

SYNTHESIS AND CHARACTERIZATION OF BENZODITHIOPHENE
CONTAINING CONJUGATED POLYMERS FOR ORGANIC BULK
HETEROJUNCTION SOLAR CELLS

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CONTAINING CONJUGATED POLYMERS FOR ORGANIC BULK
HETEROJUNCTION SOLAR CELLS**

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF BENZODITHIOPHENE CONTAINING CONJUGATED POLYMERS FOR ORGANIC BULK HETEROJUNCTION SOLAR CELLS

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Bulk heterojunction organic solar cells (BHJ-OSCs) have drawn attention as a renewable energy source due to their flexibility, lightweight and low cost in large-area applications. Besides the design of novel polymeric materials with different building blocks, the device architectures of the solar cells have been improved significantly to increase the power conversion efficiency (PCE) of solution-processed OSCs over the last years. Up to now, PCE for single layer BHJ-OSCs has reached 18%, and high performance of 18.6% was recorded in the tandem OSCs. Some requirements for designing ideal polymeric donor-acceptor (D-A) type materials should be considered to obtain high-efficiency BHJ-OSCs: a) wide and strong absorption spectra in the visible and near-infrared range to get high short circuit current (J_{SC}); b) high molecular weight and good solubility in common organic solvents; c) suitable energy levels between polymeric donor and acceptor materials to obtain high open-circuit voltage (V_{OC}); d) good morphology and high charge carrier mobility to facilitate fill factor (FF). With these aim, the D-A type conjugated polymers as the donor materials in the active layer of the OSCs were designed to obtain a narrower band gap and improve the intramolecular charge transfer (ICT) between donor and acceptor building blocks. This thesis investigated

a wide range of polymeric materials containing benzodithiophene moiety to construct organic bulk heterojunction solar cells to obtain high power conversion efficiency. The novel conjugated polymers with benzothiadiazole, quinoxaline, thienopyrroledione, benzotriazole and isoindigo acceptor moieties were studied in detail. The electrochemical, spectroelectrochemical and photovoltaic behaviors are examined for the conjugated polymers. The effect of the number of the F atom substitution on the benzothiodiazole based polymers was investigated. With the incorporation of fluorine atom, HOMO energy level of the PBDTSe-FBT and PBDTSe-FFBT were decreased compared to the polymer PBDTSe-BT. For the optimized active layer of benzothiodiazole based polymers, PBDTSe-FFBT showed the best PCE of 2.63%. Quinoxaline derivatives were synthesized with thiophene and selenophene π -bridge. The effect of the π -bridge and side groups on the benzodithiophene were investigated. PCE of 4.47% were obtained for PBDT-TQx with an increase in all photovoltaic parameters. Benzothiodiazole and thienopyrroledione based random polymers were obtained to investigate the effect of the different acceptor moieties and F atom substitution. The best device performance was found with the addition of one F atom substitution, RP2, giving 3.38% of PCE. Different side groups on benzodithiophene were used with benzotriazole acceptor to synthesize PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz. The optimized studies showed the best performance as 3.49% of PCE for PBDTT-BTz. Isoindigo containing polymers resulted broad absorption in UV-Vis spectra. Preliminary results showed a PCE of 2.03% for PBDTTT-IID.

Keywords: Benzodithiophene, D-A Alternating Polymers, Organic Solar Cell, Power Conversion Efficiency, Morphology of Active Layer

ÖZ

ORGANİK BULK HETEROEKLEM GÜNEŞ PİLLERİ İÇİN BENZODİTİYOFEN İÇEREN KONJÜGE POLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

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Bulk heterobağlam organik güneş pilleri (BHJ-OSC'ler), geniş alan uygulamalarında esneklikleri, hafiflikleri ve düşük maliyetleri nedeniyle yenilenebilir bir enerji kaynağı olarak dikkat çekmiştir. Farklı yapı taşlarına sahip yeni polimerik malzemelerin tasarımının yanı sıra, güneş pillerinin cihaz mimarileri, son yıllarda çözücü ile işlenmiş OSC'lerin güç çevrim verimliliğini (PCE) artırmak için önemli ölçüde iyileştirildi. Şimdiye kadar, tek katmanlı BHJ-OSC'ler için PCE %18'e ulaştı ve tandem OSC'lerde %18,6'lık yüksek bir performans kaydedildi. Yüksek verimli BHJ-OSC'ler elde etmek için ideal polimerik donör-alıcı (D-A) tipi malzemelerin tasarlanması için bazı gereksinimler dikkate alınmalıdır: a) yüksek kısa devre akımı (J_{sc}) elde etmek için görünür ve yakın kızılötesi aralıkta geniş ve güçlü absorpsiyon spektrumları; b) yaygın organik çözücülerde yüksek moleküler ağırlık ve iyi çözünürlük; c) yüksek açık devre voltajı (V_{oc}) elde etmek için polimerik verici ve alıcı malzemeler arasında uygun enerji seviyeleri; d) dolum faktörünü (FF) kolaylaştırmak için iyi morfoloji ve yüksek yük taşıyıcı hareketliliği. Bu amaçlarla, OSC'lerin aktif katmanındaki verici malzemeler olarak D-A tipi konjuge polimerler, daha dar bir bant aralığı elde etmek ve verici ve alıcı yapı taşları arasındaki molekül içi yük transferini (ICT) iyileştirmek için tasarlandı. Bu tez, organik bulk

heteroeklem güneş hücrelerinin inşası için benzoditiyofen içeren çok çeşitli potansiyel polimerik malzemelerin araştırmasını sunmaktadır. Benzothiadiazole, quinoxaline, tienopyroledion, benzotriazole ve isoindigo akseptör kısımlarına sahip yeni konjuge polimerler detaylı olarak incelendi. Konjuge polimerlerin elektrokimyasal, spektroeletrokimyasal ve fotovoltatik davranışları incelendi. F atomu sayısının benzotiyodiazol bazlı polimerler üzerindeki etkisi araştırıldı. Flor atomunun dahil edilmesiyle, PBDTSe-FBT ve PBDTSe-FFBT'nin HOMO enerji seviyesi, PBDTSe-BT polimerine kıyasla azaldı. Benzotiyodiazol bazlı polimerler ile yapılan çalışmaların PBDTSe-FFBT kullanılarak optimize edilmiş aktif katmanı için %2.63 ile en iyi PCE'yi gösterdi. Kinoksalin türevleri, tiyofen ve selenofen π -köprüsü ile sentezlendi. π -köprü ve yan grupların benzoditiyofen üzerindeki etkisi araştırıldı. Tüm fotovoltatik parametrelerde bir artışla PBDT-TQx için %4.47'lik PCE elde edildi. Farklı alıcı kısımların ve F atomu etkisini araştırmak için benzotiyodiazol ve tienopirolidion bazlı random polimerler elde edildi. En iyi cihaz performansı, %3.38 PCE veren bir F atomu içeren RP2 ile elde edildi. PBDTPh-BTz, PBDTT-BTz ve PBDTTT-BTz sentezlemek için benzotriazol akseptörü ile benzoditiyofen üzerindeki farklı yan gruplar kullanıldı. Optimize edilmiş çalışmalar, PBDTT-BTz için %3.49'luk PCE ile en iyi performansı gösterdi. İzindigo içeren polimerler, UV-Vis spektrumlarında geniş absorpsiyon ile yapılan ön çalışmalar, PBDTTT-IID için %2.03'lük bir PCE ile sonuçlandı.

Anahtar Kelimeler: Benzoditiyofen, D-A Alternatif Polimerler, Organik Güneş Pili, Güç Çevrim Verimliliği, Aktif Katman Morfolojisi



To my family

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CHAPTER 1

INTRODUCTION

Due to global warming and environmental concerns, the insufficient reserve of fossil fuels, and the continuous increase in the world population, it is essential to investigate more efficient technologies providing clean, renewable and low-cost energy for promoting the economic improvement of society. By hoping to solve the current energy concerns and accompanying environmental issues, remarkable research from both industry and academia has been devoted to the development of new photovoltaic technologies (PV), which can efficiently harvest energy from sunlight. The conversion of solar irradiation into electric power can enable green and sustainable energy technology. Hence, there is a demand for PV technology, and among all developed PV technology, organic photovoltaics (OPVs) offer great potential for accomplishing low-cost production due to comprising earth-abundant materials, such as carbon, oxygen, hydrogen, etc. In addition to meeting the cost-effective goal, fast roll-to-roll production, along with their fabrication on flexible substrates, lightweight, and even transparent properties, might give them considerable advantages over inorganic photovoltaics.¹⁻³

In 1954, Bell Laboratory developed the first solar cell with 4% efficiency based on silicon. This type of solar cell is attributed as the first generation due to the usage of the crystal form of silicon materials. Currently, these solar cells are mainly present in the market with above 25% efficiency.⁴ Diminishing the cost of materials has become the main aim of producing low-cost solar cells to accomplish the objective of the large-scale use of solar cells. To establish this idea, the second generation solar cells were developed from thin-film technology, which includes cadmium telluride (CdTe), amorphous silicon and copper indium gallium diselenide (CIGS) materials.^{5,6}

The third generation, unlike the second generation solar cell, has a goal of increasing the power conversion efficiency with low-cost production. This type of solar cell is based on a dye, semiconductor nanocrystals, nanoporous materials, or conjugate polymer which are used in perovskite solar cells, organic solar cells, dye-sensitized solar cells and quantum dot solar cells.⁷⁻⁹

Figure 1.2, which was prepared by National Renewable Energy Laboratory (NREL), demonstrates the development of the power conversion efficiencies of different types of solar cells up to now. Figure 1.2 shows the development of the emerging PV technology.

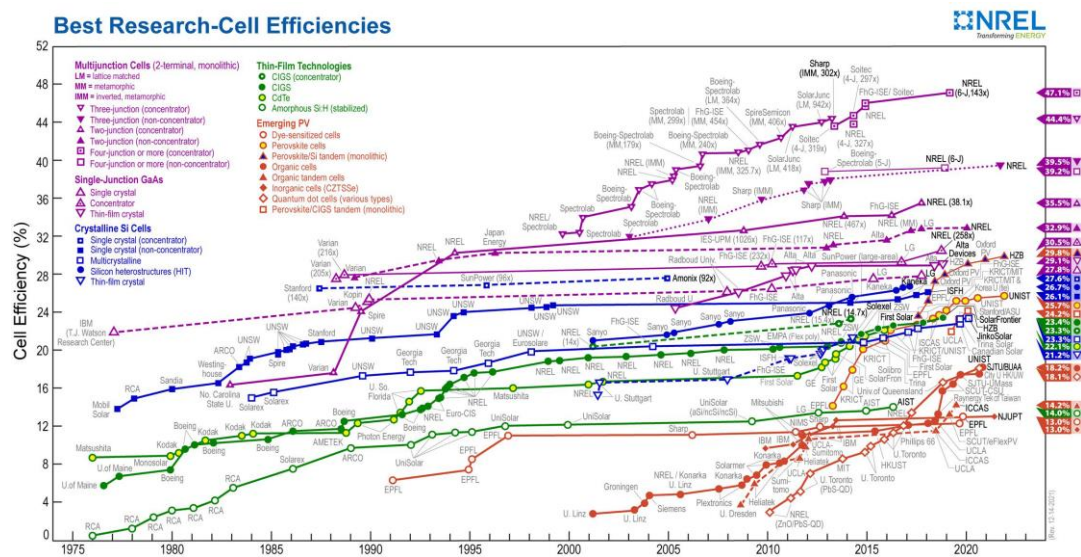


Figure 1.1. Best cell efficiencies (NREL)

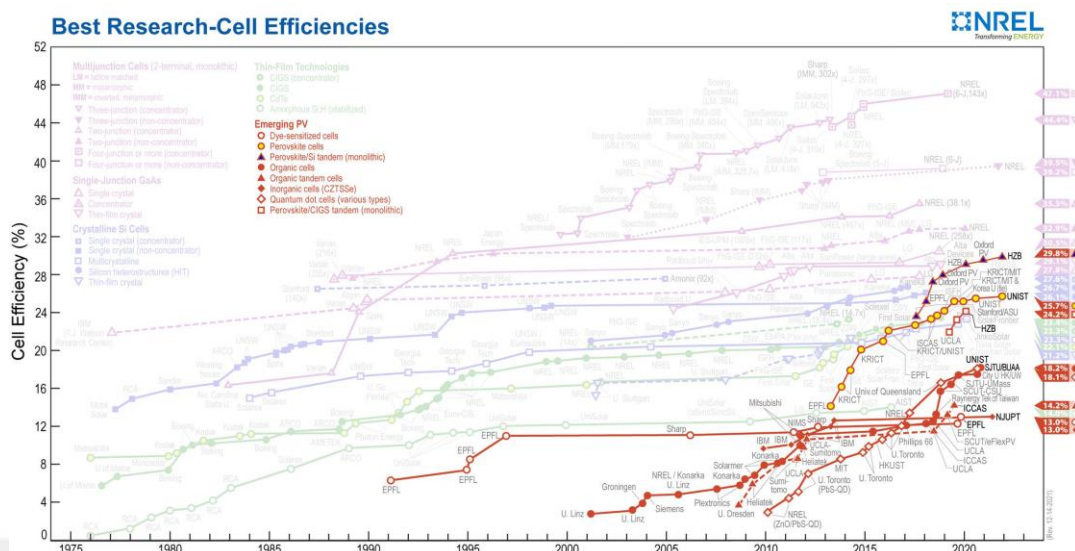


Figure 1.2. Best cell efficiencies for emerging PV (NREL)

As a result, over the last years, research conducted in the fields of science and industry has caused an increase in the efficiency of solar cell devices, reduction of materials, and low-cost of production which has eventually led to the current PV technologies, namely organic photovoltaics.

1.1 Organic Solar Cells: Background

1.1.1 Organic Semiconductors

Due to having the mechanical properties of plastics and the electrical properties of semiconductors, organic materials such as polymers, oligomers, and small molecules enable the development of producing OSC technology.

The high conductivity in doped polyacetylene was discovered by Heeger, Shirakawa, MacDiarmid et al. in the late 1970s.¹⁰ They won the 2000 Nobel Prize in Chemistry for the finding and development of conductive polymers. This discovery indicated that organic compounds are able to transport current, and the conductivity can be tuned by the doping process and appropriate molecular design.¹¹

Organic semiconductors are molecular or polymeric materials with conjugated double and single bonds, which results in the delocalization of the π electrons. Organic compounds, therefore, possess molecular π orbitals that give rise to the bonding (π) and antibonding (π^*) molecular orbitals. These discrete energy levels consisting of molecular orbitals comprise the valence and conduction bands of the organic semiconductors, which were identified as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively.¹² The ability of the charge transportation by the charge carriers is closely related to HOMO and LUMO energy levels and the energy difference between HOMO and LUMO energy levels which is in the range of 1 to 3 eV.¹³ When the repeating unit becomes large enough, the splitting of the orbitals might push the HOMO and LUMO close together. The material is called a semiconductor when the E_g is closer toward the energy of UV or visible light.¹⁴

This energy bandgap reveals semiconductor behavior and intense interactions with visible and near-infrared (NIR) photons. Therefore, the molecular design and engineering of organic semiconductors have an essential role for possible tuning of the conductivity.

It should be reminded that organic semiconductors generally possess considerably lower material costs than conventional inorganic semiconductors. They are soluble in organic solvents which can easily form a thin film by a low-temperature inexpensive process such as spin coating, roll-to-roll processing, inkjet printing.¹⁵ Moreover, thanks to the high absorption coefficients, the thickness of the layer that is used as an active layer can be very thin (~ 100 nm) so that semitransparent property of organic solar cells can be observed and the color of the device can be tuned.¹⁶ Organic semiconductors can also be light-weight due to compatibility with flexible substrates, and the mechanical flexibility of these types of materials results in specific applications such as wearable electronics and portable devices.¹⁷ Hence, organic semiconducting materials are mainly suited for lightweight, low cost, flexible and large-area device applications.

1.1.2 Device Architectures

Organic solar cells vary from classical inorganic solar cells with regards to light absorption process, carrier binding energy, and mobility besides design, active layer architecture and thickness. Free charge carriers are not immediately created upon absorption of light in the organic semiconductors, unlike inorganic traditional solar cells; an electrically neutral electron-hole pair named as exciton actually forms during the process. The design and the geometry of the organic solar cells have significantly impacted by this exciton formation from organic semiconductors for the past few years.^{18,19} An exciton consisting of electron-hole pair bound coulombic attractions has a lifetime of the order of nanoseconds. Therefore, the exciton must dissociate in time to get a photovoltaic effect in the organic solar cells. The energy produced by exciton dissociation should then surpass the exciton binding energy; in other words, the photons bearing more substantial energy than the bandgap energy of the photoactive material can be absorbed and the contribution to the energy conversion is observed.

In this part, polymer-based OSCs are classified on the basis of device structures into the following types.

1.1.2.1 Single Layer Cell

Single layer OSCs as shown in Figure 1.3 contain only one organic semiconductor material with two electrodes which become rectifying and ohmic contacts. These types of cells are often referred to as Schottky devices due to the occurrence of charge separation at the rectifying electrode (Schottky junction). The photoactive region of these types of devices is often very thin, hence the short diffusion length results in the recombination of excitons to the ground state.²⁰ Moreover, positive and negative free charges travel through the same phase leading to significant charge losses as a result of recombination. These aspects demonstrate the very low photovoltaic performances of single layer OSCs.

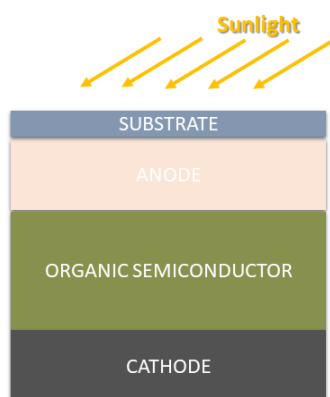


Figure 1.3. Device architecture of single layer organic solar cell

1.1.2.2 Bilayer Solar Cell

Bilayer OSCs is comprised of two closely contacted organic semiconductor (donor and acceptor semiconductor materials) layers between two electrodes as shown in Figure 1.4. the bilayer structure displays the ability to change the properties of the acceptor and the donor to maximize charge separation while providing absorption in both active layers. In this architecture, excitons are generated near the junction (less than ~ 20 nm) to give a chance to dissociate. However, the produced excitons recombine at distances greater than ~ 20 nm before reaching the photoactive interface due to the low mobility and short diffusion length. Therefore, bilayer architecture is unsuccessful in achieving high power conversion efficiency since a large number of generated excitons are not able to reach the donor-acceptor interface. This structure also limits the thickness of layers, resulting in ultra-thin layers and preventing the work with thick films with greater light absorption.^{21,22}

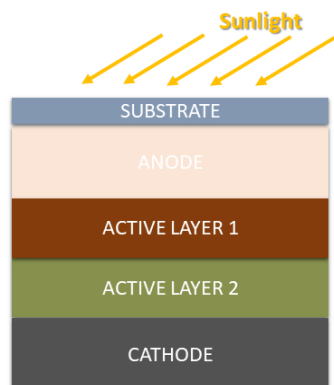


Figure 1.4. Device architecture of bilayer organic solar cell

1.1.2.3 Bulk Heterojunction Solar Cell

A new type of organic solar cell architecture was developed to overcome the restrictions on the device thickness imposed by organic materials with short exciton diffusion lengths. Bulk heterojunction solar cells are constructed with a blend of the donor and the acceptor material in a single layer while maximizing the interfacial surface area of the photoactive layer. The device architecture of the bulk heterojunction solar cell is presented in Figure 1.5. If the length of the donor and the acceptor blend domains is related to the length scale of exciton diffusion, most of the generated excitons in the blend domains may reach the interface of the bulk heterojunction before decaying. This significantly extends the probability of exciton dissociation and enables the applications of the thicker films to increase the photon harvesting in solar cells.^{23–25}

However, the blending of the donor and the acceptor into small domains has a tendency to reduce the arrangement in the molecular packing which may lead to discontinuous pathways. The isolated domains, resulting in recombination losses may exist. Therefore, poor control over the phase morphology of the solar device limits the power conversion efficiency of the bulk heterojunction solar cell. Furthermore, the increased interfacial area facilitates recombination, and poor

distribution of phase morphology suggests the presence of shunt pathways. To balance the higher photogeneration yield with the increased recombination losses, the microstructure of the blended film should be optimized.^{26–28}

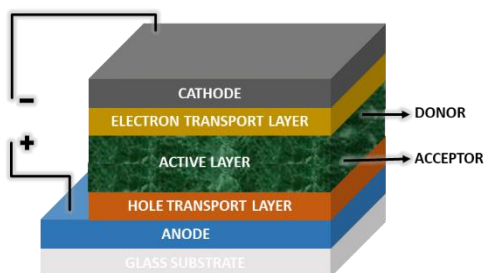


Figure 1.5. The device architecture of bulk heterojunction solar cells

Despite the challenge of adequately matching the various parameters that enhance the relative BHJ OSC efficiency, in recent years, considerable advancements have been made in the BHJ OSC performance, which has already exceeded 18% and is presently improving.²⁹

1.2 Introduction to Bulk Heterojunction Solar Cells

1.2.1 Operational Mechanisms in Organic Solar Cells

The photovoltaic effect occurs when a semiconductor is irradiated with light of a suitable wavelength, causing light excitation and the formation of an electric field within the semiconductor. The photovoltaic effect is the basic theory for photoelectric energy conversion in organic solar cells. The photoelectric conversion process of organic solar cells, as shown in Figure 1.6, consists of four steps:

- Absorption of light and exciton generation;
- Exciton dissociation;
- Charge carrier transport;

- Charge carrier collection.

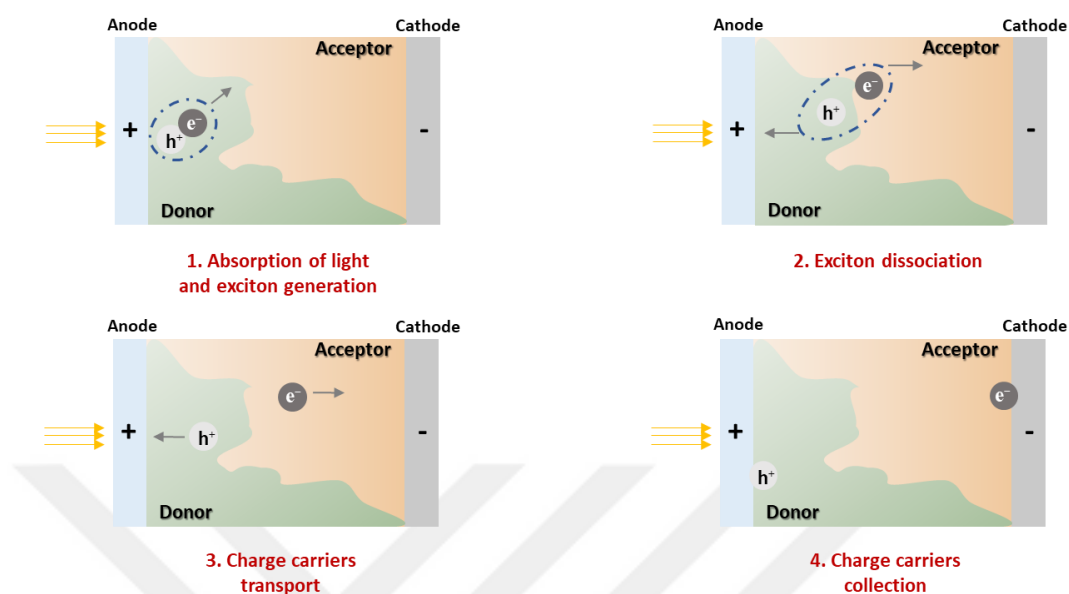


Figure 1.6. Working principle of bulk heterojunction solar cell

Light is typically absorbed by the donor material in a BHJ OSC device, such as a conjugated polymer. An electron is stimulated from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) upon photon absorption. To produce electron-hole pairs known as excitons, the gap between LUMO of the donor and the LUMO of the acceptor should be in the range of 0.1-1.4 eV. The excitons must diffuse to the donor-acceptor barrier, where there is enough potential energy loss to separate them into free charge carriers, namely, electrons and holes.¹⁴ Followed by separating into free charge carriers, each one must be transferred to the appropriate electrode via a bicontinuous interpenetrating path that avoids recombination and charge trapping. During these phases, several limits and losses may arise, such as absorption loss because of spectrum incompatibility, thermalization loss, inadequate energy needed for exciton splitting, and charge recombination. Below is a brief description of each step of the process, from light absorption through charge carrier collection.

1.2.1.1 Absorption of Light and Exciton Generation

The photoactive layer should absorb the maximum amount of incoming sunlight as the first and most fundamental prerequisite for attaining maximum performance. While the conjugated polymers have a high absorption coefficient, they can absorb light at the maximum of their absorption spectrum with a very thin photoactive layer (usually less than 100 nm) in comparison to their inorganic silicon based counterparts, which require hundreds of micrometers thickness. As a result of poor charge-carrier mobilities in most polymers, the thickness of the polymer-based active layer is generally restricted to 100 nm. Therefore, lower photocurrent production results from low absorption in conjugated polymers. An electron is stimulated from the HOMO to the LUMO when sunlight passes from the transparent anode side and the photon is absorbed. This process is similar to inorganic semiconducting materials where the electron is stimulated from the valence band to the conduction band. As a consequence, an electron-hole pair named as exciton is formed with a Coulomb binding energy in the range of 0.1-1.4 eV. After then, the excitons are transported to the donor-acceptor interface.

1.2.1.2 Exciton dissociation

In an organic solar cell, the excitons at the donor/acceptor interface must be dissociated to achieve a photovoltaic effect. Only photons with an energy greater than the band-gap of the photoactive material can be absorbed and contribute to the energy conversion if the energy obtained by this process surpasses the exciton binding energy. Once they overcome their mutual Coulomb attraction, they either recombine or dissociate into free charge carriers. The exciton binding energy in organic solar cells is typically in the range of 0.3-1.0 eV. Compared to their inorganic counterparts, this quantity of energy is regarded to be large. The distance traveled by an exciton prior to recombination is described as diffusion length. For most conjugated polymers, the diffusion lengths are confined to only a few nanometers

due to the short lifetime of the excitons (<20 nm). Hence, excitons must be produced within their diffusion length in order to generate charge efficiently. As a result, the photoactive layer thickness is vital for effective charge formation

1.2.1.3 Free charge carriers transport

The charges should be transferred towards the corresponding electrodes after the exciton dissociation into free charge carriers, which is shown in Figure 1.6. In organic semiconductors, charge carriers are primarily transported via hopping from one local state to the next. Because of the Fermi level difference between the electrodes, an internal electric field promotes the movement of free charge carriers towards their respective electrodes. An internal electric field is created by a low work function of the cathode and a high work function of the anode which determines the cell's V_{OC} . Either carrier diffusion or electric field-mediated drift promotes the movement of free charge carriers.

The recombination of free charge carriers before reaching their respective electrodes is the major difficulty for the effective transport of free charge carriers towards the anode and cathode. The mobility of charge carriers in the photoactive layer influences both charge carrier transport and loss caused by charge carrier recombination. The generated electrons and holes in low mobility semiconductor materials are still constrained by the Coulomb potential. As a consequence, they are unable to overcome their intrinsic attraction which leads recombining of the electrons and holes prior to charge collection at the corresponding electrodes. Thus, the solar cell loses a considerable amount of photogenerated current. The photogenerated electrons and holes have a path length that is proportional to the thickness of the photoactive layer. While the photoactive layer thickens, the probability of the charge carrier recombination increases, causing a significant reduction in the device performance.

1.2.1.4 Charge Collection

Charge carriers produced by photons that do not recombine are subsequently removed from the photoactive layer and delivered to the electrodes. To enhance charge extraction, the potential barrier at interface of the photoactive layer/electrodes must be decreased. As a consequence, the work function of the anode should meet the HOMO of the donor material, whereas the work function of the cathode should be equal to the LUMO of the acceptor material. The contacts are defined as Ohmic contacts if the work functions match properly as stated. Conversely, suppose the anode and cathode are mismatched with the HOMO of the donor or the LUMO of the acceptor. In that case, respectively, any Ohmic contacts are developed which will subsequently decrease the performance of the solar cell. As illustrated in Figure 1.6, the charge collection at the corresponding electrodes completes the processes from light absorption to photocurrent production.

Al, Ca, and Ag are frequently reported electrode materials utilized as electron collecting contacts in BHJ OSC devices (low WF needed). Their charge extraction performance varies based on the organic electron transporting material type. High WF materials like Au, on the other hand, are chosen as hole collecting contacts. Particularly thin metal layers might be employed since one contact must be at least partly transparent, allowing light to get through the device (e.g. about 15-20 nm of Au). Additionally, Indium Tin Oxide (ITO), a semiconductor material, is mainly employed as a transparent electrode because of its large bandgap (about 3.7 eV) and strong conductivity caused by its oxygen vacancies.

Various possible interactions might occur at the organic/electrode interface, relying on not only the alignment of the corresponding organic and electrode energy levels, but also those of physical and chemical properties. Dipole generation, charge carrier transportation, wavefunction hybridization, physical blending, chemical reactions and other interactions are common cases. All of these factors have an impact on the charge extraction processes at the electrodes and the efficiency of the solar cell. As a result, a thin intermediate layer, also known as a buffer layer, is usually used to

separate the organic BHJ film from the cathode/anode electrode. Buffer layers are generally made of semiconductor films that create appropriate ohmic contact either with the cathode's LUMO or the anode's HOMO. Buffer layers also function as a protective boundary, a surface rectifier, an energy level connector, and an optical spacer. Anode buffer layers include PEDOT:PSS and metal oxides such as V_2O_5 and MoO_3 , whereas cathode buffer layers include LiF, ZnO, and TiO_2 .

1.2.2 Basic Photovoltaic Concepts

The power conversion efficiency (PCE) of a solar cell is determined by three main parameters: short circuit current (J_{SC}) is the current that penetrates the electrodes without any applied field. Open circuit voltage (V_{OC}) is the highest potential provided by the device. The fill factor (FF) is the ratio of maximum generated power to the product of J_{SC} and V_{OC} , and it indicates the feature of the solar cell. The product of these three parameters divided by input power (P_{in}) yields the PCE.

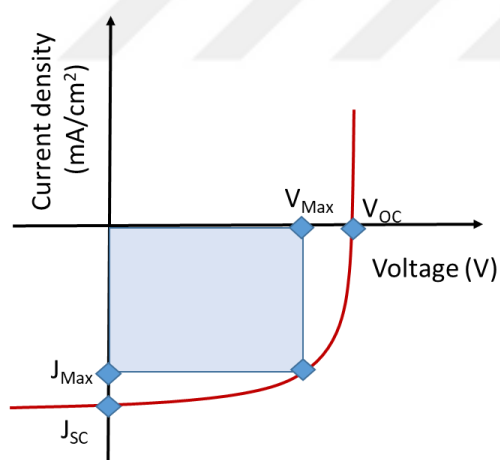


Figure 1.7. Representative J-V curve

The voltage and current density at maximum output power, respectively, are V_{Max} and J_{Max} . A typical Current Density-Voltage (J-V) curve for a solar cell is shown in Figure 1.7. It shows the V_{OC} , J_{SC} , FF, as well as the J_{Max} and V_{Max} values. The FF is

shown by the shaded area in the graph. At the maximum power output, the product of current and voltage has the highest yield (Max).

A basic overview of each of them is given below.

1.2.2.1 Short circuit current density (J_{sc})

The J_{sc} displays the number of charge carriers produced and subsequently collected at the corresponding electrodes at zero applied potential ($V_{oc}=0$). In other words, it reflects the maximum photocurrent density obtained at zero applied potential. Even though no power is generated at this stage, the J_{sc} represents the beginning of the power.

1.2.2.2 Open circuit voltage (V_{oc})

The maximum output voltage while no current passes through a solar cell is known as V_{oc} . It is one of the most significant parameters influencing device efficiency. Many researches have shown that the V_{oc} of a solar cell is determined by the energy gap between the HOMO energy level of the donor and the LUMO energy level of the acceptor.

1.2.2.3 Fill factor (FF)

The FF is a significant factor that influences the PCE of the organic solar cell. The FF, which is the proportion of the maximum output power to the product of J_{sc} and V_{oc} , specifies the structure of the J-V characteristics of solar cell.

1.2.2.4 Power conversion efficiency (PCE)

PCE is a measure of how much electrical power is created in accordance to the incident solar spectrum (AM 1.5G), and this is associated to the three variables

mentioned above via Equation 2. In fact, these important OSC performance factors play a critical role in measuring and enhancing solar cell performance.

$$FF\% = \frac{V_{Max} \times J_{Max}}{V_{oc} \times J_{sc}} \times 100 \quad \text{Equation 1}$$

$$PCE\% = \frac{V_{oc} \times J_{sc} \times FF}{100 \text{ mW/cm}^2} \times 100 \quad \text{Equation 2}$$

1.2.2.5 External Quantum Efficiency (EQE)

External quantum efficiency is an essential feature of OSCs. The incident photon-to-electron conversion efficiency (IPCE) is also known as the external quantum efficiency (EQE). The number of photogenerated electrons recovered at the electrode divided by the number of incoming photons onto the device yields EQE. Figure 1.8 shows an example external quantum efficiency spectrum of the organic solar cell.

$$EQE\% = \frac{N(coll.el.)_{\lambda}}{N(photons)_{\lambda}} \times 100 \quad \text{Equation 3}$$

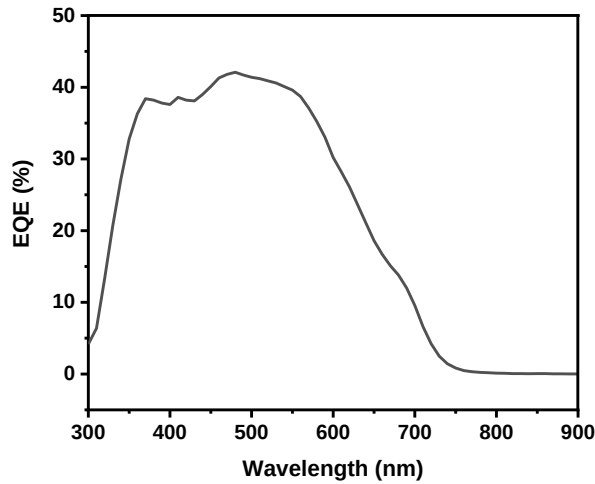


Figure 1.8. An example external quantum efficiency spectrum of organic solar cell

1.2.3 Photoactive Materials in the Bulk Heterojunction Solar Cells

In the active layer of OSCs, in which donor and acceptor materials are mixed with each other to construct a so bulk heterojunction, the photoactive materials receive sunlight and transform into free charge carriers. There seems to be no doubt that the advancement of materials for the light-harvesting layer has contributed significantly to the increase in PCEs of OSCs.

Fullerene derivatives have been widely used as electron acceptors owing to their high electron affinity and great electron-transport capabilities. Fullerene's three-dimensional nature, in particular, provides a distinct packing ability in a blend layer, allowing it to construct electron transport channels easily. The most widely used fullerene derivatives are shown in Figure 1.9. A significant variety of polymeric or small molecular donor materials have been synthesized and evaluated to obtain satisfactory compatibility with PCBM in respect of absorption spectra and molecular energy levels.

Yu et al. announced the first BHJ solar cell in 1995, using a MEH-PPV/C₆₀ and its functionalized derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM).³⁰ Under AM 1.5 illumination, the efficiency of devices based on this approach remained just around 1% after several years of development. By adjusting the casting process, Shaheen et al. achieved a 2.5% PCE with V_{OC} of 0.82 V and a J_{SC} of 5.25 mA/cm², from a more processable mixture of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) and PC₆₁BM in 2001.³¹

By employing LiF, the efficiency of the MDMO-PPV/PC₆₁BM device may be improved by around 3%.³² Another efficiency enhancement came from switching from PC₆₁BM to PC₇₁BM. Because PC₇₁BM absorbs more light in the visible range than PC₆₁BM, the MDMO-PPV/[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) device has a higher J_{SC} and a 3% increase in efficiency.³³ Because of their relatively wide bandgap (2.2 eV), PPV materials could mainly capture light below

600 nm, and they generally possess limited hole mobility, which restricts the development of these solar cells.

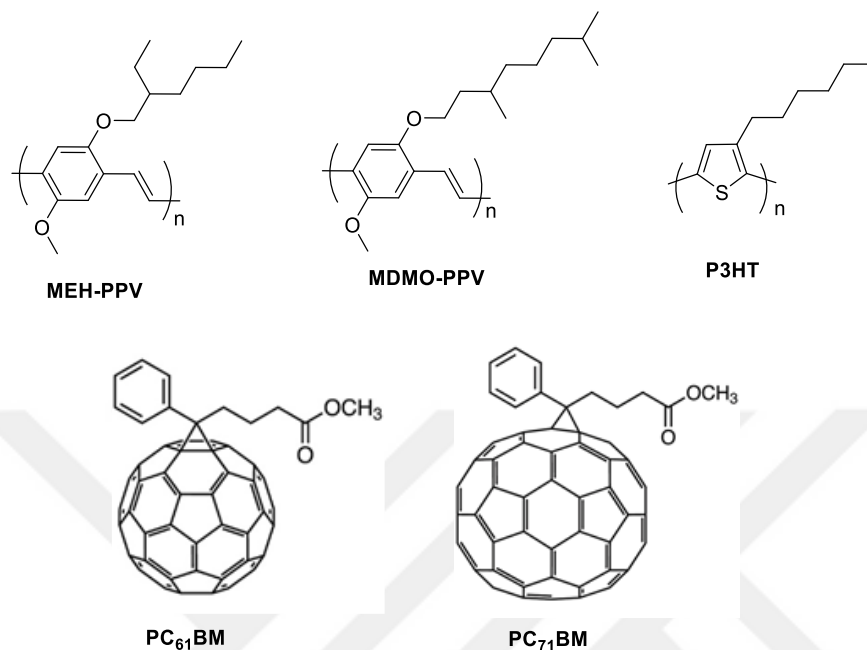


Figure 1.9. Example of first conjugated polymer and fullerene derivatives

During this period, considerable advancements were made in the modulation of these polymers' synthetic consistency, as well as their regioregularity and molecular weight. However, it had become evident that the comparatively high band gap of PPV-based materials and with their poor charge carrier mobilities would severely constrain the maximum power conversion efficiencies of photovoltaics manufactured using these donor materials. As a consequence, the effort has switched to novel polymer donor materials, particularly poly(alkyl-thiophenes), such as poly(3-hexylthiophene) (P3HT).

Owing to its stronger optical absorption, high hole mobility, and solution processability, P3HT has shown to be the best alternative for OSC than PPVs. Materials features and operating circumstances have a significant effect on the performance of P3HT/PCBM solar cells. Schilinsky et al. were able to manufacture devices with a maximum EQE of 76% in 2002, which was the first positive result

for P3HT/PC₆₁BM solar cells.³⁴ Padinger et al. showed in 2003 that subsequent thermal annealing with external voltage increased the efficiency of the P3HT/PC₆₁BM system by roughly 3.5%, which had a tenfold enhancement over the untreated system (0.4%) as a result of improved morphology.³⁵ Kim et al. discovered that the regioregularity of P3HT has a considerable impact on the performance of P3HT/PC₆₁BM solar cells due to the improvement in crystallinity.³⁶

While P3HT has been the top investigated polymer for OPV, it has been clear that a narrower band gap polymer having a low HOMO energy level and higher hole mobilities are necessary to improve the research. As a result, new materials with better efficiency are required to accomplish the required performance in polymer solar cells for commercial utilization.

In literature, two common approaches for reducing the band gap of conjugated polymers have appeared: designing polymeric materials with alternating electron-poor and electron-rich moieties along the polymeric chains, known as donor/acceptor (D/A) type polymers, and stabilizing the quinoidal form of semiconducting polymer backbones. The orbital intermixing of these donor and acceptor heterocycles therefore causes the band gap to narrow in D/A type polymers.³⁷

Numerous of D-A type polymers have been developed for solar cell applications so far. It is also important to note that the efficiency of OSC devices is influenced by not only the inherent electrochemical characteristics of the polymer, but also the order of polymer and nano/micro-scale phase separation between acceptor materials such as PCBM.²¹

Janssen et al. reported a polymer PBBTDPP2 comprised of diketopyrrolo-pyrrole and thiophene with a low optical bandgap of 1.40 eV. The manufacturing solvent has a significant impact on the photovoltaic efficiency of PBBTDPP2. The blend with weight ratio of 1:2 in chloroform/*o*-dichlorobenzene solvent mixture was used to produce an optimum PBBTDPP2:PC₇₁BM solar cell with a V_{OC} of 0.61 eV a J_{SC} of 11.3 mA/cm², an FF of 0.58 resulting in PCE of 4.0%.³⁸ Huo et al. represented another diketopyrrolopyrrole polymer PDPP-BDP which has a derivative of

benzodithiophene moiety on the polymer backbone. The PDPP-BDP:PC₇₁BM based solar cell device resulted in 4.4% of PCE.³⁹

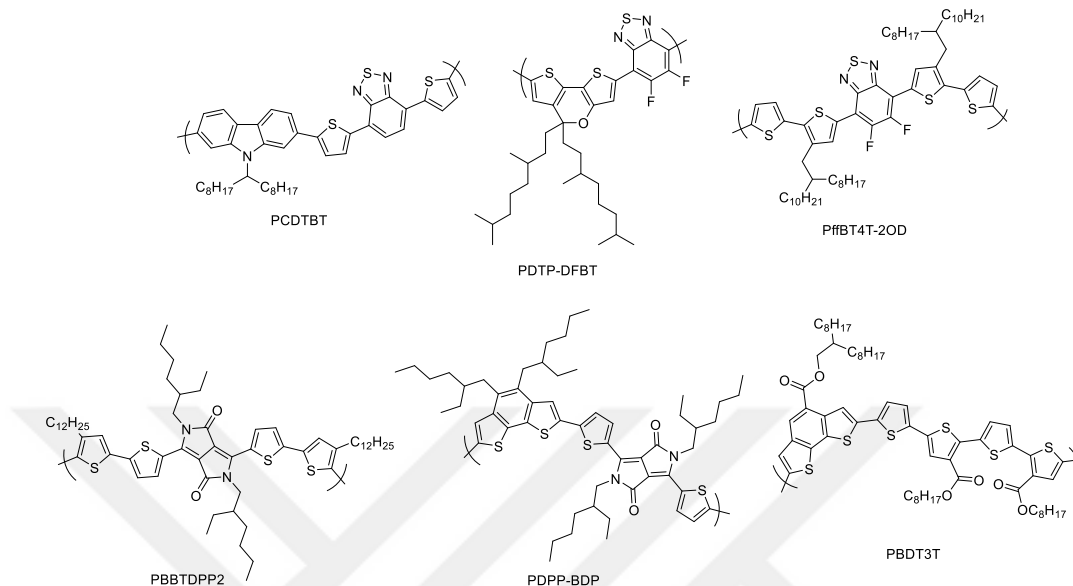


Figure 1.10. Some examples of conjugated polymers with various building blocks

Park et al. designed PCDTBT polymer which has electron rich unit carbazole, electron deficient benzothiadiazole moiety and thiophene as π -bridge. This polymer resulted in red shifted absorption spectrum that reaches around 700 nm. The devices constructed with this polymer have attained 5.9% power conversion efficiency.⁴⁰ You et al. obtained a branched alkoxy chain containing a fused bithiophene ring. The resulted dithienopyron (DTP) unit has asymmetric structure and significantly electron-rich characteristics, which led to a very low optical bandgap E_g of 1.38 eV. The device based on PDTP-DFBT polymer has a PCE of 8.0% along with wide absorption up to 900 nm.⁴¹

The effect of many fabrication factors (solution concentration, temperature, solvent selection and spin coating rate), including the impacts of polymer molecular weight, was examined by Ma et al. for PffBT4T-2OD:PC₇₁BM based devices. During the spin coating process, it was observed that molecular packing and the alignment of the molecules could be controlled with low solution temperature and low spin

coating rate. The best PCE was obtained as 10.3% employing 800 rpm of spin coating rate at 100 °C which yields smooth film provided with sufficient aggregates.⁴² Penconi et al. reported an optimum PBDT3T:PC₇₁BM based solar cell with approximately 100 nm thickness and 1:1 weight ratio with 3.0% butanedithiol (BT) solvent addition. The treatment of the active layer with the addition of BT resulted in an improvement of photovoltaic parameters. The J_{SC} of 9.29 mA/cm², V_{OC} of 0.98 V and a FF of 0.72 resulted in the best PCE of 6.51%.⁴³

The benzo[1,2-b:4,5-bdithiophene (BDT) moiety is among the most promising (considered as a successful) electron-rich building blocks to synthesize polymers and small molecules. In 2008, a variety (series) of BDT-based polymers was synthesized utilizing different acceptors. These novel BDT polymers containing different acceptor units were a good example of polymer backbone optimization. Incorporating various acceptors into the polymer backbone such as, thiophene, quinoxaline, benzothiadiazole etc. resulted the tuning of the bandgaps and molecular energy levels efficiently. These polymers had absorption edges ranging from 600 nm to 1100 nm, and optical bandgaps ranging from 1.1 eV to 2.1 eV. The HOMO energy levels were also adjusted between -4.56 eV and -5.16 eV with backbone optimization (H6, H7 and H8 polymers). Despite the low PCEs of fullerene based OSC devices, this study showed that employing different D-A configurations can effectively adjust molecular energy level and the bandgaps of polymers.⁴⁴

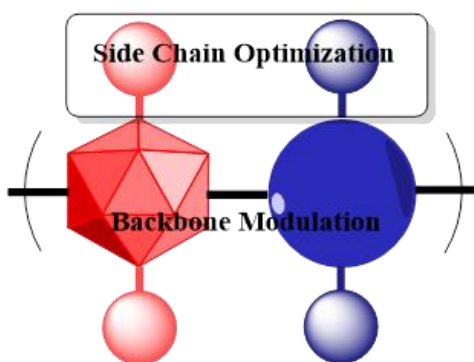


Figure 1.11. Molecular design strategy of conjugated polymers

The efficiency of the BDT-based D-A type polymers was immediately enhanced with proper side-chain design and backbone modulation of the accepted units (Figure 10). In 2009, Yu et al. polymerized an ester-functionalized thienothiophene (TT) unit with BDT unit that resulted in PTB1, PTB2 and PTB4 polymers. The polymer PTB1 had a high-lying HOMO energy level of -4.90 eV that limits the V_{OC} to 0.56-0.58 V. Therefore, the structure of BDT and TT moieties were appropriately adjusted with the substitution of branched alkyl chains and F atoms to improve the photovoltaic parameters. As a result of these changes, higher results of PCE (5.10% and 5.90% for PTB2 and PTB4, respectively) were obtained compared to PTB1 which had 4.76% of PCE.⁴⁵

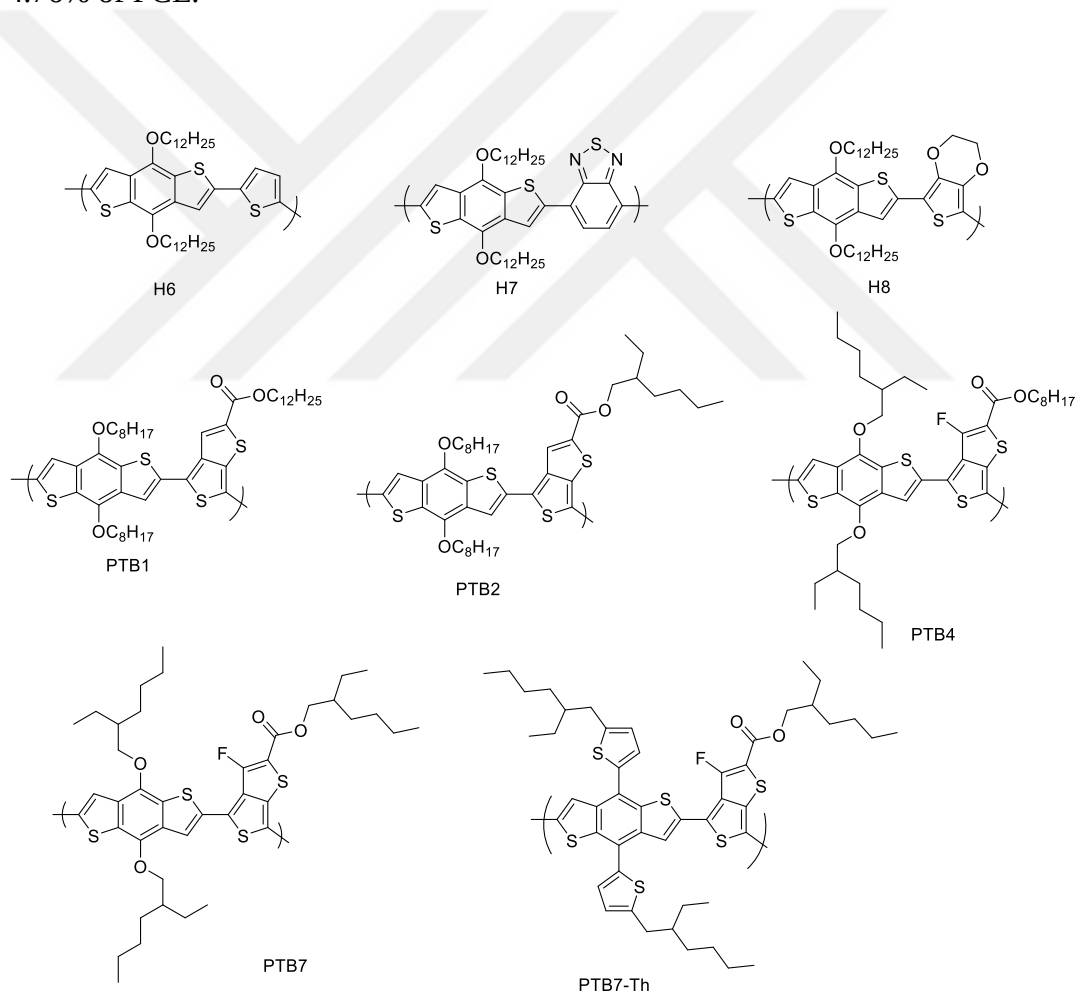


Figure 1.12. Some examples of benzodithiophene based conjugated polymers

PTB7 was synthesized in 2010 by Yu et al. who investigated the photovoltaic performance of conventional solar cells with ITO/PEDOT:PSS/PTB7:PCBM/Ca/Al device structure using dichlorobenzene/diiodooctane (DIO) or chlorobenzene (CB)/DIO solvents. A PCE of 7.4% with J_{sc} of 14.50 mA/cm² V_{OC} of 0.74 V and a FF of 69% was obtained from the device utilizing PC₇₁BM and CB/DIO solvent after device optimizations.²⁴

A successful 2D-BDT usage was achieved with PTB7-Th. Chen et al. found that by changing the alkoxy of PTB7 with a thienyl group, the absorption spectra of PTB7-Th was broadened by 25 nm toward a higher wavelength. HOMO energy level of PTB7-Th was calculated as 80 mV lower than that of PTB7, according to a CV measurement. The GIWAXS analysis also revealed that the intermolecular arrangement of the PTB7-Th/PC₇₁BM solar cell film was better than that of the PTB7/PC₇₁BM. The conventional inverted solar device resulted in a fair PCE of 7.6%, while the inverted OSC device of PTB7-Th produced a high PCE of 9.35% using a new zinc oxide doped fullerene derivative (ZnO-C60) as the electron-transporting layer (ETL). PTB7-Th has become the first and well-known polymer to exceed the 10% efficiency barrier in PSCs, receiving the label "PCE10".⁴⁶

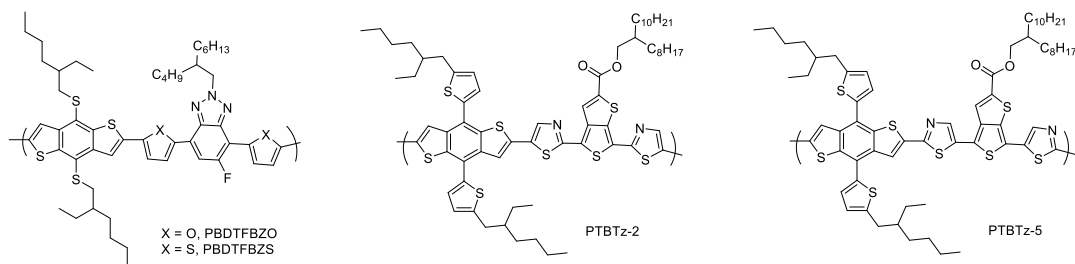


Figure 1.13. Some examples of benzodithiophene based conjugated polymers (continued)

BDT-based polymers with satisfactory HOMO/LUMO energy levels and absorption spectrum have the potential to produce high-efficiency OSC devices when combined with different acceptors. Many research groups have accomplished quite a remarkable PCEs. Peng et al. developed two novel polymers (PBDTFBZO and

PBDTFBZS) based on a monofluorinated BTz unit, with the furan and thiophene units serving as the π -bridges, respectively, to minimize HOMO levels. Both polymers had smaller bandgaps, deeper HOMO levels, and larger hole mobilities, resulting in better PCEs of 6.3% for PBDTFBZO and 7.7% for PBDTFBZS. Thiophene-based polymer PBDTFBZS was also used in a subcell to achieve high efficiency (PCE: 9.4%) tandem cell because of the low bandgap.⁴⁷

Yang et al. compared two isomeric polymers, PTBTz-2 and PTBTz-5, with varied thiazole ring configurations with respect to the TT unit. Both polymers have high crystallinities and low HOMO levels, especially PTBTz-2. It, therefore, displayed better cooperation with PC₇₁BM to facilitate optimum BHJ morphology, resulting in a remarkable PCE of 9.7%.⁴⁸

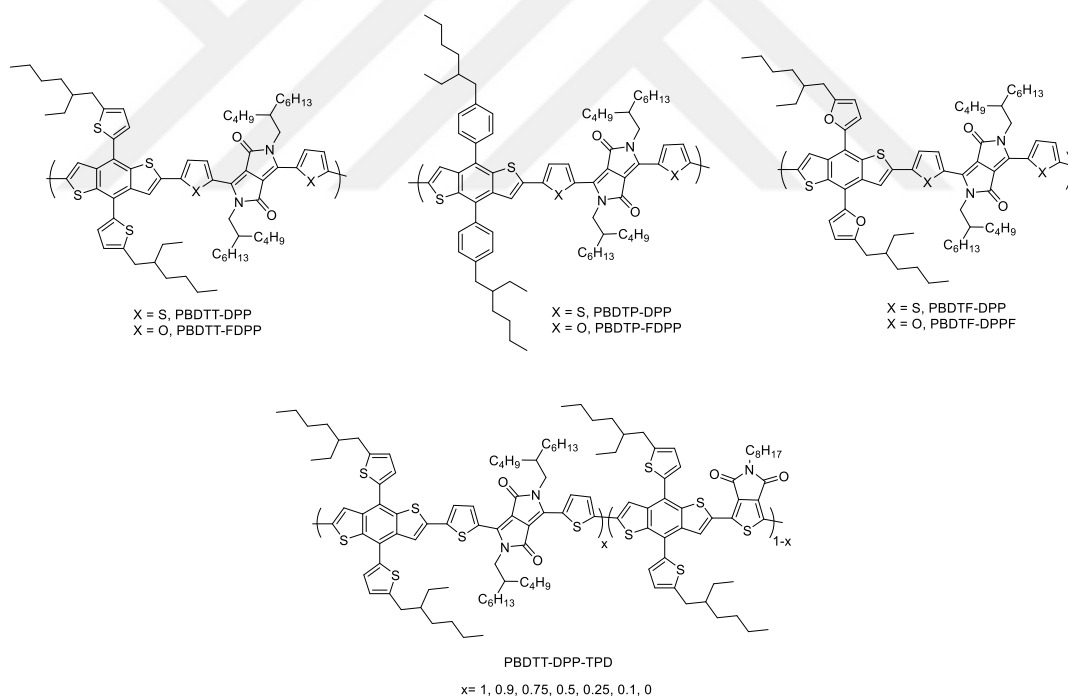


Figure 1.14. Some examples of benzodithiophene based conjugated polymers (continued)

Moreover, copolymerizing with the DPP acceptor unit resulted in functional low bandgap 2D BDT-based polymers that are particularly attractive for manufacturing multiple junction PSCs due to their broad absorption. Yang et al., for example, molecularly modified various substituents on the BDT unit and the π -bridges to produce a sequence of 2D-BDT-DPP polymers. All of these polymers had optical bandgaps of less than 1.6 eV.⁴⁹ Furthermore, they discovered that attaching phenyl groups to the BDT unit lowers HOMO energy levels further while introducing furan as the π -bridge raises HOMO levels. PCEs of 6.6%, 5.8%, 6.2%, and 3.3% were found in single-junction OSCs based on PBDTT-DPP, PBDTT-FDPP, PBDTP-DPP and PBDTP-FDPP, respectively, whereas PCEs of 9% were found in tandem cells based on PBDTT-DPP-derived rear subcell. In 2013, Ge et al. copolymerized the DPP unit with a furan-substituted BDT unit to produce PBDTF-DPP and PBDTF-DPPF polymers. Both polymers had optical bandgaps around 1.5 eV, while PBDTF-DPPF, which had a furan π -bridge, had a PCE of 5.1% and a V_{OC} of 0.72 V.⁵⁰

As reported in the literature, lower aromaticity of selenophene with respect to the thiophene results in an improvement in the quinoid character of the polymer, which leads to lower band-gap energy, increased effective conjugation length and enhanced planarity.^{51,52} Selenophene-based materials have also improved conductivity and charge mobility due to larger π -overlap leading to the greater π -orbitals of Se atoms and intermolecular Se-Se interactions.^{53,54} Moreover, the Se atom has a much larger size and less electronegativity than the chalcogenophene homolog of the S atom; as a result, Se comprising polymers are more efficient at broadening the absorption spectrum near the infrared region.^{55,56} Jiang et al. studied a series of polymers by changing S-atoms with Se-atoms on the side chains of the donor moiety, the acceptor units, and the π -bridge to examine the effect of Se-atom substitution and they reported a maximum PCE of 3.3% for PBDTTTBS containing thiophene substituted BDT and 4.0% for PBDTSTBS containing Se substituted BDT moiety.⁵⁵

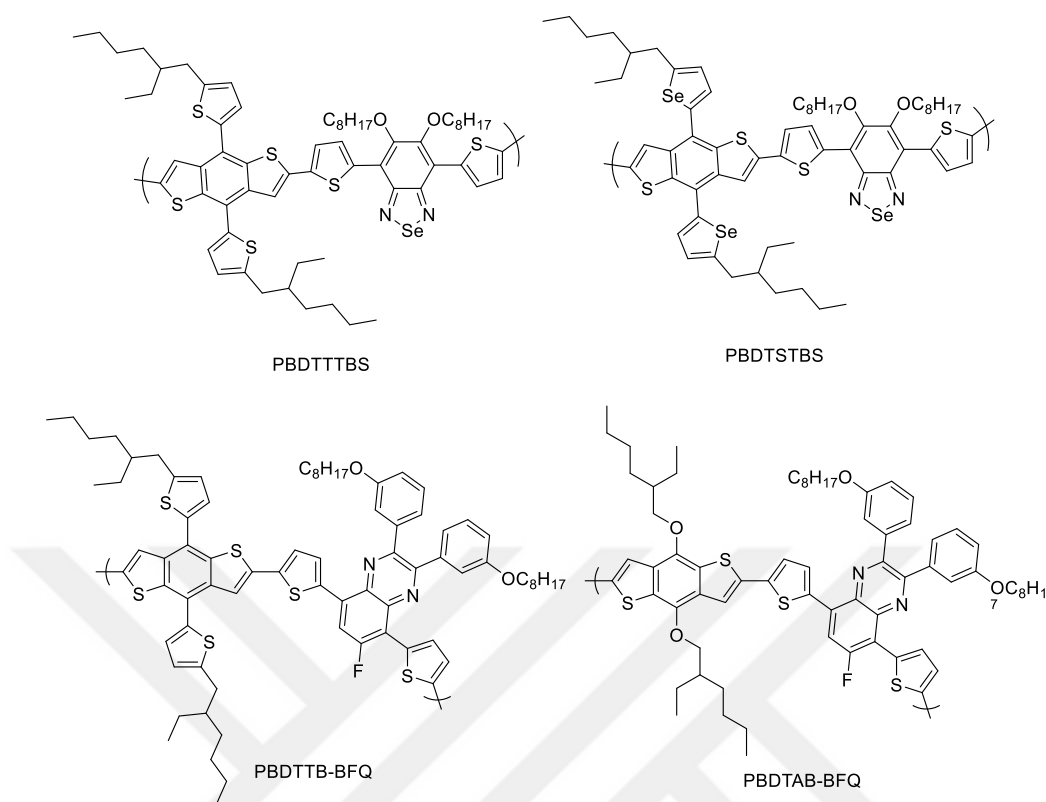


Figure 1.15. Some examples of benzodithiophene based conjugated polymers (continued)

Xu et. al synthesized new conjugated copolymers which consist of BDT moiety with different side groups and monofluorinated Qx moiety. The degree of dimensionality was investigated using alkoxy and alkylthienyl groups for organic solar cells. The photovoltaic results exhibited the best device performance of 5.0% of PCE for PBDTTB-BFQ 2.4% of PCE for PBDTAB-BFQ by utilizing an inverted solar cell device configuration.⁵⁷ Therefore, side-chain engineering can offer an effective method to promote the device efficiencies of organic solar cells.

By combining one donor and one acceptor, the D-A alternating copolymers have shown a significant breakthrough in developing extremely efficient organic solar cell devices. Constructing copolymers with three or more building components that is called as terpolymer, appears innovative and possible to take advantage of the various donors/acceptors' capabilities. The molecular structures of the terpolymers

became more complicated than those of the D-A copolymers when the number of copolymerization monomers expanded to three. In characterizing the properties of the resultant terpolymers, the ratio of the three monomers is especially critical. Kim et al. synthesized a variety of PBDT-DPP-TPD terpolymers with different monomer ratios ($x = 1, 0.9, 0.75, 0.5, 0.25, 0.1$, and 0), and the effect of the random terpolymer composition on electronic and optical properties was examined extensively. The band gaps in the terpolymers consistently began to increase as the TPD content varied from 0 to 100%, while the HOMO levels became deeper at the same time.⁵⁸

1.3 Aim of the Study

Based on this information, benzodithiophene (BDT) based polymers were synthesized and used in solar cell applications. BDT, having a planar and rigid structure, has been extensively used by scientists to produce D-A type conjugated polymers due to highly tunable molecular energy levels and optical band gaps. Furthermore, the BDT unit allows for easier molecular stacking and has high hole mobility, making BDT-based polymers capable of achieving outstanding photovoltaic performances for PSC applications. Meanwhile, backbone modulation, the addition of functional groups to the conjugated backbone and substituents, can manipulate the electronic properties of donor materials, especially bandgap and energy levels. These approaches can be achieved by careful consideration of the molecular design used by synthetic chemists.

A polymer chemist's viewpoint on the research area is brought to this dissertation. By modifying the materials at the molecular level, or molecular engineering, we hope to overcome the limitations of various donor-acceptor type polymers. These structural changes are accomplished by the different approaches, which are covered in more detail in the following chapters.

This thesis aimed to investigate a wide range of polymeric materials containing benzodithiophene (BDT) moiety to construct organic bulk heterojunction solar cells

in order obtaining high power conversion efficiency. The successful molecular design of novel conjugated polymers with benzothiadiazole (BT), quinoxaline (Qx), thienopyrroledione (TPD), benzotriazole (BTz) and isoindigo (IID) acceptor moieties were studied in detail.

In Chapter 2; 2-ethylhexyl selenophene substituted BDT was used as the donor unit and benzo[c][1,2,5]thiadiazole (BT) was selected as the acceptor unit in an investigation of the effects of the fluorine substitution on the benzothiadiazole acceptor moiety. The n-hexylthiophene unit was introduced to the polymer backbone as π -bridges to improve the solubility and photovoltaic performance of benzothiadiazole-based polymers.

In Chapter 3; a series of novel conjugated polymers based on BDT and quinoxaline (Qx) were produced using Stille coupling polymerization to investigate the effect of the π bridge between the D-A groups and side groups attached to BDT moiety.

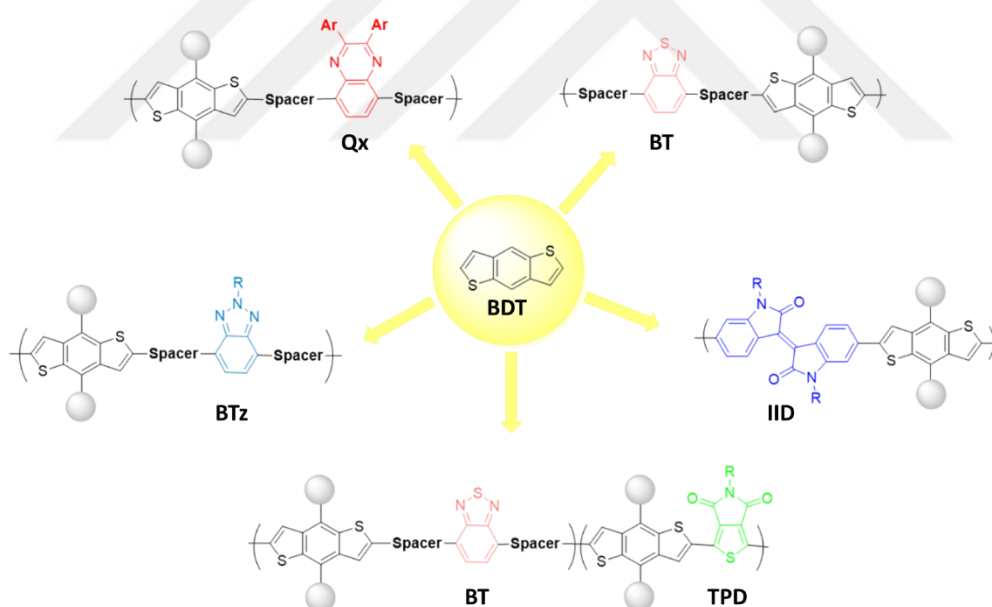


Figure 1.16. Summary of thesis

In Chapter 4; BDT, BT and thienopyrroledione (TPD) were used to synthesize conjugated terpolymers to optimize the backbones of conjugated photovoltaic

polymers. The incorporation of TPD into the donor-acceptor backbone and the effect of the number of fluorine atoms on electrochemical, spectroelectrochemical, and photovoltaic properties of the novel polymers were inspected thoroughly.

In Chapter 5; two-dimensional (2D) BDT and benzotriazole (BTz) were used to synthesize conjugated polymers in order to construct solar cells. Different aromatic side groups (phenyl, thienyl and thienothienyl) were utilized to investigate the effect on the electronic and photovoltaic properties of the conjugated polymers.

In Chapter 6; the structure and photovoltaic relationship were investigated for BDT and isoindigo (IID) based polymers. Four different alternating conjugated polymers were synthesized, and selenophene was utilized as a π -bridge along the conjugation backbone.

The successful molecular design and the detailed studies for the characterization of these polymers were performed in the thesis.

CHAPTER 2

SELENOPHENE SUBSTITUTED BENZODITHIOPHENE AND FLUORINATED BENZOTHIADIAZOLE BASED CONJUGATED POLYMERS

This work was published in the following reference:⁵⁹

Taskaya Aslan, S.; Cevher, D.; Bolayır, E.; Hizalan Ozsoy, G.; Arslan Udum, Y.; Yıldırım, E.; Toppare, L.; Cirpan, A. Synthesis of Selenophene Substituted Benzodithiophene and Fluorinated Benzothiadiazole Based Conjugated Polymers for Organic Solar Cell Applications. *Electrochim. Acta* **2021**, 398 (139298), 1–12.

(Theoretical calculations were performed by Asst. Prof. Erol Yıldırım in this chapter.)

Several conjugated polymers involving electron donor and acceptor units in their main chain backbone or two-dimensional configurations (2-D) have been designed to tune the energy levels and harvest more photons from the solar light. As reported in the literature, lower aromaticity of selenophene with respect to the thiophene results in an improvement in the quinoid character of the polymer, which leads to lower band-gap energy, increased effective conjugation length and enhanced planarity.^{60,61} Selenophene-based materials have also improved conductivity and charge mobility due to larger π -overlap leading to the greater π -orbitals of Se atoms and intermolecular Se-Se interactions.^{53,54} Moreover, the Se atom has a much larger size and less electronegativity than the chalcogenophene homolog of the S atom; as a result, Se comprising polymers are more efficient at broadening the absorption spectrum near the infrared region.^{55,56}

Recent studies have indicated that fluorination of the backbone of conjugated copolymers has been established to construct high-performance BHJ solar cell

devices.^{62,63} Because of the strong electron-withdrawing property, incorporating fluorine atoms into D-A conjugated polymers results in lower HOMO energy levels leading to an increased V_{oc} . Moreover, the non-covalent interaction of fluorine atoms with the adjacent atoms ($F\cdots H/S/F/N$) can cause strong π - π interactions which may induce fine-tuning of its morphology with fullerene. This interaction also may increase the charge mobility and the crystallinity of the active layer resulting in higher J_{sc} and FF.^{64–69}

In the present study, 4,8-bis(5-(2-ethylhexyl)selenophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-Se) was used as the donor unit and 4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole was selected as the acceptor unit in an investigation of the effects of the fluorine substitution on the benzothiadiazole acceptor moiety. According to the literature, incorporating thiophene or other heteroaromatic rings into the D-A polymers can greatly affect the optoelectronic and photovoltaic properties of the organic solar cells (OSCs).^{70–72} Three conjugated polymers based on selenophene substituted BDT and benzothiadiazole building blocks were synthesized and used in OSCs. The n-hexylthiophene unit was introduced to the polymer backbone as π -bridges to improve the solubility and photovoltaic performance of benzothiadiazole-based polymers. Fluorine atoms were included in the benzothiadiazole structure. The effect of the number of fluorine atoms on electrochemical, spectroelectrochemical, and photovoltaic properties of the novel polymers was inspected thoroughly. The change in the morphology of blends with polymers and PCBM was also discussed in this study.

2.1 Experimental

2.1.1 Materials

The starting materials and all reagents were purchased from commercial sources and used without further purification unless stated otherwise. The solvents used during the experiments were dried over common standard methods when needed. All

reactions were performed under a nitrogen atmosphere unless otherwise noted. Column chromatography was carried out with Merck Silica Gel 60 (particle size: 0.063–0.200 mm, 70–230 mesh ASTM) as the stationary phase with different solvent systems for the purification of crude materials.

2.1.2 Instrumentation

Thermal properties were determined by a thermal gravimetric analyzer (Perkin Elmer Pyris 1 Thermogravimetric Analysis(TGA)) and Perkin Elmer Diamond Differential Scanning Calorimeter (DSC) with a heating rate of 10°C/min under N₂. ¹H and ¹³C Nuclear Magnetic Resonance Spectra were obtained via Bruker Spectrospin Avance DPX-400 Spectrometer with regard to trimethylsilane (TMS) as an internal reference. Gel permeation chromatography (GPC) technique (polystyrene as the Standard-Universal Calibration method) was used to determine the average molecular weights of the synthesized polymers PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT in THF via Malvern-OmniSEC. In order to accomplish the spectroelectrochemical studies of PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT, Varian Cary 5000 UV–Vis Spectrometer was used at ambient temperature. Gamry 600 potentiostat was used with a three-electrode consisting of a platinum wire, Ag wire, and Indium Tin Oxide (ITO)-coated glass configuration in 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile (TBAPF₆/ACN) electrolyte/solvent couple at 100 mV/s scan rate to achieve cyclic voltammetry studies of these polymers.

2.1.3 Synthesis of Monomers

2.1.3.1 Synthesis of Compound 2-1

To a solution of selenophene (1.0 g, 7.6 mmol) in dry THF (40 mL) n-BuLi (2.5 M, 3.36 mL, 8.4 mmol) was added at 0°C. After 30 minutes, the mixture was cooled to

-15°C, and 2-ethylhexyl bromide (1.62 g, 8.4 mmol) was added. The mixture was heated to 50°C and stirred for 12 hours. It was then hydrolyzed by the addition of a saturated NH₄Cl solution and extracted with diethyl ether. The organic phase was dried over MgSO₄ and filtered. The organic phase was removed under reduced pressure. The resulting residue was purified by column chromatography over silica gel using hexane/CH₂Cl₂ (20:1) mixture system to give compound 2-1 as a pale yellow oily liquid (1.2 g, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (dd, *J* = 5.6, 1.0 Hz, 1H), 7.13 (dd, *J* = 5.6, 3.6 Hz, 1H), 6.92 (dd, *J* = 3.6, 1.1 Hz, 1H), 2.83 (dd, *J* = 6.8, 0.7 Hz, 2H), 1.59 – 1.52 (m, 1H), 1.42 – 1.27 (m, 8H), 0.89 (t, *J* = 7.4 Hz, 6H).

2.1.3.2 Synthesis of Compound 2-2

N-BuLi (2.5 M, 2.7 mL, 6.8 mmol) was added dropwise to a solution of compound 2-1 (1.24 g, 5.10 mmol) in dry THF (50 mL) at 0°C under argon atmosphere. The temperature of the reaction mixture was raised to 50°C and stirred for 1.5 hours. To the reaction mixture, benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.386 g, 1.7 mmol) was added at 50°C and then stirred at the same temperature for 2 hours. To the reaction mixture, the room temperature was added tin (II) chloride dihydrate (SnCl₂·2H₂O) (3.18 g, 14.1 mmol) in 15% HCl solution (10 mL) and then stirred for 2 hours. The resulting reaction mixture was poured into cold water. The reaction mixture was extracted with diethyl ether, the organic phase was dried over anhydrous MgSO₄, and the solvent was evaporated to give the crude compound as a brown oil. The crude product was then purified by column chromatography on silica gel using hexane as the eluent to afford compound 2-2 as a yellow viscous oil (1.0 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 5.7 Hz, 2H), 7.45 (d, *J* = 5.7 Hz, 2H), 7.40 (d, *J* = 3.7 Hz, 2H), 7.04 (d, *J* = 3.6 Hz, 2H), 2.92 (d, *J* = 6.6 Hz, 4H), 1.69 – 1.60 (m, 2H), 1.50 – 1.31 (m, 16H), 0.97 – 0.92 (m, 12H). ¹³C NMR (100 MHz) δ 153.9, 142.8, 138.8, 136.2, 130.0, 127.6, 127.4, 126.3, 123.6, 42.2, 37.0, 32.5, 29.0, 25.7, 23.1, 14.2, 10.9.

2.1.3.3 Synthesis of Compound 2-3

To a dry two-neck flask filled with argon, compound 2-2 (1.00 g, 1.49 mmol) was dissolved in 25 mL of anhydrous THF. To the solution, n-BuLi (2.5 M, 1.8 mL, 4.46 mmol) was added dropwise at 0°C. The reaction mixture was stirred for 40 min. at room temperature. The reaction mixture was then cooled to 0°C, and trimethyltin chloride (1.0 M, 4.8 mL, 4.76 mmol) was added via a syringe at once. The reaction mixture was stirred at 0°C for 20 min and then at room temperature for 2 h. To the reaction mixture was added 50 mL of water and then extracted with diethyl ether. The organic phase was dried with anhydrous MgSO₄ and concentrated under a vacuum to give a yellow viscous crude product. Further purification of the compound was achieved by recrystallization from isopropyl alcohol (1.1 g, 74%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 2H), 7.43 (d, *J* = 3.7 Hz, 2H), 7.05 (d, *J* = 3.7 Hz, 2H), 2.93 (dd, *J* = 6.3, 3.9 Hz, 4H), 1.73 – 1.61 (m, 2H), 1.52 – 1.29 (m, 16H), 0.99 – 0.89 (m, 12H), 0.39 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 153.6, 143.6, 143.1, 142.3, 137.1, 137.0, 131.3, 129.8, 127.5, 42.3, 37.1, 32.5, 29.0, 25.9, 23.1, 14.2, 11.0, -8.3.

2.1.3.4 Synthesis of Compound 2-4

Benzothiadiazole (2.50 g, 18.4 mmol) was dissolved in 30 mL of HBr. A mixture of Br₂ (3.0 mL, 55 mmol) and 15 mL of HBr was added dropwise to the reaction flask. The temperature was increased to 120°C and the reaction was continued for 16 hours. The reaction was then brought to room temperature and saturated NaHSO₃ solution was added. The mixture was precipitated by pouring into water and filtered. The solid remaining on the filter was washed sequentially with plenty of water and diethyl ether. After drying in the oven, dark yellow solid was obtained (3.9 g, 72%). ¹H-NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ 152.7, 132.4, 114.3.

2.1.3.5 Synthesis of Compound 2-5

3-hexylthiophene (2.00 g, 11.9 mmol) and 30 mL of distilled tetrahydrofuran were flaked. The reaction medium was brought to -78°C with the help of dry ice. In an argon atmosphere, n-butyl lithium (in 2.0 M hexane, 5.2 mL, 12.9 mmol) was added dropwise to the reaction medium. After the addition was complete, the reaction was brought to room temperature. After 2 hours the temperature was brought back to -78°C and tributyltin chloride (3.50 mL, 12.9 mmol) was added slowly. After addition, the reaction continued for 20 hours at room temperature. After evaporation of the reaction solvent, brine was added and extraction was done with dichloromethane. The organic phase was dried with MgSO_4 and the solvents were removed in a rotary evaporator. It was used in the next reaction (NMR yield 80%) without further purification.

2.1.3.6 Synthesis of Compound 2-6

In an argon atmosphere, compound 2-4 (0.28 g, 0.95 mmol) and compound 2-5 (1.10 g, 2.41 mmol) were taken in a two-neck flask and dissolved in 15 mL of THF. After addition of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.034 g, 0.048 mmol), the temperature was brought to 70°C and the reaction was continued for 16 hours. The solvent was evaporated with rotary evaporator and the residue was purified by column chromatography on silica gel using hexane/chloroform (2:1). Compound 2-6 was obtained as an orange solid (79%). ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 1.2$ Hz, 2H), 7.82 (s, 2H), 7.04 (d, $J = 1.1$ Hz, 2H), 2.69 (t, $J = 7.7$ Hz, 4H), 1.80 – 1.63 (m, 4H), 1.54 – 1.20 (m, 12H), 0.90 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.6, 144.4, 135.1, 129.0, 125.9, 125.5, 121.6, 31.7, 30.5, 27.7, 22.7, 21.2, 14.1.

2.1.3.7 Synthesis of Compound 2-7

Compound 2-6 (0.202 g, 0.431 mmol) was dissolved in 20 ml distilled THF. The reaction flask was sealed with aluminum foil to provide a dark environment. NBS (0.169 g, 0.949 mmol) was added in small portions. The reaction was continued at room temperature for 8 hours. The THF was then removed and extracted with NH_4Cl solution and DCM. The organic phase was dried over anhydrous MgSO_4 , and the solvent was evaporated to give the crude compound. The crude product was then purified by column chromatography on silica gel using hexane as eluent to yield compound 2-7 as a red solid (0.205 g, 76%). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (s, 2H), 7.64 (s, 2H), 2.62 (t, $J = 7.7$ Hz 4H), 1.74-1.61 (m, 4H), 1.44-1.29 (m, 12H), 0.98-0.84 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 143.0, 138.5, 128.01, 125.2, 124.7, 111.6, 31.7, 29.7, 29.7, 29.0, 22.7, 14.1.

2.1.3.8 Synthesis of Compound 2-8

Commercially available 4-fluoro-1,2-phenylenediamine (1.00 g, 7.93 mmol) was taken into a two-neck flask and CHCl_3 (20 mL) and triethylamine (4.40 ml, 31.7 mmol) were added to the reaction flask. The reaction mixture was stirred until completely dissolved. The solution was placed in an ice bath and SOCl_2 (1.16 ml, 15.8 mmol) was added slowly. After addition, it was stirred at 70°C for 8 hours. After the reaction was cooled to room temperature, water was added and dichloromethane was used to extract the crude. The organic phase was dried with MgSO_4 and the solvent was removed by rotary evaporation. Compound 2-8 was obtained by column chromatography on silica gel using hexane/DCM (1:3) as the eluent to afford a pale yellow solid (0.92 g, 75%). ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J_{\text{HF}} = 9.5$ Hz, $J = 5.2$ Hz, 1H), 7.61 (dd, $J = 8.7$, 2.5 Hz, 1H), 7.43 (ddd, $J_{\text{HF}} = 9.5$ Hz, $J = 8.7$, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.5 (d, $^1J_{\text{CF}} = 253.0$ Hz), 154.9 (d, $^3J_{\text{CF}} = 14.2$ Hz), 152.0, 122.5 (d, $^3J_{\text{CF}} = 10.8$ Hz), 121.4 (d, $^2J_{\text{CF}} = 29.4$ Hz), 104.8 (d, $^2J_{\text{CF}} = 23.8$ Hz).

2.1.3.9 Synthesis of Compound 2-9

Br₂ (2.3 mL, 45.4 mmol) in 10 mL HBr was added slowly into 5-fluoro-2,1,3-benzothiadiazole (0.70 g, 4.54 mmol) and HBr (20 mL) mixture. Then, the reaction was heated at 120°C for 2 days. After the reaction was completed, saturated NaHSO₃ solution was added. The mixture was poured into water and solid was filtered. After recrystallization with ethanol, the product was obtained as yellow solid (0.74 g, 52%). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J*_{HF} = 8.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 157.7 (d, ¹*J*_{CF} = 255.6 Hz), 150.3 (d, ³*J*_{CF} = 7.1 Hz), 147.9, 121.4 (d, ²*J*_{CF} = 32.1 Hz), 111.6 (d, ³*J*_{CF} = 11.5 Hz), 95.8 (d, ²*J*_{CF} = 24.3 Hz).

2.1.3.10 Synthesis of Compound 2-10

In a 250 mL flame-dried 2-neck round-bottom flask with a condenser, compound 2-9 (0.35 g, 1.12 mmol), excess of compound 5 (1.17 g, 2.55 mmol) and 20 mL of dry THF were added. After the mixture was purged with nitrogen for 30 min, bis(triphenylphosphine)palladium(II) dichloride (PdCl₂(PPh₃)₂) (0.039 g, 0.056 mmol) was added and the heat of the resultant mixture was increased to reflux temperature. The reaction mixture was stirred for 24 hours and then cooled to room temperature. The solvent of the reaction was evaporated and the crude product was purified by column chromatography with hexane/dichloromethane (1:1) as eluent. The organic solvent was evaporated and the final product was recrystallized from isopropyl alcohol as orange solid (0.39 g, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 2H), 7.97 (s, 1H), 7.71 (d, *J*_{HF} = 13.0 Hz, 1H), 7.14 (s, 1H), 7.08 (s, 1H), 2.70 (dd, *J* = 15.7, 7.9 Hz, 4H), 1.77-1.49 (m, 8H), 1.46-1.20 (m, 8H), 0.96-0.73 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 157.2 (d, ¹*J*_{CF} = 253.6 Hz), 151.8 (d, ³*J*_{CF} = 11.1 Hz), 148.1, 142.83, 141.8, 135.9, 130.5 (d, ⁴*J*_{CF} = 5.5 Hz), 129.8 (d, ³*J*_{CF} = 7.9 Hz), 128.2, 124.2 (d, ³*J*_{CF} = 11.2 Hz), 121.2 (d, ⁴*J*_{CF} = 7.0 Hz), 121.0, 115.0 (d, ²*J*_{CF} = 32.4 Hz), 109.6 (d, ²*J*_{CF} = 15.5 Hz), 30.1, 30.0, 28.9, 28.9, 28.8, 27.4, 27.4, 21.0, 12.4.

2.1.3.11 Synthesis of Compound 2-11

A solution of compound 10 (0.250 g, 0.514 mmol) was dissolved in 25 ml of distilled THF. NBS (0.183 g, 1.027 mmol) was added in the dark. The reaction was terminated by stirring at room temperature for 6 hours. After removal of THF, extraction was carried out with brine and DCM. Recrystallization from isopropyl alcohol gave an orange solid (49%). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.76 (s, 1H), 7.67 (d, $J_{\text{HF}} = 13.0$ Hz, 1H), 2.65 (dd, $J = 15.3, 7.5$ Hz, 4H), 1.70 – 1.64 (m, 4H), 1.44 – 1.30 (m, $J = 2.4$ Hz, 12H), 0.99 – 0.81 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.7 (d, $^1J_{\text{CF}} = 254.9$ Hz), 152.7 (d, $^3J_{\text{CF}} = 9.3$ Hz), 149.2, 143.1, 142.3, 136.9 (d, $^4J_{\text{CF}} = 2.7$ Hz), 132.1 (d, $^4J_{\text{CF}} = 5.9$ Hz), 130.9 (d, $^3J_{\text{CF}} = 9.8$ Hz), 128.6, 124.7 (d, $^3J_{\text{CF}} = 10.9$ Hz), 115.6 (d, $^2J_{\text{CF}} = 32.4$ Hz), 113.3 (d, $^4J_{\text{CF}} = 8.9$ Hz), 113.1, 110.5 (d, $^2J_{\text{CF}} = 14.9$ Hz), 31.7, 29.8, 29.7, 29.6, 29.6, 29.0, 22.7, 14.2.

2.1.3.12 Synthesis of Compound 2-12

To a round bottom flask was added 1,2-diamino-4,5-difluorobenzene (1.22 g, 8.46 mmol), CHCl_3 (50 mL) and triethylamine (4.72 mL, 33.86 mmol). The solution was stirred until 1,2-diamino-4,5-difluorobenzene was completely dissolved. SOCl_2 (2.0 g, 1.23 mL, 16.93 mmol) was added drop wise and the mixture was heated to boiling for 5 hours. The mixture was then cooled to room temperature and extracted with CH_2Cl_2 (100 mLx3). The organic phase was combined and dried over MgSO_4 . The solvent was evaporated and column chromatography using hexane/ethyl acetate (1:4) as the eluent gave white snow-like crystalline compound 2-12 (1.05 g, 72%). ^1H NMR (400 MHz, CDCl_3) δ 6.52 (t, $J_{\text{HF}} = 9.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.8 (dd, $^1J_{\text{CF}} = 260.2, ^2J_{\text{CF}} = 20.1$ Hz), 150.8 (t, $^{3,4}J_{\text{CF}} = 5.6$ Hz), 106.1 (dd, $^3J_{\text{CF}} = 14.9, ^4J_{\text{CF}} = 6.8$ Hz).

2.1.3.13 Synthesis of Compound 2-13

To a solution of compound 2-12 (1.02 g, 5.95 mmol) in concentrated H₂SO₄ (60 mL) N-bromosuccinimide (NBS) (4.24 g, 23.82 mmol) was added in three portions. The reaction mixture was heated to 70°C and stirred for 4 hours by sealing the reaction flask with aluminum foil to protect it from light. The reaction mixture was cooled to room temperature, and poured into an ice-water mixture to give a large white precipitate. The resulting solid was filtered off, washed with water and then dried. Purification was then carried out by recrystallization from isopropyl alcohol to afford compound 2-13 as a white wool solid (1.0 g, 50%). ¹³C NMR (CDCl₃, 100 MHz) δ 151.9 (dd, ¹J_{CF} = 261.5 Hz, ²J_{CF} = 21.3 Hz) 148.9 (t, ^{3,4}J_{CF} = 2.2 Hz) 99.5 (dd, ²J_{CF} = 14.4 Hz, ³J_{CF} = 9.0 Hz).

2.1.3.14 Synthesis of Compound 2-14

To a 250 mL dried flask with condenser, compound 2-13 (0.354 g, 1.07 mmol), compound 2-5 (1.35 g, 2.36 mmol) and 50 mL of dry toluene were charged and argon gas was introduced into the reaction mixture for 40 minutes. Pd(PPh₃)₄ (8.7 mg, 7.5 mmol) was then added and the reaction mixture was stirred at 110°C for 5 days. The reaction mixture was cooled to room temperature and the solvent was evaporated. The crude orange product was subjected to column chromatography with hexane/CH₂Cl₂ (5:1) as eluent to give compound 2-14 as a light orange solid (0.287 g, 52%). ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 2H), 7.21 (s, 2H), 2.72 (t, *J* = 7.6 Hz, 4H), 1.75 – 1.66 (m, 4H), 1.43 – 1.30 (m, 12H), 0.90 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 149.8 (dd, ¹J_{CF} = 259.4 Hz, ²J_{CF} = 20.3 Hz), 148.9 (t, ^{3,4}J_{CF} = 4.2 Hz), 143.7, 132.2 (t, ^{3,4}J_{CF} = 3.8 Hz), 131.2, 123.9 (t, ^{3,4}J_{CF} = 2.6 Hz), 111.7 (dd, ²J_{CF} = 14.4 Hz, ³J_{CF} = 9.0 Hz), 31.7, 30.5, 30.5, 29.0, 22.6, 14.1.

2.1.3.15 Synthesis of Compound 2-15

To a round flask compound 2-14 (0.26 g, 0.52 mmol) and NBS (0.184 g, 1.03 mmol) were added in 70 mL chloroform. After stirring at room temperature for 18 hours, the solvent was removed and the crude material was purified by column chromatography with hexane/CH₂Cl₂ (1:1) to give compound 2-15 as an orange solid (0.320 g, 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 2H), 2.56 (t, *J* = 7.7 Hz, 4H), 1.62 – 1.52 (m, 4H), 1.36 – 1.22 (m, 12H), 0.83 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 149.4 (dd, ¹*J*_{CF} = 260.3 Hz, ²*J*_{CF} = 20.3 Hz), 148.1 (t, ^{3,4}*J*_{CF} = 4.1 Hz), 142.5, 131.5 (t, ^{3,4}*J*_{CF} = 4.7 Hz), 131.2, 114.5 (t, ^{3,4}*J*_{CF} = 3.7 Hz), 110.7 (dd, ²*J*_{CF} = 8.2 Hz, ³*J*_{CF} = 4.6 Hz), 31.7, 29.7, 29.5, 29.0, 22.7, 14.1.

2.1.4 Synthesis of Polymers

2.1.4.1 Synthesis of PBDTSe-BT

Compound 2-3 (0.15 g, 0.15 mmol) and compound 2-7 (94 mg, 0.15 mmol) were dissolved with 15 mL of toluene and 40 minutes of argon gas passed and PdCl₂(PPh₃)₂ (5.3 mg, 7.5 μmol) catalyst was added. The reaction mixture was heated to reflux and stirred for 42 h. Tributyl (thiophen-2-yl) stannane (0.118 g, 0.3 mmol) was added and stirred for a further 4 hours, followed by the addition of 2-bromo thiophene (0.05 g, 0.3 mmol) for 4 hours. The reaction mixture was then brought to room temperature and the polymer was precipitated by the addition of 50 mL of methanol. The precipitate was then extracted with Soxhlet with methanol, hexane, and chloroform. The polymer in the chloroform fraction was recovered as a purple solid by precipitation from methanol. The solid was dried under vacuum (120 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 8.21 – 6.45 (Aromatic H), 2.95 (-CH₂), 1.88 – 0.61 (-CH₂, -CH₃).

2.1.4.2 Synthesis of PBDTSe-FBT

The same procedure was performed for PBDTSe-FBT using compound 2-3 (0.15 g, 0.15 mmol) and compound 2-11 (97 mg, 0.15 mmol) and the purple polymer was obtained from chloroform fraction (126 mg, 72%). ^1H NMR (400 MHz, CDCl_3) δ 8.28 – 6.38 (Aromatic H), 2.96 (-CH₂), 1.98 – 0.66 (-CH₂, -CH₃).

2.1.4.3 Synthesis of PBDTSe-FFBT

The same procedure was performed for PBDTSe-FFBT using compound 2-3 (0.15 g, 0.15 mmol) and compound 2-15 (0.1 g, 0.15 mmol) and the purple polymer was obtained from chlorobenzene fraction (70 mg, 39%).

2.1.5 Computational Methods

Density functional theory (DFT) calculations were conducted for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT using tight convergence criteria in Gaussian09.Rev. A.02 software package at the B3LYP hybrid functional and 6-311G(d) basis set level, similar to the recent studies that have concordant results with the experimental studies.^{73–80} Calculations were performed on model tetramer structures with four donors, four acceptors and eight bridge structures. Hexyl side chains on the thiophene bridges and 2-ethylhexyl units on donor were replaced with methyl groups in calculations not to exceed our computational capacity. Geometry optimizations were started from different initial conformations by altering the dihedral angle between consecutive repeating donor, acceptor and bridging units. Electrostatic potential surface (ESP), first three highest occupied molecular orbitals (HOMO, HOMO-1, HOMO-2), and three lowest unoccupied molecular orbitals (LUMO, LUMO+1, LUMO+2) were mapped onto the optimized model structures. Direct band gap (E_g) was calculated calculation of energy difference between the HOMO and LUMO for the optimized ground state, and the optical E_g^{opt} was

determined by the $S_0 \rightarrow S_1$ transition, the first vertical excitation energy of the singlet excited state obtained by time-dependent density-functional theory (TDDFT). Vertical ionization potential (VIP) and vertical electron affinity (VEA) in addition to the adiabatic ionization potential (AIP), and adiabatic electron affinity (AEA) were also calculated by considering the transition from the neutral ground state to the charged structures at the ground state geometry and optimized charged geometries for cation and anions, respectively. Hole reorganization energies (λ_{reorg}) were determined based on Bredas *et al.*⁸¹ formulation. The total atomic charges (δ) on the acceptor units based on the ESP fitting method of Merz-Kollman (MK),⁸² dipole moment (μ), isotropic dipole (α) polarizability, anisotropy ($\Delta\alpha$) of the polarizability and first order hyperpolarizability (β) were calculated to elucidate experimental observations.

2.1.6 Fabrication of Photovoltaic Devices

Organic solar cell parameters for the PBDTSe-BT, PBDTSe-FBT, and PBDTSe-FFBT were investigated with the device structure of ITO/PEDOT:PSS/Polymer:PC₇₁BM/LiF/Al. The construction of the BHJ solar cell device was as follows; etching and cleaning of ITO, coating of the PEDOT:PSS, coating of the active layer and evaporating the metal. ITO coated glass substrates purchased from Visiontek were etched using an acid solution. The substrates were sonicated in an ultrasonic bath, respectively, using toluene, detergent (Hellmanex), water and isopropyl alcohol for 15 minutes. The substrates were dried with an N₂ gun after that O₂ plasma treatment was used to enhance the work function of ITO via removing organic impurities as well as to reduce the surface tension of ITO. PEDOT:PSS was filtered through a 0.45 μm PES syringe filter and coated on the ITO surface. Subsequently, the substrates were annealed at 135°C for 15 minutes on the hot plate to evaporate the residual water. Polymer:PC₇₁BM mixtures were prepared with different weight ratios, concentrations and additives, filtered through a 0.22 μm pore-sized PTFE syringe filter and coated on a PEDOT:PSS layer in the nitrogen-filled

glove box. Lastly, the devices were completed by thermal evaporation of LiF and Al metal in a vacuum evaporation chamber on the Polymer:PC₇₁BM layer. After the device construction, the current density voltage characteristics were tested using the Keithley 2400 under the Atlas Material Testing Solutions solar simulator (AM 1.5G).

2.2 Results and Discussion

2.2.1 Synthesis and Characterization of BDT and BT Based Polymers

The structure of the polymer and the structures of the modified donor and acceptor units required for their synthesis are given below. All the intermediates and monomers were synthesized according to the given references. In our synthetic design, 2-ethylhexylselenophene substituted benzodithiophene and fluorinated benzothiadiazole derivatives were taken as the donor and acceptor units, respectively. The synthetic route for the donor compound is given in Figure 2.1. Commercially available selenophene was reacted with commercial 2-ethylhexylbromide in the presence of *n*-butyl lithium to obtain compound 2-1. After that, the synthesis of compound 2-2 was achieved in high yield by the reaction of benzo[1,2-b:4,5-b']dithiophene-4,8-dione with lithium derivative of compound 2-1⁸³ followed by reduction of the corresponding diol with stannous chloride dihydrate in hydrochloric acid solution. The lithiation of compound 2-2 with *n*-buthyl lithium followed by quenching the lithium derivative with trimethyltin chloride resulted in the monomer compound 2-3 successfully.⁸³

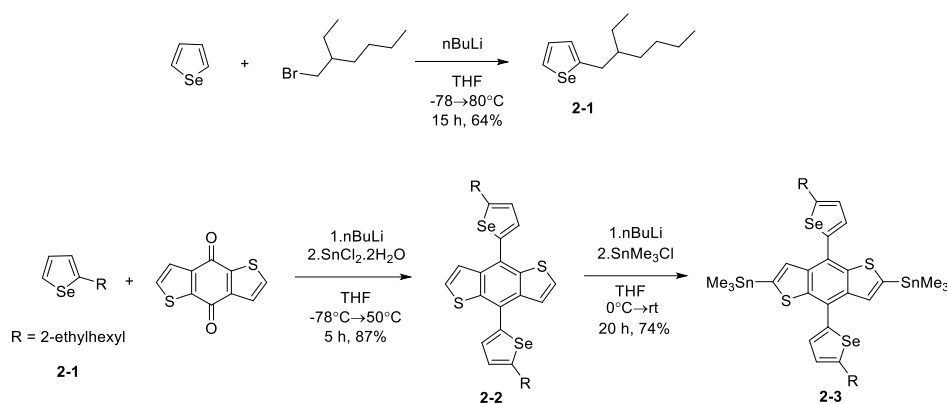


Figure 2.1. Synthetic pathway of donor monomer

The detailed synthetic routes followed for the acceptor compounds 2-7, 2-11, and 2-15 are given in Figure 2.2. Compound 2-4⁸⁴ and Compound 2-5⁸⁵ were synthesized according to previously reported procedures. The Stille cross-coupling reaction between compound 2-4 and compound 2-5 afforded compound 2-6, which was treated with N-bromosuccinimide to yield compound 7⁸⁶. The diamine derivatives of mono fluorinated and difluorinated benzene were purchased commercially. The ring closure reactions were performed with thionyl chloride to obtain compound 2-8 and compound 2-12. The halogenation reactions were performed according to the procedures reported in the literature.^{85,87} The treatment of compounds 2-9 and 2-13⁸⁸ with tributyl (thiophen-2-yl)stannane (2-5) under Stille coupling reaction conditions produced the target molecules 2-10 and 2-14 which were brominated with N-bromosuccinimide to yield target monomers 2-11 and 2-15.^{88,89}

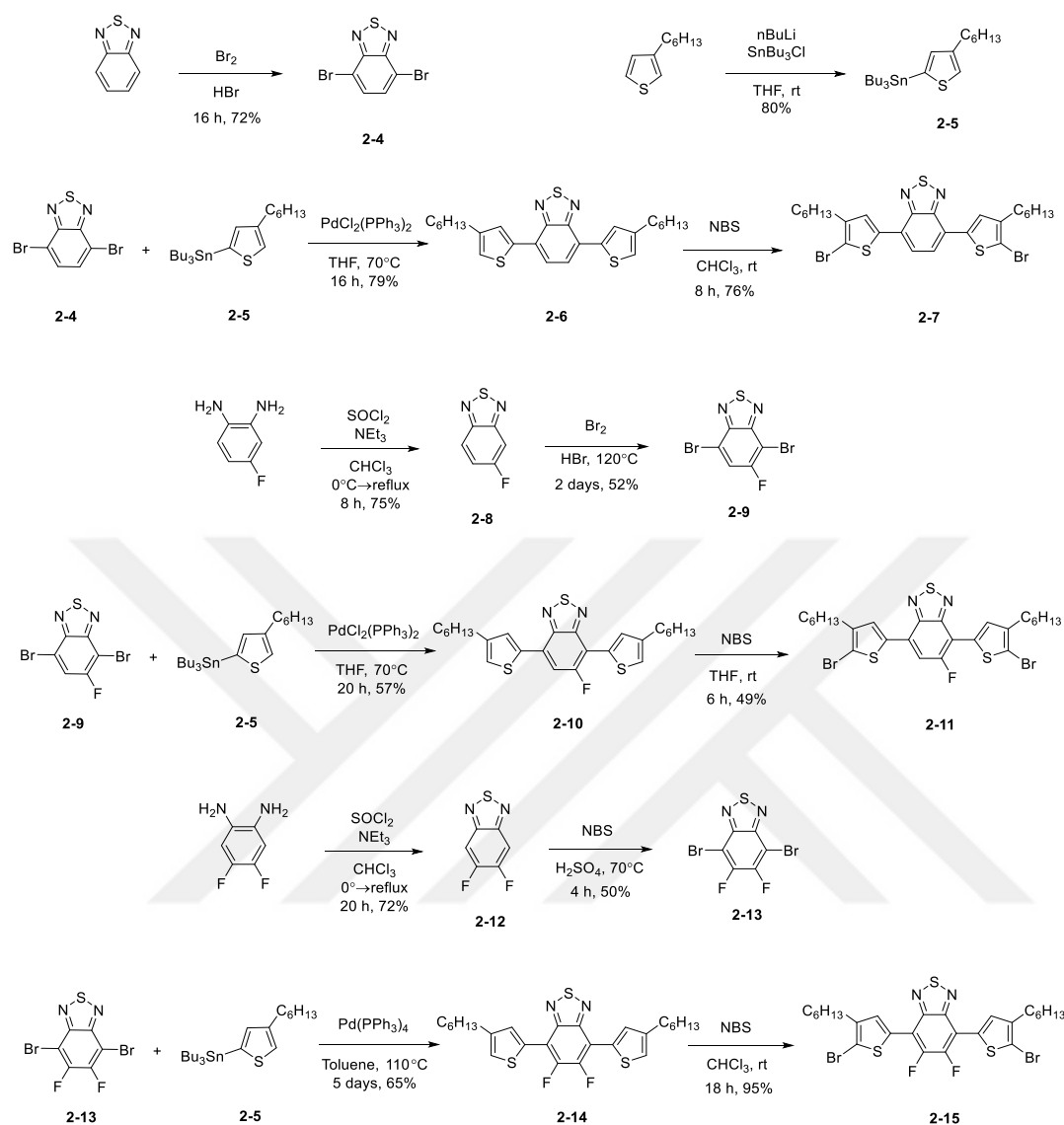


Figure 2.2. Synthetic pathway of acceptor monomers

The routes for the synthesis of three polymers are shown in Figure 2.3. PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT were prepared via typical Stille cross-coupling reaction between organotin monomer of BDT (2-3) and bromothiophene flanked benzothiadiazole derivatives (2-7, 2-11 and 2-15) using tetrahydrofuran as solvent and bis(triphenylphosphine)palladium(II) dichloride ($\text{PdCl}_2(\text{PPh}_3)_2$) as the catalyst.

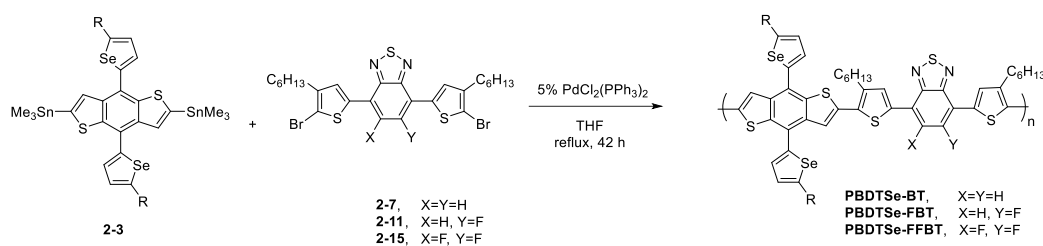


Figure 2.3. Synthetic pathway of polymers

The gel permeation chromatography (GPC), which measured the molecular weights and polydispersity index (PDI) of the three polymers are displayed in Table 2.1. All polymers show good solubility in chloroform, chlorobenzene (CB) and other common solvents, which are favorable for film fabrication.

Table 2.1 Summary of GPC and TGA studies

	<i>M_n/kDa</i>	<i>M_w/kDa</i>	<i>PDI</i>	<i>T_d[*]/°C</i>
PBDTSe-BT	8.7	29.6	3.4	443
PBDTSe-FBT	10.1	29.7	2.9	437
PBDTSe-FFBT	13.5	91.7	6.8	400

*corresponding to 5% weight loss in the thermogravimetric analysis

2.2.2 Thermal Studies of BDT and BT Based Polymers

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were utilized to determine the thermal properties of the polymers. PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT have good thermal stability with degradation temperatures over 400°C, which are sufficient for the application in an organic solar cell. The TGA measurements showed that 5% weight loss degradation temperatures (*T_d*) of PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT were 443°C, 437°C and 400°C, respectively. The synthesized polymers did not display any phase transition up to 300°C.

2.2.3 Computational Results of BDT and BT Based Polymers

HOMO, HOMO-1, HOMO-2 orbital surfaces given in Figure 2.4.a-c showed that HOMO orbitals were distributed along the chain similar to previous studies.^{68,69,71} LUMO orbitals were highly localized on the acceptor groups. LUMO, LUMO+1 and LUMO+2 are positioned on different acceptor units due to different chemical environments in the middle part and end groups of the tetramers which is also valid for HOMO, HOMO+1 and HOMO+2 frontier orbitals showing a complementary behavior along the chain. Although their distribution for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT looks similar, there are small differences in the details. LUMO orbitals were extended to the fluorine atoms in the acceptor unit for PBDTSe-FBT and PBDTSe-FFBT. In addition, the extension of HOMO orbitals on the acceptor units has a different shape and distribution for different copolymers. The difference in the electron density distribution can be seen more clearly from the ESP surface mapped onto the model structures where electron rich sites were concentrated on the donor and bridge groups, displayed in red color, while electron deficient sites were concentrated on the acceptor and alkyl side chains, displayed in blue color (Figure 2.4.d-f). Weak extension of electron rich sites on the PBDTSe-BT acceptor, especially on its phenyl group of benzothiadiazole, was not observed after fluorine substitution in PBDTSe-FBT and PBDTSe-FFBT. Both phenyl and thiadiazole rings donate electrons upon the substitution of fluorine atoms which leads to the enhanced acceptor capacity for the fluorine substituted benzothiadiazole unit in the polymer backbone (Figure 2.4.g-i).

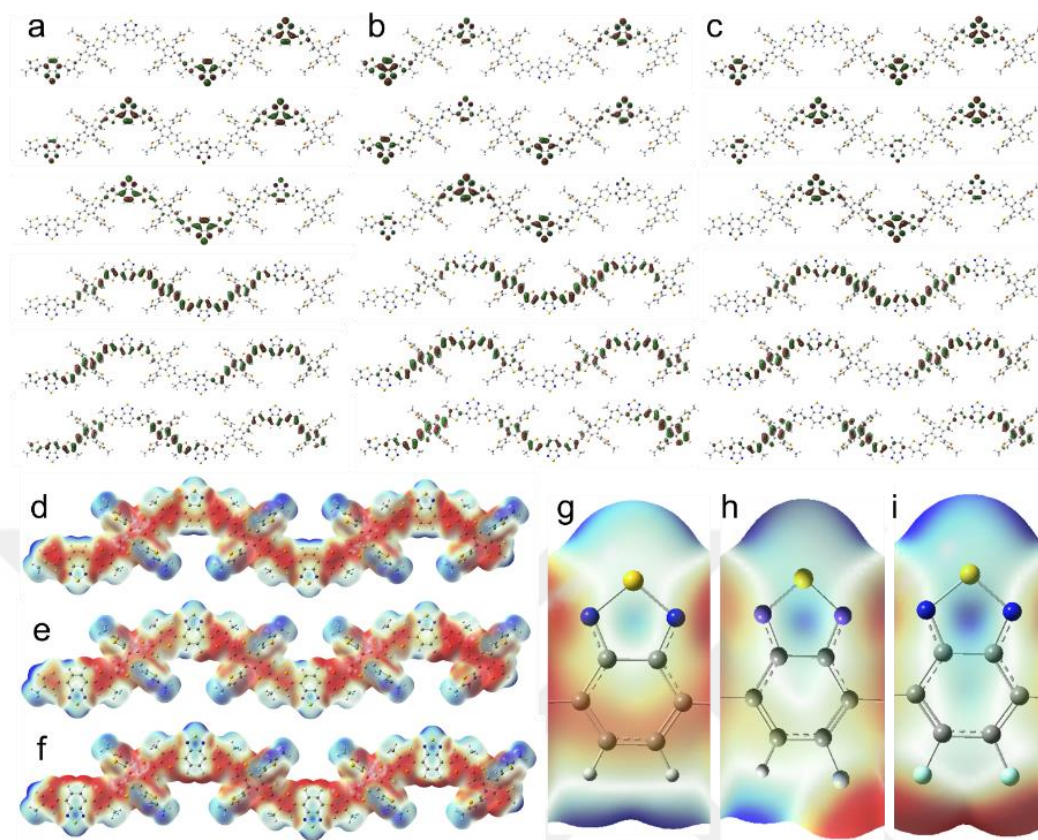


Figure 2.4. Frontier molecular orbital surfaces (from top to down: LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2) for a) PBDBTSe-BT, b) PBDBTSe-FBT, c) PBDBTSe-FFBT and electrostatic potential surface (ESP) for the d) PBDBTSe-BT, e) PBDBTSe-FBT, f) PBDBTSe-FFBT tetramers. ESP for the acceptor units in the middle of the chain for g) PBDBTSe-BT, h) PBDBTSe-FBT, i) PBDBTSe-FFBT

DFT calculations showed that HOMO energies have more negative values by incorporation of the fluorine atoms as observed experimentally that is relevant for the enhanced V_{OC} values. LUMO levels also have lower values that result in the close band gap values for polymers where PBDBTSe-FBT has slightly lower band gap values. Although calculations predicted close E_g^{opt} values with experiments, there is a difference in their order at experimental and theoretical results which is mainly due to the molecular weight difference and lack of intermolecular interactions in the computational results that can affect electronic structure by fluorine substitution. Vertical and adiabatic ionization potentials (VIP and AIP) were increased and

electron affinities (VEA and AEA) were decreased due to improved electronegativities by fluorine incorporation. Hole reorganization energies (λ_{reorg}) that indicate ease of hole mobility along the chain were low for all chains and slightly improved by fluorine incorporation. The most significant change was observed in the delocalization or resonance energy (π_{del}) where fluorine substitution decreased π -electron energy in the conjugated polymer backbone, particularly from the benzodithiophene acceptor rings. This is supported by the electrostatic potential surfaces in Figure 2.4. This hypothesis was tested by the calculation of the total average atomic charges on the acceptor. The average total atomic charge on acceptor units (δ_{Acceptor}) obtain more negative value by fluorine substitution. However, total atomic charges only on the acceptor ring excluding hydrogens and fluorine atoms are increasing and became a positive number as given in parenthesis which indicates improved acceptor potential. Although fluorine atoms attracted electrons from other units and increase overall electron density on the acceptor unit, this electron density is concentrated on the fluorine atoms and total electron density on the acceptor ring is decreased. The average torsional angle between acceptor and bridging units (θ (A-B)) presented that planarity of the chains was improved by fluorine substitution that can lead to the increased quinoid character, better chain packing leading to the enhanced intra-charge transport and inter-chain hopping.⁹⁰ It should be noted that the two sides of PBDTSe-FBT acceptor were not identical where the fluorine side has a lower dihedral angle compared to the side hydrogen side. This asymmetrical structure of PBDTSe-FBT leads to the higher dipole moment (μ), static polarizability (α) and anisotropy in the polarizability ($\Delta\alpha$) compared to PBDTSe-BT and PBDTSe-FFBT. First order hyperpolarizability (β) which is a measure for the induced dipole formation in an electric field that was reported as an indication for decreased bond length alternation in conjugated chains with higher β values.^{75,91} Increasing β values by fluorine substitution points out enhanced donor, bridge and acceptor unit coupling with lower bond length alternation.

Table 2.2 Results of DFT calculations for the structural and electronic properties of PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT tetramers. (Energies are in eV, dipole moments are debye, polarizabilities are in a.u.)

	<i>HOMO</i>	<i>LUMO</i>	E_g	E_g^{op}
PBDTSe-BT	-4.98	-2.98	-2	1.68
PBDTSe-FBT	-5.01	-3.04	-1.97	1.66
PBDTSe- FFBT	-5.05	-3.07	-1.99	1.68
	<i>VIP</i>	<i>AIP</i>	<i>VEA</i>	<i>AEA</i>
PBDTSe-BT	5.44	5.36	-2.5	-2.55
PBDTSe-FBT	5.46	5.39	-2.56	-2.6
PBDTSe- FFBT	5.51	5.44	-2.59	-2.63
	λ_{reorg}	π_{del}	$\delta_{Acceptor}$	$\theta (A-B)$
PBDTSe-BT	0.142	5320	0.07 (-0.30)	8.79
PBDTSe-FBT	0.139	3734	-0.02 (-0.09)	3.76
PBDTSe- FFBT	0.138	540	-0.13 (0.11)	1.7
	μ	α	$\Delta\alpha$	β
PBDTSe-BT	0.16	3778	5263	14978
PBDTSe-FBT	7.26	3801	5328	18361
PBDTSe- FFBT	0.29	3787	5299	23409

2.2.4 Electrochemical Properties of BDT and BT Based Polymers

The cyclic voltammetry (CV) measurements were executed for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT between the suitable potentials to investigate the redox performances of the resulted polymers at a constant 100 mV/s scan rate at room temperature. The experimental study of CV was conducted via a three-electrode setup in which indium tin oxide (ITO) was used as the working electrode, Ag wire as the reference electrode and Pt as the counter electrode. Acetonitrile (ACN) was the solvent and tetrabutylammoniumhexafluorophosphate (TBAPF₆) was the supporting electrolyte during the measurements. Doping/dedoping potentials, onset oxidation potentials (E_{onset}^{ox}) and onset reduction potentials (E_{onset}^{red}) of polymers were explored from the cyclic voltammograms. As depicted in Figure 2.5, all polymers showed both p-dopable and n-dopable character. All the electrochemical properties were summarized in Table 2.3. The E_{onset}^{ox} were measured as 0.5 eV, 0.77 eV and 0.81 eV while E_{onset}^{red} were detected as -1.09 eV, -0.93 eV and -1.16 eV for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT respectively. The electron-withdrawing nature of the fluorine atom may be the result of the variation in the oxidation potential of the polymers. These electron-withdrawing effect results in lower electron density on benzothiadiazole moiety in the polymer backbone of PBDTSe-FBT and PBDTSe-FFBT. Therefore, doping/dedoping processes occur at higher oxidation potentials. Moreover, high occupied molecular orbital (HOMO) and low occupied molecular orbital (LUMO) energy levels were deduced from the onset oxidation potentials and onset reduction potentials of the corresponding polymers according to the following equations;

$$HOMO = -(4.75 + E_{onset}^{ox})$$

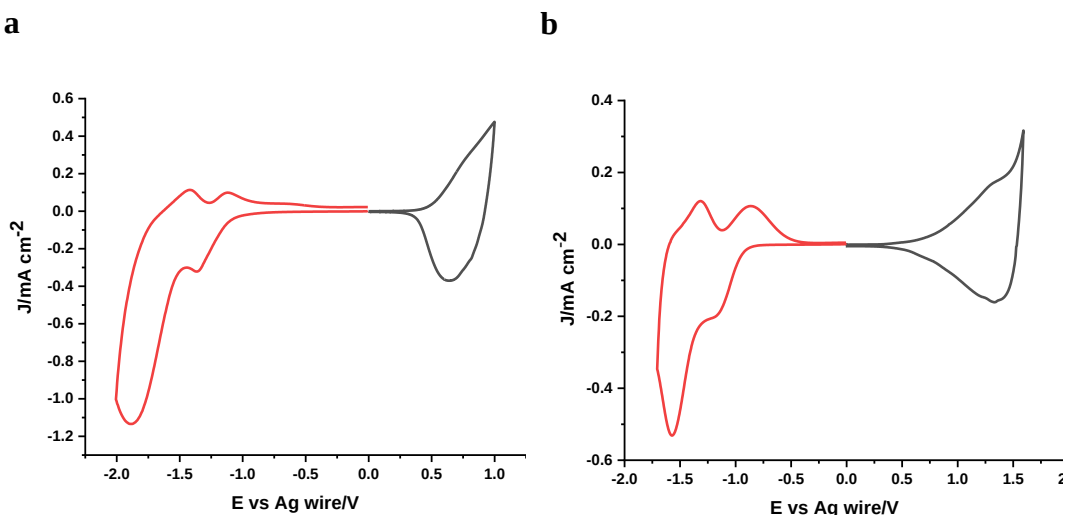
$$LUMO = -(4.75 + E_{onset}^{red})$$

Standard Hydrogen Electrode (SHE) vs. vacuum level was adopted as 4.75 eV. The electronic band gaps (E_g^{el}) of PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT were calculated from the energy level difference between HOMO and LUMO. The

following equation was used for the calculation of the electronic band gaps of polymers;

$$E_g^{el} = \text{HOMO-LUMO}$$

HOMO energy levels for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT were found as -5.28 eV, -5.52 eV and -5.56 eV whereas LUMO energy levels were calculated as -3.65 eV, -3.82 eV and -3.59 eV, respectively. Therefore, the electronic band gaps of PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT were deduced to be 1.63 eV, 1.70 eV and 1.97 eV. The HOMO energy level of the synthesized polymers decreases dramatically upon fluorine substitution with approximately 0.3 eV energy difference between the difluorinated (PBDTSe-FFBT) and the non-fluorinated (PBDTSe-BT) polymers. The deeper HOMO energy level of the polymer was associated with the strong electron-withdrawing characteristic of benzothiadiazole acceptor and weak electron-donating nature of alkylselenophene side chain which has π -conjugation to BDT moiety. Moreover, the electronic band gap of non-fluorinated polymer PBDTSe-BT exhibited lower band gap energy than fluorinated PBDTSe-FBT and PBDTSe-FFBT which may arise from the strong electronegativity of fluorine atom and enhanced inter-/intramolecular interaction among polymer backbones.⁹²⁻⁹⁴



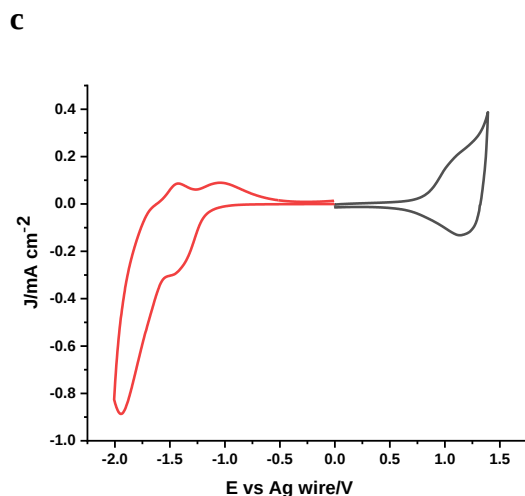


Figure 2.5. Single scan cyclic voltammograms of polymers a) PBDTSe-BT, b) PBDTSe-FBT, and c) PBDTSe-FFBT in 0.1 M TBAPF₆/ACN electrolyte solution at 100 mV s⁻¹ scan rate

While different HOMO levels are obtained from theoretical and experimental methods for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT conjugated polymers, these values reveal the same trend; i.e., with the introduction of F atoms onto the benzothiadiazole moiety the HOMO level of polymers can be diminished, and also the number of fluorination on these polymers has a synergetic impact on reducing the HOMO level.⁹⁵

Table 2.3 Summary of electrochemical and optical properties of polymers

	$E_{p-doping}$ (V)	$E_{p-dedoping}$ (V)	$E_{n-doping}$ (V)	$E_{n-dedoping}$ (V)	E_{onset}^{ox} (V)	E_{onset}^{red} (V)
PBDTSe	0.75	0.64	-1.36/-	-1.12/-	0.53	-1.10
-BT			1.88	1.42		
PBDTSe	1.35	1.33	-1.18/-	-0.87/-	0.77	-0.93
-FBT			1.57	1.32		
PBDTSe	1.20	1.16	-1.47/-	-1.05/-	0.81	-1.16
-FFBT			1.95	1.42		
	$HOMO$ (eV)	$LUMO$ (eV)	E_g^{ec} (eV)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{op} (eV)
PBDTSe	-5.28	-3.65	1.63	620	763	1.62
-BT						
PBDTSe	-5.52	-3.82	1.70	600	754	1.65
-FBT						
PBDTSe	-5.56	-3.59	1.97	590	745	1.67
-FFBT						

2.2.5 Spectroelectrochemical Properties of BDT and BT Based Polymers

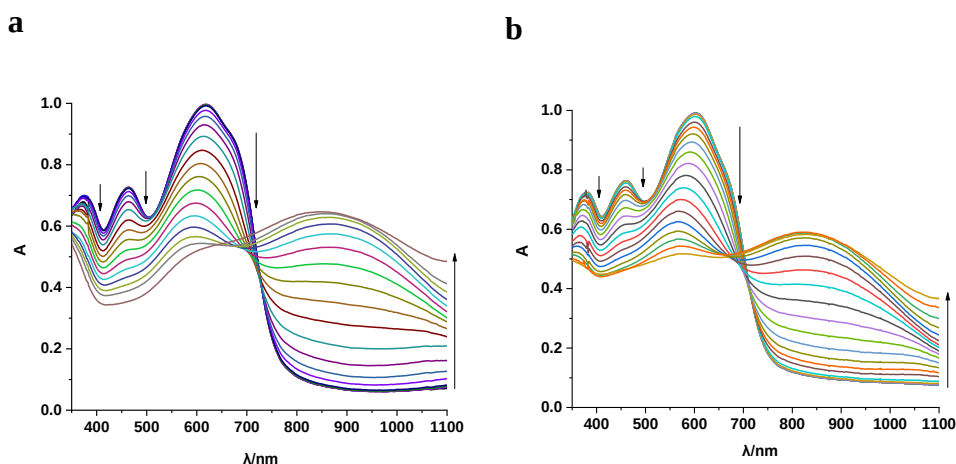
In order to investigate the spectroelectrochemical properties of the polymers, a three-electrode system was used. PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT were dissolved in chloroform and deposited onto ITO coated glass substrate via spray coating at room temperature. All polymers have good solubility in chloroform and homogenous solutions were obtained for the spectroelectrochemical analysis. The analysis of three polymers was performed with UV-Vis-NIR spectrophotometer via step by step increment of the applied potential in 0.1 M TBAPF₆/ACN solution. Constant potentials were carried out to remove the charges or ions trapped into polymers and record the neutral states correctly before applying the oxidation potentials. Absorption spectra were obtained by stepwise oxidation and while the

neutral state absorptions (λ_{max}) were steadily declining, polarons (radical cations) and bipolarons (bications) absorption bands were observed in the NIR region as expected. The absorption behaviors of polymers in the UV-Vis region give essential information, especially for organic solar cell applications. For this purpose, optical band gaps (E_g^{op}) and maximum absorption wavelengths (λ_{max}) of the polymers were obtained from Figure 2.6 and all data were summarized in Table 2.3. The λ_{max} values were found as 620 nm, 600 nm and 590 nm for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT, accordingly. The optical bandgaps (E_g^{op}) were calculated from the onset point of the lowest energy $\pi-\pi^*$ transitions (λ_{onset}) in the UV-Vis-NIR absorption spectrum of the polymer thin films by using the following equation;

$$E_g^{op} = \frac{1241}{\lambda_{onset}}$$

The band gaps (E_g^{op}) were calculated as 1.62 eV, 1.65 eV and 1.67 eV for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT correspondingly. The backbone fluorination slightly increased the optical band gaps and the changes in the absorption spectra clearly reveal the effect of substitution of fluorine atom. Similar results have also been published for fluorine atom substituted conjugated polymer by other groups.

93,94,96,97



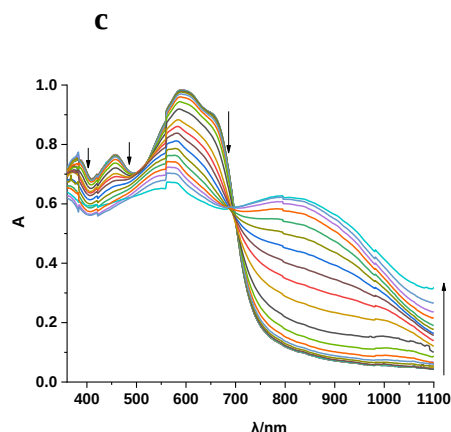


Figure 2.6. Normalized UV–Vis–NIR absorption spectra of thin film of a) PBDTSe-BT, b) PBDTSe-FBT, and c) PBDTSe-FFBT upon oxidative doping potentials in 0.1 M TBAPF₆/ACN electrolyte solution

All the polymers displayed an absorption shoulder peak in thin-film state and the existence of strong intermolecular interactions caused by better π – π stacking between the neighbor polymer chains might be the reason for this phenomenon. On the other hand, when fluorine atoms are substituted to the polymer backbone, PBDTSe-FFBT showed pronounced absorption shoulder around 650 nm demonstrating strong polymer aggregation at room temperature. Therefore, the strong aggregation in PBDTSe-FFBT may be caused by intermolecular interactions of F...F, C-F...H, and C-F... π_F .^{98,99} Due to the introduction of fluorine atoms leading to more pronounced aggregation, PBDTSe-FFBT demonstrates a lower wavelength in the absorption spectrum compared to PBDTSe-FBT and PBDTSe-BT which may result in a slightly larger band gap of 1.67 eV.

2.2.6 Photovoltaic Performance of BDT and BT Based Polymers

BHJ photovoltaic devices of these three polymers were fabricated to explore and analyze the influence of the substituting fluorine atom on the resultant photovoltaic performance. Organic solar devices with standard configuration, ITO/PEDOT:PSS/Polymer:PC₇₁BM/LiF/Al, were employed using PBDTSe-BT,

PBDTSe-FBT and PBDTSe-FFBT as donors and PC₇₁BM as an acceptor counterpart into the active layer of the devices. While determining the processing solvent of the active layer, different weight ratios of the polymer to PC₇₁BM and the concentration of the active layer were investigated. Moreover, a small amount of 1,8-diiodooctane (DIO) was used to optimize the photovoltaic performance of the devices. The thicknesses of the active layers were optimized by altering the spin coating rate which was found as 1000 rpm for all polymers. The active layers were blended by using solvents of 1,2-dichlorobenzene (*o*-DCB) for PBDTSe-BT and chlorobenzene (CB) for PBDTSe-FBT and PBDTSe-FFBT with PC₇₁BM. The photovoltaic parameters, including open-circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) of the devices using polymers PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT are summarized in Table 2.4-2.6. Figure 2.7 shows the resultant current density-voltage (J-V) plots of the most efficient devices, which were investigated under AM 1.5G simulated solar illumination at an irradiation intensity of 100 mW cm⁻².

Table 2.4 Summary of photovoltaic studies of PBDTSe-BT

PBDTSe- BT:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Treatment
1:4 (4%) ^a	5.43	0.67	39.4	1.43	-
1:4 (4%) ^b	4.84	0.67	43.9	1.42	-
1:4 (4%) ^c	6.10	0.67	41.9	1.71	-
1:4 (4%) ^c	5.67	0.66	45.6	1.70	1% DIO
1:4 (4%)^c	6.58	0.66	55.3	2.39	2% DIO
1:4 (4%) ^c	6.22	0.67	54.0	2.26	3% DIO
1:4 (4%) ^c	6.48	0.67	52.8	2.29	2% DIO, MeOH

^a Spin coating rate of 500 rpm; ^b Spin coating rate of 750 rpm; ^c Spin coating rate of 1000 rpm

Table 2.5 Summary of photovoltaic studies of PBDTSe-FBT

PBDTSe-FBT:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Treatment
1:2 (3%) ^a	3.34	0.65	39.1	0.85	-
1:2 (3%) ^b	6.17	0.66	36.1	1.47	-
1:2 (3%) ^c	6.00	0.65	39.2	1.53	-
1:2 (3%) ^c	7.09	0.68	34.0	1.64	2% DIO
1:2 (3%)^c	7.23	0.67	34.6	1.68	3% DIO
1:2 (3%) ^c	6.16	0.65	31.1	1.25	4% DIO

^a Spin coating rate of 500 rpm; ^b Spin coating rate of 750 rpm; ^c Spin coating rate of 1000 rpm

Table 2.6 Summary of photovoltaic studies of PBDTSe-FFBT

PBDTSe- FFBT:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Treatment
1:1 (2%) ^a	4.99	0.70	38.8	1.36	-
1:1 (2%) ^b	5.75	0.70	49.2	1.99	-
1:1 (2%) ^c	6.40	0.70	50.4	2.26	-
1:1 (2%) ^c	6.15	0.72	50.5	2.23	2% DIO
1:1 (2%)^c	7.24	0.72	50.6	2.63	3% DIO
1:1 (2%) ^c	6.76	0.71	47.4	2.28	4% DIO

^a Spin coating rate of 500 rpm; ^b Spin coating rate of 750 rpm; ^c Spin coating rate of 1000 rpm

Among all three polymers, difluorinated PBDTSe-FFBT:PC₇₁BM revealed the highest photovoltaic performance achieving 2.63%, with J_{sc} of 7.24 mA cm⁻², V_{oc} of 0.72 V and FF of 50.6%. Whereas PBDTSe-BT:PC₇₁BM exhibited the best PCE as 2.39%, and the device reached the highest efficiency up to 1.68% for PBDTSe-FBT:PC₇₁BM. Polymer PC₇₁BM weight ratio of the blend in the active layer is essential to optimize the photovoltaic parameters. Since the function of the acceptor

material in the active layer is associated with the charge transport, the balance between the charges (the hole and the electron) transportations are enhanced by changing the weight ratio of the electron accepting material PCBM in the blend. As a result of this enhancement, efficient charge separation occurs and more separated charge carriers can be transported and collected at the proper electrodes, which arises higher PCE. However, this increase of the acceptor material causes a decrease in the content of the donor material, which plays a vital role in the absorption of sunlight in the active layer. Therefore, the optimization of the weight ratios of the donor and acceptor materials is an essential process to obtain efficient PCE. Consequently, the best device performances were found with a blend ratio of 1:4 (w/w), 1:2 (w/w) and 1:1 (w/w) for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT, respectively.

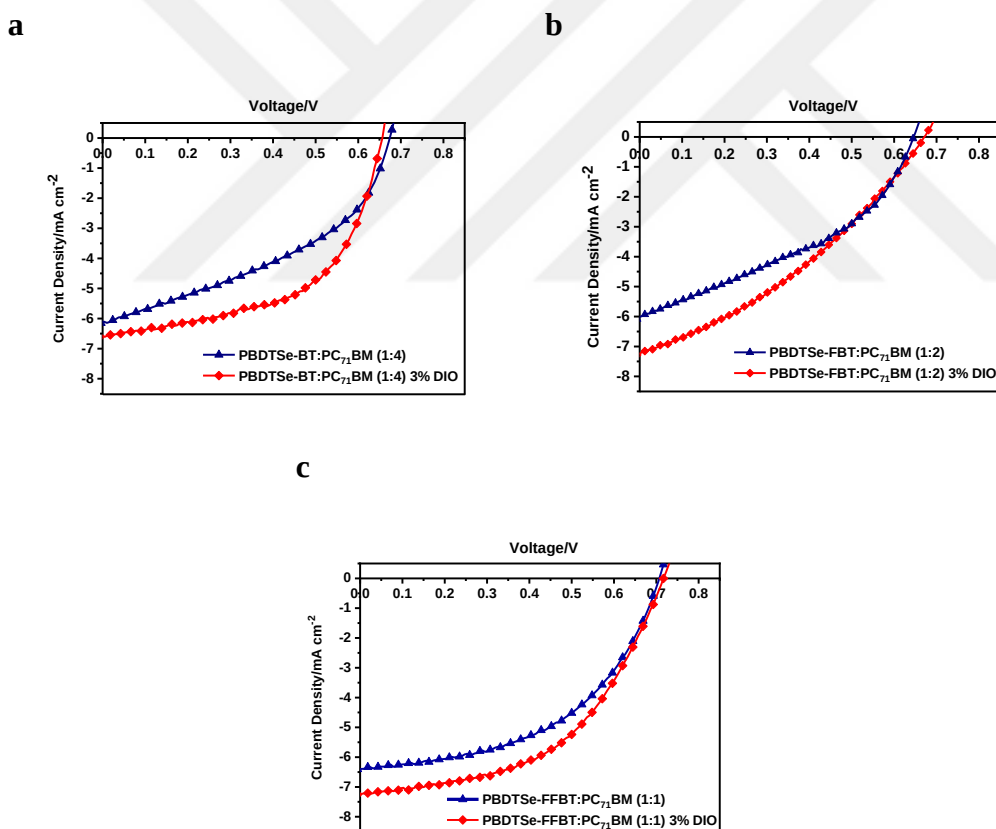


Figure 2.7. Current density-voltage curves of OSCs based on a) PBDTSe-BT:PC₇₁BM, b) PBDTSe-FBT:PC₇₁BM, and c) PBDTSe-FFBT:PC₇₁BM without additive and with additive in the active layer

Further improvement in the PCE was observed by the addition of a trace amount of DIO to the active layer of the OSC. With the addition of 1% DIO to the active layer, device efficiency of PBDTSe-BT:PC₇₁BM (1:4, 4%) remained unchanged while an improvement from 41.9% to 45.6% in the FF% obtained. An increase in the J_{sc} from 5.67 to 6.58 mA cm⁻² and FF from 45.6% to 55.3% was observed by the addition of 2% DIO resulting 2.39% of PCE. Further DIO and methanol treatment for PBDTSe-BT resulted in lower photovoltaic parameters. The studies for the optimum amount of the DIO were carried out for PBDTSe-FBT and PBDTSe-FFBT. The results showed that the best device efficiency was found 1.68% for PBDTSe-FBT and 2.63% for PBDTSe-FFBT with the addition of 3% DIO. It is believed that the donor can form pure and ordered self-assembly phases in the film due to the high boiling point property of DIO, which promotes and stimulates the generation of crystal structures.¹⁰⁰

The substitution of the fluorine atom along the conjugation backbone provides effective tuning of the molecular energy levels as well as enhanced intramolecular interactions.¹⁰¹ DFT calculations and experimental results indicated that PBDTSe-FFBT including two F atoms into its polymer backbone has a deeper HOMO level in regards to PBDTSe-BT and PBDTSe-FBT. Therefore, an increase in V_{OC} of the best solar cell device was observed that might lead to higher PCE of the solar cell. Moreover, according to the DFT calculations, hole mobility along the polymers chain slightly improved by F incorporation due to increased hole reorganization energies (λ_{reorg}) listed in Table 2.2. Higher charge carrier mobility may also be one of the reasons for the high photovoltaic performance of PBDTSe-FFBT based solar cell.

Overall, the efficiencies of the synthesized polymers was moderately reported in this work, however, several factors such as HOMO-LUMO energy level, device structure, the molecular weight of the polymers, band gap etc. affect the device efficiency.^{14,102,103} Although the benzothiadiazole-based conjugated polymers exhibit great properties for photovoltaics, the molecular weight of the polymer was recognized to be significant.^{27,104} The high molecular weight of the polymer is

usually expected to provide an efficient path for charge transport and blend morphology.¹⁰⁵ Due to the insufficient growth of the polymer chains during the Stille cross-coupling polymerization, the low molecular weight of polymers was synthesized. Therefore, the lower PCEs were revealed for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT.

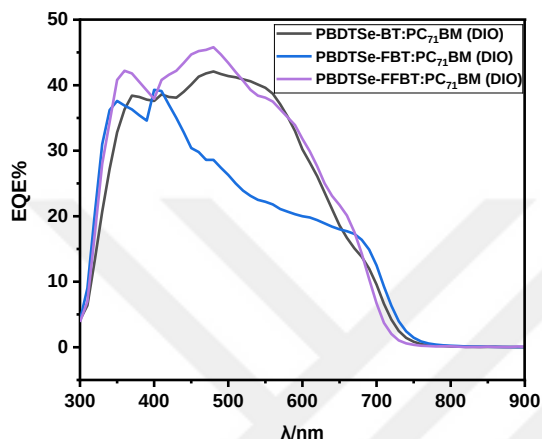


Figure 2.8. EQE curves for the best performance solar cells

External quantum efficiency (EQE) curves of the devices based on PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT without DIO addition and with DIO addition via using the optimum conditions were shown in Figure 2.8. The conversion efficiencies measured for the best device performances were observed over the wavelength range of 300–900 nm which are in agreement with the absorption spectra of the polymers. The highest EQE% values were found as 42.1%, 39.3% and 45.8% for PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT with the addition of DIO, respectively.

2.2.7 Morphology Studies of BDT and BT Based Polymers

In order to gain information about the morphology and topography of the photo-active layer of OSC devices, transmission electron microscopy (TEM) and atomic force microscopy (AFM) were utilized. TEM images of PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT polymers as the active layers of best OSC with DIO

addition were shown in Figure 2.9, respectively. As seen from Figure 2.9, PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT based solar cells display homogenous and nanoscale phase separation with DIO treatment.¹⁰⁶ As mentioned before in computational results, the torsional angles θ (A-B) decreased with fluorine substitution, which indicates better planarity resulting in improved chain packing and interchain hopping. Therefore, the nanoscale morphology of the active layer promotes the exciton separation and charge transportation causing an increase in J_{SC} and FF.^{107,108}

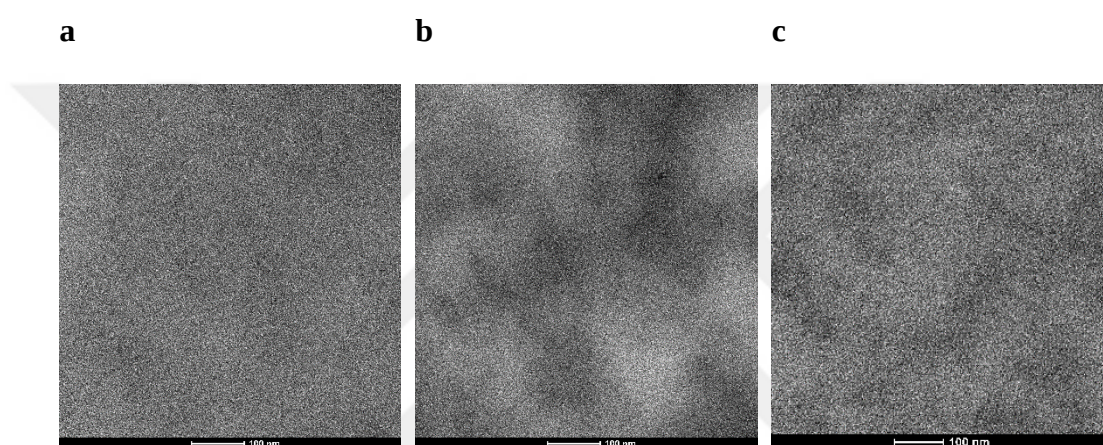


Figure 2.9. TEM images of a) PBDTSe-BT, b) PBDTSe-FBT and c) PBDTSe-FFBT based active layers processed with o-dcb and DIO

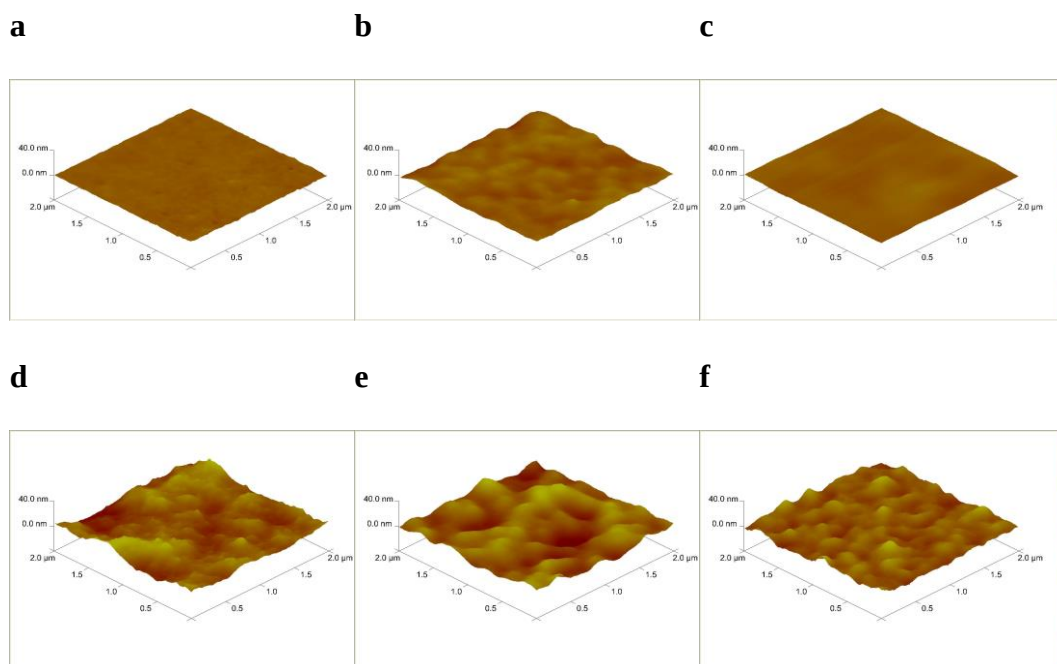


Figure 2.10. 3D AFM images of a) PBDTSe-BT, b) PBDTSe-FBT and c) PBDTSe-FFBT without the additive DIO; d) PBDTSe-BT, e) PBDTSe-FBT and f) PBDTSe-FFBT with the additive DIO

The 3D AFM height images of the most efficient devices without DIO and with DIO are shown in Figure 2.10. The root mean square roughness of the blend of PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT with PCBM were calculated as 0.66 nm, 1.81 nm and 0.97 nm as cast polymer blends; 4.61 nm, 5.43 nm and 3.21 nm for DIO treatment, respectively. The active layer thickness values were found as 107.6 nm, 150.7 nm and 120.2 nm without DIO addition; 123.5 nm, 117.0 nm and 64.7 nm with DIO addition, correspondingly. As can be seen from Figure 2.10.a and Figure 2.10.c, the blend of the PBDTSe-BT and PBDTSe-FFBT had the lowest roughnesses. As DIO was added to the active layer, the roughness values increased significantly. With the addition of DIO, which enhances the solubility of PCBM, PCBM aggregates tend to form near the surface resulting in an increase in surface roughness.¹⁰⁹

CHAPTER 3

INVESTIGATION THE EFFECT OF π BRIDGE AND SIDE CHAIN ON PHOTOVOLTAIC PROPERTIES OF BENZODITHIOPHENE AND QUINOXALINE BASED CONJUGATED POLYMERS

This work was published in the following reference:¹¹⁰

Taskaya Aslan, S.; Alemdar Yılmaz, E.; Hacıfendioğlu, T.; Arslan Udum, Y.; Toppare, L.; Yıldırım, E.; Cirpan, A. Investigation the Effect of π Bridge and Side Chain on Photovoltaic Properties of Benzodithiophene and Quinoxaline Based Conjugated Polymers. *Eur. Polym. J.* **2022**, 169, 111141.

(Theoretical calculations were performed by Asst. Prof. Erol Yıldırım and Tuğba Hacıfendioğlu in this chapter.)

Among various D-A type polymers, quinoxaline building block has been utilized as an electron-withdrawing moiety due to its easily modified structure and versatility.¹¹¹ Quinoxaline derivatives with strong quinoid properties provide a wider light absorption and improved charge carrier transport due to the relatively stable and strong electron-withdrawing features that are conducive to enhancing the intramolecular charge transfer (ICT) effect.¹¹²

Backbone modulation of the conjugated polymers and side-chain engineering can offer an effective method to promote the device efficiencies of organic solar cells. In selenium-based materials, the larger π -overlap leads to increased π -orbitals of Se atoms and intermolecular Se-Se interactions, which improve conductivity and charge mobility.^{53,54} Furthermore, because the Se atom is significantly bigger and has less electronegativity than the chalcogenophene homolog of the S atom, Se-containing polymers are more effective at expanding the absorption spectra near the infrared range.⁵⁶ Over the years of researches, BDT moieties were established by involving

different units attached to the central benzene such as alkoxy, alkyl, aromatic groups etc.^{113,114}

Considering all of the factors mentioned above, a series of novel conjugated polymers based on BDT and Qx were produced using Stille coupling polymerization to investigate the effect of the π bridge between the D-A groups and side groups attached on BDT moiety. Because of the correlation between the molecular structures of the polymers, a comparison will be beneficial in determining the impact of the π bridge and the different substituents on benzodithiophene along with the conjugated structure on the photovoltaic characteristics.

3.1 Experimental

3.1.1 Materials

Unless otherwise specified, all starting substances and reagents were obtained commercially and utilized without additional purification. When necessary, the solvents used in the studies were dried using conventional standard techniques. Unless otherwise specified, all reactions were carried out in a nitrogen environment. For the purification of crude materials, column chromatography was used with Merck Silica Gel 60 (particle size: 0.063–0.200 mm, ASTM 70–230 mesh) as the stationary phase and various solvent mixtures as the eluent.

3.1.2 Instrumentation

Thermal characteristics were measured using the thermogravimetric analysis (TGA) (Perkin Elmer Pyris 1) and differential scanning calorimeter (DSC) (Perkin Elmer Diamond) at a heating rate of 10°C/min under N₂. Bruker Spectrospin Avance DPX-400 Spectrometer was used to acquire ¹H and ¹³C Nuclear Magnetic Resonance Spectra with trimethylsilane (TMS) as the internal reference. The average molecular weights of the polymers in CHCl₃ were determined using gel permeation

chromatography (GPC) (polystyrene as the standard reference-Universal Calibration procedure). A Varian Cary 5000 UV–Vis Spectrometer was utilized at room temperature to conduct spectroelectrochemical investigations on PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx, and PBDT-SeQx. To study the electrochemical properties of these polymers, a Gamry 600 potentiostat was utilized using a three-electrode system with Indium Tin Oxide (ITO) coated glass, platinum wire and Ag wire in 0.1 M tetra-butylammonium hexafluorophosphate/acetonitrile (TBAPF₆/ACN) at 100 mV s⁻¹ scan rate.

3.1.3 Synthesis of Monomers

3.1.3.1 Synthesis of Compound 3-2

Compound 3-1 (5.0 g, 17.0 mmol) and 300 mL of EtOH was put into reaction flask. After dissolution, mixture was cooled to 0°C in an ice bath. NaBH₄ (6.43 g, 0.17 mol) powder was added slowly and carefully to the reaction flask. After gas evolution was stopped, temperature was brought to the room temperature and stirred for 20 hours. After evaporation of EtOH solvent from the reaction medium, water was added to crude product and extraction was performed with diethyl. The organic phase was washed with brine and MgSO₄ was used for removing residual water. The organic phase was evaporated and compound 3-2 was obtained as faint yellow solid (2.7 g, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.77 (s, 2H), 3.75 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 133.74, 123.3, 109.7.

3.1.3.2 Synthesis of Compound 3-3

Thiophene (1.0 g, 11.9 mmol) and 30 mL of distilled tetrahydrofuran were flaked. The reaction medium was brought to -78°C with the help of dry ice. In an N₂ atmosphere, n-butyl lithium (2.5 M in hexane, 5.2 mL, 13.1 mmol) was added dropwise to the reaction medium. After the addition was complete, the reaction was

brought to room temperature. After 2 hours the temperature was brought back to -78°C and tributyltin chloride (4.0 ml, 14.2 mmol) was added slowly. After addition, the reaction continued for 20 hours at room temperature. After evaporation of the reaction solvent, brine was added and extraction was done with dichloromethane. The organic phase was dried with MgSO₄ and the solvents were removed in a rotary evaporator. It was used in the next reaction (NMR yield 80%) without further purification.

3.1.3.3 Synthesis of Compound 3-4

Selenophene (1.00 g, 7.6 mmol) and 30 mL of distilled tetrahydrofuran were flaked. The reaction medium was brought to -78°C with the help of dry ice. In an N₂ atmosphere, n-butyl lithium (2.5 M in hexane, 3.4 mL, 8.4 mmol) was added dropwise to the reaction medium. After the addition was complete, the reaction was brought to room temperature. After 2 hours the temperature was brought back to -78°C and tributyltin chloride (2.60 ml, 9.1 mmol) was added slowly. After addition, the reaction continued for 20 hours at room temperature. After evaporation of the reaction solvent, brine was added and extraction was done with dichloromethane. The organic phase was dried with MgSO₄ and the solvents were removed in a rotary evaporator. It was used in the next reaction (NMR yield 75%) without further purification.

3.1.3.4 Synthesis of Compound 3-5

1,2-bis(decyloxy)benzene (2.1 g, 5.38 mmol), urea (0.32 g, 5.38 mmol), and AlCl₃ (1.25 g, 9.4 mmol) were dissolved in 10 mL of DCM at 0°C in a nitrogen-filled bottom flask with a two-necked. Dropwise additions of oxalyl chloride (0.23 mL, 2.7 mmol) were added to the reaction mixture at 0°C before allowing it to warm to room temperature. Overnight, the mixture was stirred at room temperature. The chilly water was filled to the brown suspension. DCM was used to extract the organic phase

from aqueous phase. After that, a NaHCO_3 solution was used to wash the organic phase and was dried over MgSO_4 . The organic phase was evaporated via rotary. The purification was performed by precipitation using methanol to obtain a milk white solid (0.9 g, 40% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 1.9 Hz, 2H), 7.43 (dd, J = 8.4, 1.9 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 4.05 (td, J = 6.6, 1.9 Hz, 8H), 1.88–1.79 (m, 8H), 1.50 – 1.41 (m, 8H), 1.27 (s, 52H), 0.88 (m, 12H).

3.1.3.5 Synthesis of Compound 3-6

In a two necked bottom flask compound 3-5 (0.55 g, 2.1 mmol) and compound 3-2 (1.73 g, 2.1 mmol) was dissolved with ethanol (20 mL) and catalytic amount PTSA was added. The reaction mixture was stirred at room temperature for 20 h and then the solution was poured into cold water. Precipitate was washed with cold ethanol (2x250 mL). The solution was filtered and the crude product was purified by column chromatography on silica gel using Hexane/ CHCl_3 (1:1) as eluent. Yellow solid was further purified via recrystallization with ethanol to yield the resultant compound (1.87 g, 85%).

3.1.3.6 Synthesis of Compound 3-7

Compound 3-6 (0.60 g, 0.56 mmol) and compound 3-3 (0.46 g, 1.24 mmol) were dissolved in 10 mL of anhydrous toluene, then, nitrogen gas was passed through the reaction medium for 40 min. $\text{Pd}(\text{PPh}_3)_4$ (32 mg, 0.03 mmol) was added at room temperature. The reaction mixture was allowed to react at 110°C for 20 h under N_2 atmosphere. After the reaction was finished, the mixture was poured into 150 mL of 1.0 M HCl solution. The organic phase was extracted with chloroform, dried over anhydrous MgSO_4 . After evaporation of the solvent, the residue was separated by column chromatography using a 60:1:3 (Hexane: EtOAc: THF) mixture to give a yellow solid (0.50 g, 83%). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 2H), 7.77 (dd, J = 3.7, 1.0 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.21 (dd, J = 8.3, 2.0 Hz, 2H), 7.09 (dd, J =

5.1, 3.8 Hz, 2H), 6.77 (d, $J = 8.4$ Hz, 2H), 3.95 (t, $J = 6.6$ Hz, 4H), 3.87 (t, $J = 6.7$ Hz, 4H), 1.82 – 1.66 (m, 8H), 1.45 – 1.08 (m, 66H), 0.84 – 0.76 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 148.4, 147.0, 137.2, 135.2, 129.7, 129.3, 126.9, 124.9, 124.9, 124.5, 121.9, 114.1, 111.1, 67.5, 67.5, 30.3, 28.1, 28.0, 28.0, 27.9, 27.8, 27.8, 27.8, 27.7, 27.6, 27.5, 24.5, 24.4, 21.1, 12.5.

3.1.3.7 Synthesis of Compound 3-8

After compound 3-6 (0.80 g, 0.76 mmol) and compound 3-4 (0.70 g, 1.67 mmol) were dissolved in 10 ml of anhydrous toluene, nitrogen gas was passed through the reaction medium for 40 min and $\text{Pd}(\text{PPh}_3)_4$ (44 mg, 0.04 mmol) was added at room temperature. The reaction mixture was allowed to react at 110°C for 20 h under N_2 atmosphere. After the reaction was finished, the mixture was poured into 150 mL of 1.0 M HCl solution. The organic phase was extracted with chloroform, dried over anhydrous MgSO_4 . After evaporation of the solvent, the residue was separated by column chromatography using a 1:1 (Hexane: CHCl_3) mixture to give an orange solid (0.55 g, 63%). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 2H), 8.13 (dd, $J = 5.7$, 0.6 Hz, 2H), 7.97 (d, $J = 3.3$ Hz, 2H), 7.38 (dd, $J = 5.8$, 4.0 Hz, 2H), 7.29 (d, $J = 2.0$ Hz, 2H), 7.15 (dd, $J = 8.3$, 2.0 Hz, 2H), 3.96 (t, $J = 6.7$ Hz, 4H), 3.86 (t, $J = 6.7$ Hz, 4H), 1.83 – 1.75 (m, 8H), 1.76 – 1.65 (m, 8H), 1.29 – 1.12 (m, 48H), 0.86 – 0.77 (m, 12H).

3.1.3.8 Synthesis of Compound 3-9

Compound 3-7 (0.18 g, 0.17 mmol) was dissolved in 20 mL of chloroform and N-bromosuccinimide (NBS) (61 mg, 0.34 mmol) was added. After stirring the mixture for 18 h at room temperature in the dark, it was poured into 150 mL of water. The organic phase was extracted with chloroform, dried over anhydrous MgSO_4 and then concentrated. The residue was precipitated with methanol (0.2 g, 95%) to give a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.64 (d, $J = 2.0$ Hz, 2H),

7.53 (d, $J = 4.1$ Hz, 2H), 7.11 (dt, $J = 4.4$, 2.0 Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 4.10 (t, $J = 6.5$ Hz, 4H), 4.03 (t, $J = 6.6$ Hz, 4H), 1.90 – 1.80 (m, 8H), 1.54 – 1.44 (m, 8H), 1.41 – 1.18 (m, 48H), 0.94 – 0.84 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 150.2, 149.1, 139.5, 134.0, 130.9, 130.1, 128.9, 125.0, 124.9, 123.6, 117.0, 115.4, 112.4, 69.3, 69.1, 32.0, 32.0, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 26.3, 26.1, 22.7, 14.1.

3.1.3.9 Synthesis of Compound 3-10

Compound 3-8 (0.33 g, 0.28 mmol) was dissolved in 30 mL of chloroform and N-bromosuccinimide (NBS) (0.1 g, 0.56 mmol) was added. After stirring the mixture for 18 h at room temperature in the dark, it was poured into 150 mL of water. The organic phase was extracted with chloroform, dried over anhydrous MgSO_4 and then concentrated. The residue was precipitated with methanol to give a red solid (0.35 g, 95%). ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 2H), 7.72 (d, $J = 4.4$ Hz, 2H), 7.41 (d, $J = 2.1$ Hz, 2H), 7.36 (d, $J = 4.4$ Hz, 2H), 7.07 (dd, $J = 8.3$, 2.0 Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 2H), 4.03 (dt, $J = 9.7$, 6.7 Hz, 8H), 1.94 – 1.75 (m, 8H), 1.54 – 1.19 (m, 48H), 0.93 – 0.82 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 150.2, 148.8, 142.5, 135.7, 131.9, 131.4, 130.4, 125.7, 123.9, 123.5, 123.0, 115.8, 112.4, 69.4, 69.1, 32.0, 32.0, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 26.2, 26.1, 22.7, 14.1.

3.1.4 Synthesis of Polymers

3.1.4.1 Synthesis of PBDTSe-TQx

Compound 2-3 (0.13 g, 0.13 mmol) and compound 3-9 (0.160 g, 0.13 mmol) were dissolved in 10 mL of toluene. N_2 gas was purged through the reaction flask for 40 min. $\text{Pd}_2(\text{dba})_3$ (6.0 mg, 6.5 μmol) catalyst, $\text{P}(\text{o-toly})_3$ (16.0 mg, 52.0 μmol) ligand were added and the reaction mixture was heated while stirring at boiling temperature for 24 h. 2-(Tributylstannyl)thiophene (0.118 g, 0.3 mmol) was added and stirred for

another 1 h, then 2-bromo thiophene (0.05 g, 0.3 mmol) was added and stirred for a further 1 h. Subsequently, the reaction mixture was cooled to room temperature and the resultant polymer was precipitated with 50 mL of methanol. The polymer was then purified with Soxhlet using methanol, acetone, hexane, and chloroform solvents. The chloroform fraction was recovered under reduced pressure and the solid was precipitated from methanol. The solid was then dried under vacuum to obtain polymer (0.221 g, 96%). ^1H NMR (400 MHz, CDCl_3) δ 8.02 – 6.60 (m, aromatic H), 4.23 – 3.43 (m, $-\text{OCH}_2-$), 3.33 – 2.67 (m, alkyl H), 1.96 – 0.52 (m, alkyl H).

3.1.4.2 Synthesis of PBDTSe-SeQx

Compound 2-3 (0.135 g, 0.135 mmol) and compound 3-10 (0.179 g, 0.135 mmol) were dissolved in 10 mL of toluene and after 40 min argon gas was passed through the reaction flask, $\text{Pd}_2(\text{dba})_3$ (6.2 mg, 6.8 μmol) catalyst and $\text{P}(\text{o-toly})_3$ (16.5 mg, 54.0 μmol) ligand was added and the reaction mixture was heated while stirring at boiling temperature for 24 h. 2-(Tributylstannyl)thiophene (0.118 g, 0.3 mmol) was added and stirred for another 1 h, then 2-bromo thiophene (0.05 g, 0.3 mmol) was added and stirred for a further 1 h. Subsequently, the reaction mixture was cooled to room temperature and the resultant polymer was precipitated with 50 mL of methanol. The polymer was then purified with Soxhlet using methanol, acetone, hexane, and chloroform solvents. The chloroform fraction was recovered under reduced pressure and the solid was precipitated from methanol. The solid was then dried under vacuum to obtain polymer (0.225 g, 89%). ^1H NMR (400 MHz, CDCl_3) δ 8.26 – 6.61 (br m, aromatic H), 4.26 – 3.57 (br m, $-\text{OCH}_2-$), 2.94 (br s, alkyl H), 2.06 – 0.42 (br m, alkyl H).

3.1.4.3 Synthesis of PBDT-TQx

Compound BDT-OEH (0.11 g, 0.142 mmol) and compound 3-9 (0.175 g, 0.142 mmol) were dissolved with 10 mL of toluene and after 40 min argon gas was passed through the reaction flask, $\text{Pd}_2(\text{dba})_3$ (6.5 mg, 7.1 μmol) catalyst and $\text{P}(\text{o-toly})_3$ (17.3 mg, 57.0 μmol) ligand were added and the reaction mixture was heated while stirring at boiling temperature for 22 h. 2-(Tributylstannyl)thiophene (0.3 mmol) was added and stirred for another 1 h, then 2-bromo thiophene (0.3 mmol) was added and stirred for a further 1 h. Subsequently, the reaction mixture was cooled to room temperature and the resultant polymer was precipitated with 50 mL of methanol. The polymer was then purified with Soxhlet using methanol, acetone, hexane, and chloroform solvents. The chloroform fraction was recovered under reduced pressure and the solid was precipitated from methanol. The solid was then dried under vacuum to obtain PBDT-TQX polymer (0.11 g, 50%). ^1H NMR (400 MHz, CDCl_3) δ 8.10 – 6.75 (br m, aromatic H), 4.54 – 3.64 (br m, $-\text{OCH}_2-$), 2.24 – 0.59 (br m, alkyl H).

3.1.4.4 Synthesis of PBDT-SeQx

Compound BDT-OEH (0.102 g, 0.132 mmol) and compound 3-10 (0.175 g, 0.132 mmol) were dissolved in 10 mL of toluene and after 40 min argon gas was passed through the reaction flask, $\text{Pd}_2(\text{dba})_3$ (6.0 mg, 6.6 μmol) catalyst and $\text{P}(\text{o-toly})_3$ (16.0 mg, 53.0 μmol) ligand were added and the reaction mixture was heated while stirring at boiling temperature for 22 h. 2-(Tributylstannyl)thiophene (0.3 mmol) was added and stirred for another 1 h, then 2-bromo thiophene (0.3 mmol) was added and stirred for a further 1 h. Subsequently, the reaction mixture was cooled to room temperature and the resultant polymer was precipitated with 50 mL of methanol. The polymer was then purified with Soxhlet using methanol, acetone, hexane, and chloroform solvents. The chloroform fraction was recovered under reduced pressure and the solid was precipitated from methanol. The solid was then dried under vacuum to

obtain PBDT-SEQX polymer (0.08 g, 37%). ^1H NMR (400 MHz, CDCl_3) δ 8.39 – 6.71 (br m, aromatic H), 4.54 – 3.55 (br m, $-\text{OCH}_2-$), 2.10 – 0.59 (br m, alkyl H).

3.1.5 Computational Methods

Theoretical calculations were carried out for polymers in the form of $\text{B}(\text{DBA})_4\text{B}$ (D: donors, A: quinoxaline acceptor, B: thiophene and selenophene as a π -bridging group) tetramers by using B3LYP hybrid functional and 6-311G(d) basis set with tight SCF convergence criteria in the Gaussian 2009 (Revision A.02) software package which provided successful results in the previous studies.^{73–75,77–82,91,115} Alkyl side chains were replaced with methyl groups to increase computational efficiency. Geometry optimizations were started from different initial conformations by controlling the torsional angle between connected donor, bridge and acceptor units to determine the lowest energy geometry. Electrostatic potential surface (ESP), highest occupied molecular orbitals (HOMO), and lowest unoccupied molecular orbitals (LUMO) were calculated for the optimized geometries. The band gap was calculated using two different methods: the direct differences between the HOMO energy and LUMO energy for the optimized ground state and the vertical excitation energy of the lowest singlet excited state. The singlet excited states of the oligomers were calculated by using time-dependent density-functional theory (TDDFT). Orbital composition analysis was performed using the Multiwfn wavefunction analysis program by Stout-Poltzer orbital partition scheme.¹¹⁶ Vertical ionization potential (VIP) and adiabatic ionization potential (AIP) were calculated by the energy difference between the neutral and cation state of the optimized ground state geometry and optimized cation geometry, respectively. Hole reorganization energies (λ_{reorg}) were determined based on the method by Bredas et al.⁸¹ Dipole moment (μ), isotropic polarizability (α), anisotropic polarizability ($\Delta\alpha$) and static first order hyperpolarizability (β) were calculated for the B-D-B-A-B type optimized units. Atomic charges (δ) based on the natural population analysis and bond orders as NBO based Wiberg bond indexes were calculated by using natural population analysis

scheme for the donor, acceptor and π -bridging units for the B-D-B-A-B structure were calculated by neglecting end groups to avoid end group effect.¹¹⁷

3.1.6 Device Fabrication

The bulk heterojunction organic solar cells were constructed with the device construction of glass/ITO/PEDOT:PSS/active layer/LiF/Al. The glass substrates were ready after the cleaning processes; Hellmanex, water, acetone, and isopropyl alcohol with 15 min ultrasonication for each one, respectively. The substrates were dried with an N₂ gun. After that O₂ plasma treatment was used to enhance the work function of ITO via removing organic impurities as well as to reduce the surface tension of ITO. PEDOT: PSS was filtered through a 0.45 μ m PES syringe filter and coated on the ITO surface. Subsequently, the substrates were annealed at 135°C for 15 minutes on the hot plate to evaporate the residual water. In the active layer, the optimizations of donor polymers PBDTSE-TQX, PBDTSE-SEQX, PBDT-TQX and PBDT-SEQX were studied with different thicknesses, polymer:PCBM ratios and weight percentages filtered through a 0.22 μ m pore-sized PTFE syringe filter and coated on a PEDOT:PSS layer in the nitrogen-filled glove box. LiF was used as a buffer layer with 0.6 nm thickness, and finally, Al with 100 nm was used as a cathode. While the hole transport and active layers were spin-coated, LiF and Al were deposited with a vapor deposition under low pressure. All devices were controlled with 16 different devices and the J_{SC} was corrected with IPCE. J-V curves were acquired from Keithley 2400 at AM 1.5G conditions.

3.2 Results and Discussion

3.2.1 Synthesis and Characterization of BDT and Qx Based Polymers

In our synthetic strategy, 2-ethylhexylselenophene substituted benzodithiophene (Compound 2-3) was used as the donor moiety and quinoxaline derivatives were

taken as the acceptor units. The synthetic pathway for the donor material is given in Figure 2.1 and the details to synthesize the donor moiety were mentioned in Chapter 2.

The design route followed for the acceptor materials is given in Figure 3.1. As a result of the reaction of compound 3-2 with compound 3-5 under paratoluenesulfonic acid (PTSA) catalysis, a quinoxaline derivative of compound 3-6 was successfully obtained.¹¹⁸ The treatment of compound 3-6 with 2-(tributylstannyl)thiophene (3-3) and 2-(tributylstannyl)selenophene (3-4) with Stille coupling reaction conditions resulted in the target materials 3-7 and 3-8¹¹⁹ which were reacted with N-bromosuccinimide to provide acceptor compounds 3-9 and 3-10.^{120,121} Both the intermediate compounds and the target monomers were purified with either column chromatography or precipitation from appropriate solvents.

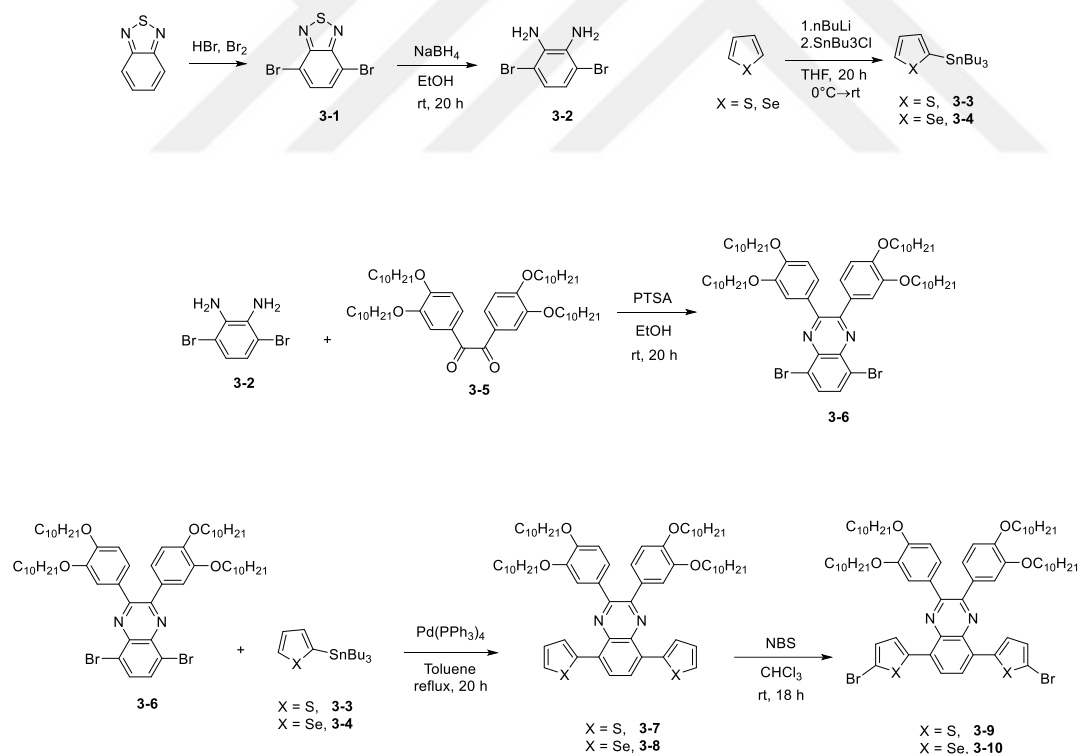


Figure 3.1. Synthesis of quinoxaline acceptor

The synthesis of polymers was achieved via Stille cross-coupling polymerization reaction between the corresponding monomers. During the polymerization, $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-tolyl})_3$ and toluene were used as the catalyst and solvent, respectively. The synthesized compound 2-3 was used as the donor for the synthesis of PBDTSe-TQx and PBDTSe-SeQx and commercially available 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (BDT-OEH) was used for the synthesis of PBDT-TQx and PBDT-SeQx. The polymerization reactions were shown in Figure 3.2. These polymers displayed good solubility in common organic solvents such as THF, chloroform, and toluene. The measurements of the GPC were carried out in chloroform as the eluent. The number average molecular weights are 138.3 kDa, 264.6 kDa, 231.2 kDa and 230.0 kDa for PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx, respectively. The gel permeation chromatography (GPC) results of the polymers are displayed in Table 3.1.

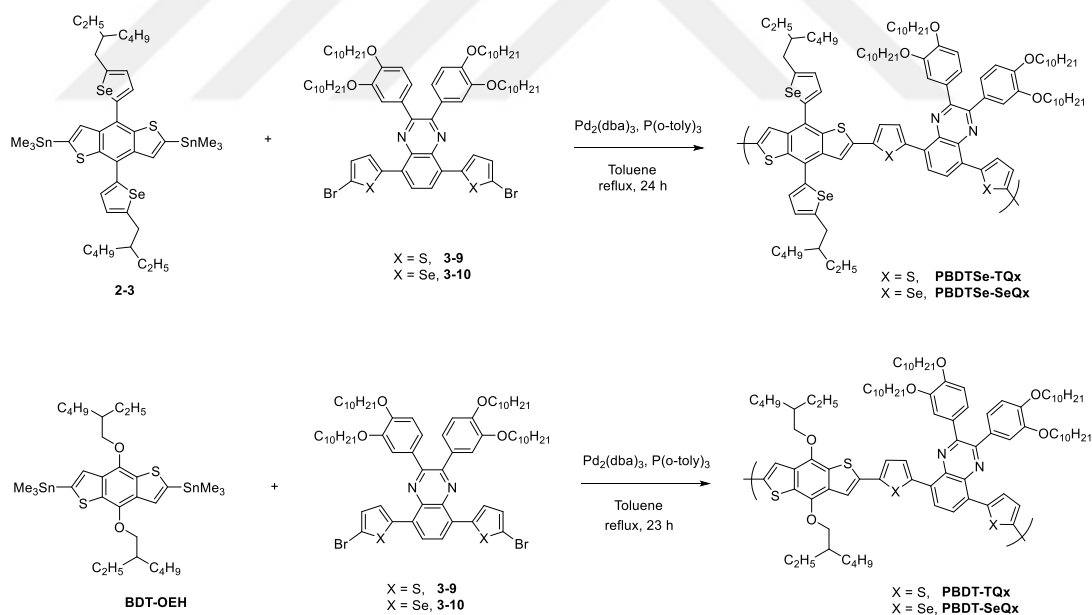


Figure 3.2. Synthesis of BDTand Qx based polymers

Table 3.1 Summary of GPC and TGA Studies

	<i>Mn (kDa)</i>	<i>Mw (kDa)</i>	<i>PDI</i>	<i>T_d[*] (°C)</i>
PBDTSe-TQx	138.3	358.1	2.59	370
PBDTSe-SeQx	264.6	369.0	1.39	389
PBDT-TQx	231.2	546.7	2.36	300
PBDT-SeQx	230.0	283.1	1.23	314

3.2.2 Thermal Studies of BDT and Qx Based Polymers

The thermal characteristics of the polymers were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx polymers have strong thermal stability, with degradation temperatures exceeding 300°C, making them suitable for an organic solar cell. TGA measurements revealed that the degradation temperatures (*T_d*) of polymers at 5% weight loss were 370°C, 389°C, 300°C and 314°C, respectively. Up to 300°C, no phase transition was observed for the produced polymers.

3.2.3 Computational Results of BDT and Qx Based Polymers

According to the electrostatic potential surface, all copolymers present donor-acceptor type consecutive electron-rich and deficient parts on the donor/ π -bridging unit and acceptor units, respectively (Figure 3.3). Although HOMOs are mostly localized on the donor and π -bridge, and LUMOs are primarily localized on the acceptor group, the extension and overlapping of both frontier orbitals were observed for all four copolymers. The more detailed analysis given in Table 3.2 shows that the percentage of LUMO on the acceptor is higher for PBDT-TQx and PBDT-SeQx than the LUMO group on PBDTSe-TQx and PBDTSe-SeQx which means more localized LUMO orbital on the same acceptor group can be controlled by alternating the

electron rich donor system. However, there is no significant difference between the percentage of HOMO orbital on the donor and bridge groups for copolymers.

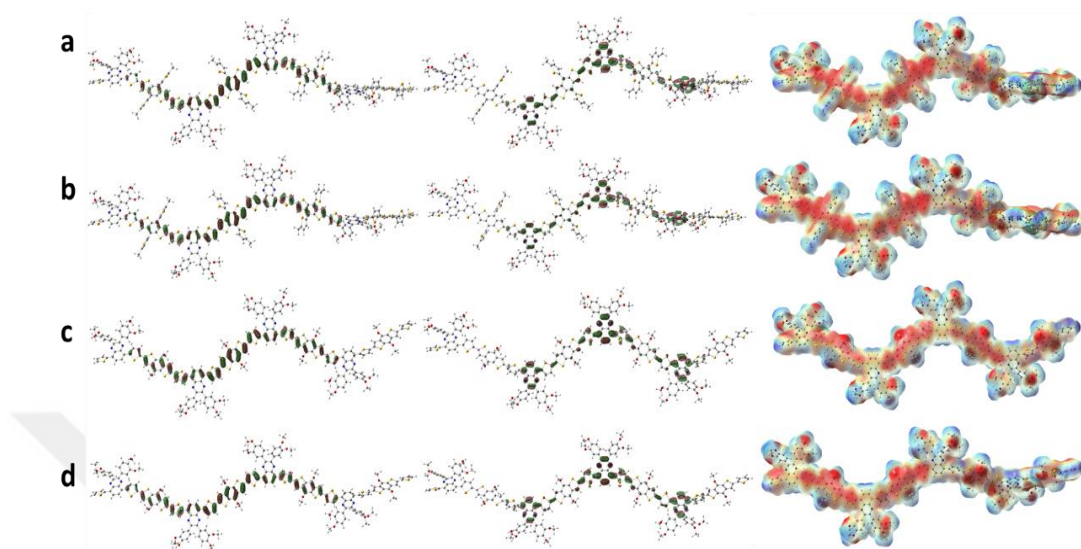


Figure 3.3. Frontier orbital surfaces (HOMO and LUMO) and electrostatic potential surfaces (ESP) for the a) PBDTSe-TQx, b) PBDTSe-SeQx, c) PBDT-TQx, d) PBDT-SeQx copolymers.

Table 3.2 Frontier molecular orbital percentage of donor and acceptor units for polymers

	<i>LUMO-acceptor (%)</i>	<i>HOMO-donor (%)</i>
PBDTSe-TQx	79.75	84.47
PBDTSe-SeQx	78.82	84.37
PBDT-TQx	82.73	84.13
PBDT-SeQx	81.60	84.11

Average dihedral angles between acceptor and donor with bridging units abbreviated as φ_{A-B} and φ_{D-B} , calculated by excluding the end group effects are given in Table 3.3. Alternating the π -bridging unit from thiophene to selenophene increases the dihedral angle between the acceptor and bridge unit, decreasing the torsion between donor and bridge for both PBDTSe-TQx and PBDT-TQx. It was observed that the

main reason for the copolymer chains' difference in planarity is the dihedral angle between acceptor unit and thiophene/selenophene based π -bridging units. The dihedral angles between corresponding atoms are shown in Figure 3.4b.

Relative values were determined for four copolymers, for the VIP, AIP and λ_{reorg} values which are directly related to charge mobility. Slightly lower VIP values of the PBDTSe-SeQx and PBDT-SeQx than the PBDTSe-TQx and PBDT-TQx show a higher electron density donating ability of selenophene rather than thiophene, which agrees well with the experimental results.

Table 3.3 Results of the DFT calculations for the electronic and structural properties of polymers

	PBDTSe-TQx	PBDTSe-SeQx	PBDT-TQx	PBDT-SeQx
HOMO (eV)	-4.91	-4.91	-4.99	-4.98
LUMO (eV)	-2.67	-2.71	-2.71	-2.76
E_g^{el} (eV)	2.24	2.2	2.28	2.23
E_g^{op} (eV)	1.9	1.86	1.93	1.89
VIP (eV)	5.35	5.34	5.44	5.43
AIP (eV)	0.04	0.05	0.05	0.05
Λ_{reorg} (eV)	0.09	0.09	0.1	0.1
δ_{Accep}	-0.085	-0.097	-0.083	-0.095
μ (Debye)	2.3	2.31	2.47	2.48
α (a.u)	1039.8	1078.1	893.1	930.8
$\Delta\alpha$ (a.u)	1011.9	1072	1043.1	1103.8
β (a.u)	8404.1	9549	8538.7	9511
φ A-B	20.72	26.66	20.33	26.94
φ D-B	13.09	12.86	17.18	14.7

Band gap calculations gave similar values for all copolymers for single chain tetramer calculations where the trend in the calculated values is in good agreement with experimental values having optical band gap values below 2 eV which was also validated by calculation by other DFT functionals such as CAM-B3LYP. The difference between calculated band gap energy values with the experimental results depends on the short chain length oligomers used in the calculations, in addition to the interchain packing interactions that are neglected in the computational studies.

Dipole moment (μ), polarizability (α), anisotropy of the polarizability ($\Delta\alpha$) and static first order hyperpolarizability (β) values are calculated to compare electronic differences by control of the donor and π -bridging unit as given in Table 3.3. Values calculated for α , $\Delta\alpha$ and β were determined for selenophene based PBDTSe-SeQx and PBDT-SeQx compared to the thiophene based PBDTSe-TQx and PBDT-TQx copolymers. There is a relation between molecular hyperpolarizability, β , and the reduction bond length alternation in donor-acceptor copolymers where β increases with increasing electron delocalization and decreased the bond length alternation.⁹¹ β values are in the order of PBDTSe-SeQx > PBDT-SeQx > PBDT-TQx > PBDTSe-TQx that agrees with the experimental results. Higher polarizability and hyperpolarizability values for PBDTSe-SeQx and PBDT-SeQx with selenophene units indicated the possibility of stronger dispersion, reduced bond length alternation and enhanced dipole–dipole intermolecular interactions with other species such as PC₇₁BM.

Finally, atomic charges (δ) calculated based on the natural population analysis method for four structures with two two different donor and two different bridging units for the B-D-B-A-B structures were determined by avoiding end groups to avoid end group effect. Negative atomic charges on the acceptors (δ_{acceptor}) with relatively higher values on PBDTSe-SeQx and PBDT-SeQx show the efficiency of selenophene bridge unit for the transfer of electron density from donor and bridging units to acceptor. These values also show the strong ability of the quinoxaline units as an acceptor. The difference between PBDTSe-SeQx and PBDT-SeQx is not significant for the electron transfer ability between units.

Wiberg bond indices corresponds to bond orders as well as bond lengths were calculated for backbone critical bonds in polymers as given in Figure 3.4c-d. Higher Wiberg bond index indicates the stronger π -bond between groups and rigidity at the backbone leads to the stronger electron delocalization. In Figure 3.4d, the average Wiberg bond index for the bonds between donor-bridge and acceptor-bridge groups for PBDT-SeQx is calculated as 1.14 on average excluding the end groups and bonds between bridging groups, which is extensively higher than PBDT-TQx bond index, calculated as 0.89. In addition, PBDTSe-SeQx has a higher π -conjugation degree with an average Wiberg bond index for the same bonds at 1.14, while PBDTSe-TQx yielded bond index is determined as 1.02. Bond lengths between the corresponding groups denoted as letters in Figure 3.4a are given in Figure 3.4d. According to these bond lengths, PBDTSe-TQx and PBDT-TQx has slightly higher bond length for the bonds with bridging units calculated as 1.45 Å, in average, excluding the end group effect, which explains the lower experimental and theoretical band gap values for PBDTSe-SeQx and PBDT-SeQx. Herewith, it was concluded that PBDTSe-SeQx and PBDT-SeQx with selenophene bridging units display stronger benzoid to quinoid transition with higher electron delocalization and rigidity compared to PBDTSe-TQx and PBDT-TQx with thiophene bridging units.

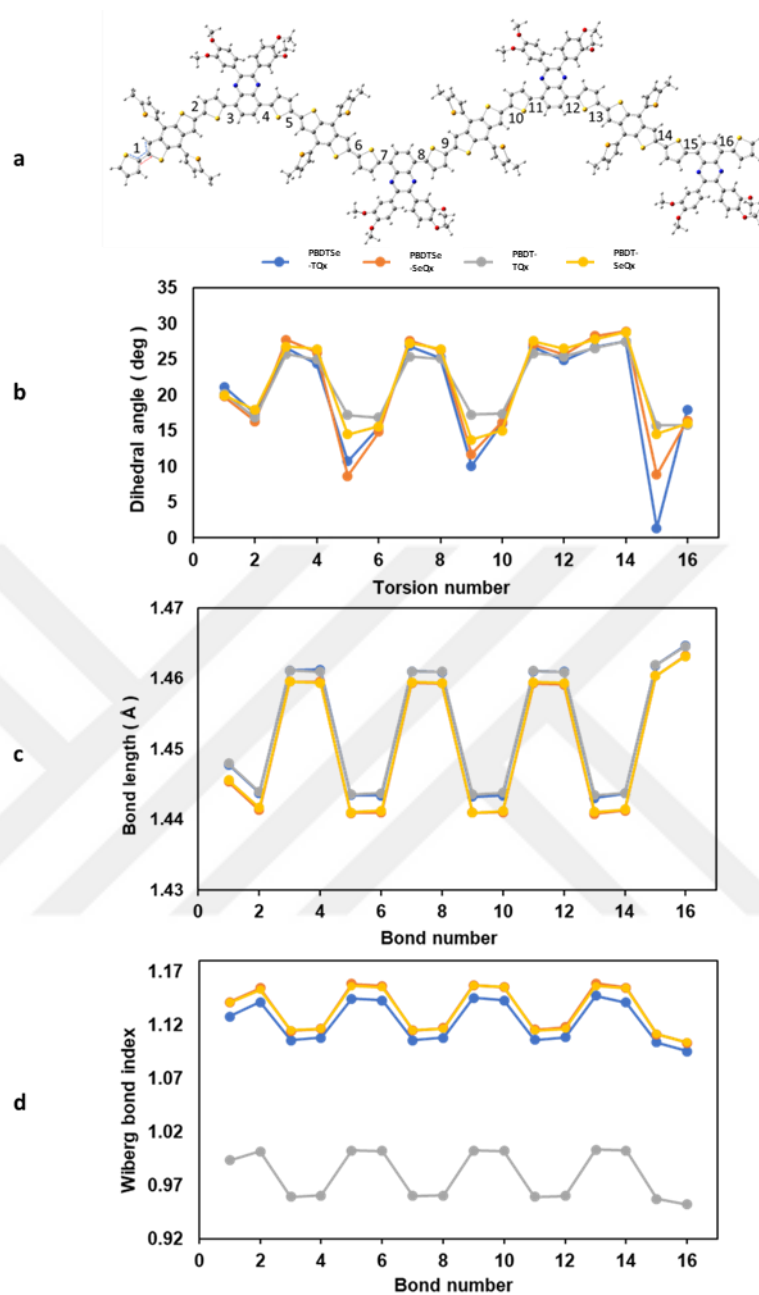


Figure 3.4. a) Representation of the angles (represented as 1,2,3..), length and bonds (represented as a,b,c..), b) Dihedral angles, c) Bond lengths d) Wiberg bond index.

3.2.4 Electrochemical Studies of BDT and Qx Based Polymers

To explore the redox behaviors of the resulting polymers, cyclic voltammetry (CV) measurements were performed for PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx between the appropriate potentials with a constant 100 mV s^{-1} scan rate at room temperature. CV experiments were carried out using a three-electrode setup with indium tin oxide (ITO), Ag wire and Pt wire as the working electrode, the reference electrode and the counter electrode, respectively. Acetonitrile (ACN) was used as the solvent during the experiments, and tetrabutylammoniumhexafluorophosphate (TBAPF₆) was used as the supporting electrolyte. Single scan CV studies were used to determine the redox behaviors, oxidation/reduction potentials, HOMO/LUMO energy levels, and polymers' electronic band gap values. For electrochemical investigations, the synthesized polymers were dissolved in chloroform (5 mg/mL) and spray-coated onto ITO-coated glass slides. Table 3.4 summarizes the electrochemical properties of these polymers. The onset oxidation potentials (E_{onset}^{ox}) values were 0.81 eV, 0.64 eV, 0.88 eV, and 0.51 eV for PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx, and PBDT-SeQx, respectively, whereas the onset reduction potentials (E_{onset}^{red}) were -1.0 eV, -1.09 eV, -0.97 eV, and -1.22 eV. The E_{onset}^{ox} and the E_{onset}^{red} of PBDTSe-SeQx and PBDT-SeQx with selenophene π -bridge in their structures were lower than PBDTSe-TQx and PBDT-TQx with thiophene π -bridge. The decreased oxidation potential of PBDTSe-SeQx and PBDT-SeQx may be attributed to the raise in electron density in the polymer backbone, resulting from a stronger electron-donating property of selenophene than that of thiophene.

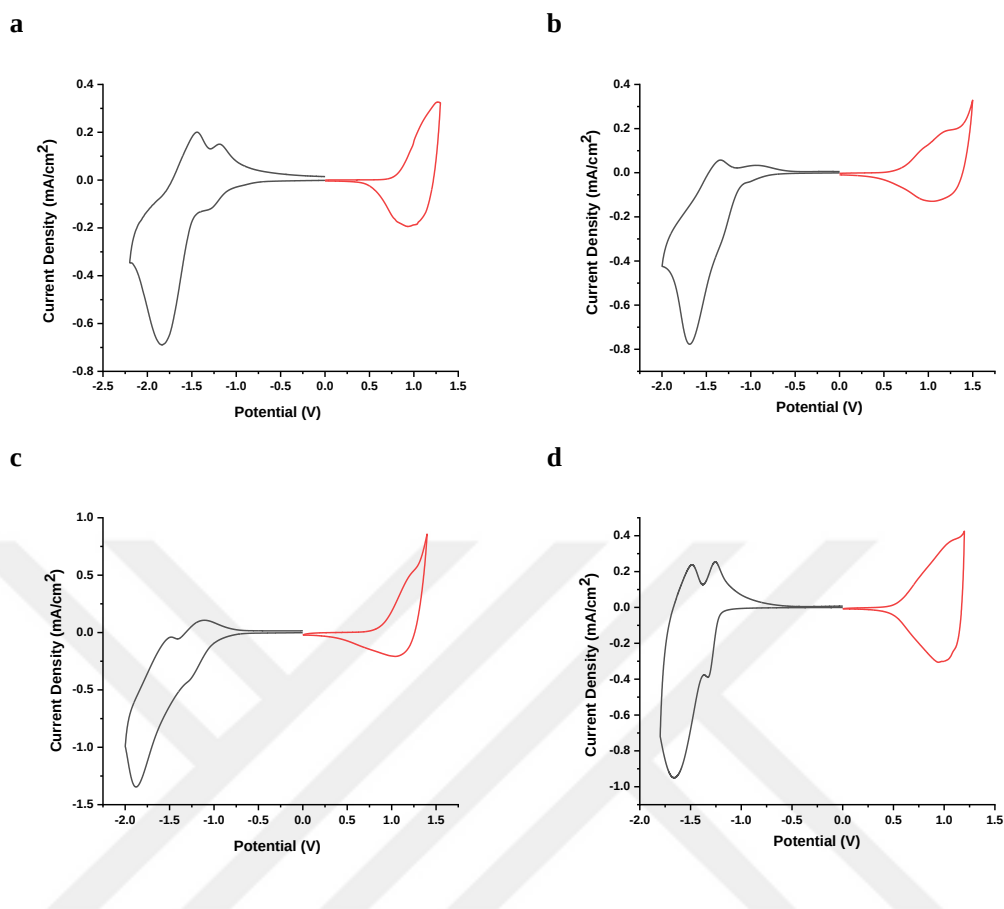


Figure 3.5. Single scan cyclic voltammograms of polymers a) PBDTSe-TQx, b) PBDTSe-SeQx, c) PBDT-TQx and d) PBDT-SeQx in 0.1 M TBAPF6/ACN electrolyte solution at 100 mV s^{-1} scan rate

HOMO and LUMO energy levels of the polymers were determined using their onset oxidation and reduction potentials due to the ambipolar nature of the polymers. The following equations were employed:

$$HOMO = -(4.75 + E_{onset}^{ox})$$

$$LUMO = -(4.75 + E_{onset}^{red})$$

The energy level difference between HOMO and LUMO was used to calculate the electronic band gaps (E_g^{el}) of PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and

PBDT-SeQx. The following equation was used to find the electronic band gaps of polymers:

$$E_g^{el} = \text{HOMO-LUMO}$$

The HOMO values for PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx were calculated to be -5.56 eV, -5.39 eV, -5.63 eV and -5.26 eV, respectively, whereas the LUMO levels were -3.75 eV, -3.66 eV, -3.78 eV and -3.53 eV. The electronic band gaps of PBDTSe-TQx and PBDT-TQx were predicted to be 1.81 eV and 1.85 eV, respectively, with PBDTSe-SeQx and PBDT-SeQx having the lowest electronic band gap of 1.73 eV.

Benzodithiophene units with two-dimensional (2D) conjugation structures are used in D/A alternative copolymer to further extend electron delocalization across the conjugation backbone of the polymers. Delocalization of the electrons results in an increased probability of transition between the ground state and excitation state, leading to a narrower bandgap.^{122,123} Therefore, PBDTSe-TQx containing the 2D-benzodithiophene structure resulted in a lower E_g^{el} than PBDT-TQx. Moreover, according to the cyclic voltammetry results, the selenophene-containing polymers PBDTSe-SeQx and PBDT-SeQx have lower band gaps than that of the thiophene-containing PBDTSe-TQx and PBDT-TQx polymers. Literature studies have revealed that incorporating the selenophene π -bridge into the conjugated polymer backbone instead of thiophene reduces the electronic band gap of the polymer.^{60,124} The reduction of steric hindrance and the elongation of π -conjugation reduce E_g , and the amount of the reduced E_g is strongly associated with the quinoidal nature of the π -bridge along with the donor-acceptor copolymer backbone.⁶¹ According to the calculated aromatic stabilization energy (ASE)¹²⁵ which is 16.7 and 18.6 kcal mol⁻¹ for selenophene and thiophene, respectively, selenophene has a more quinoidal nature than thiophene-containing copolymers.

Moreover, Wiberg bond index values were calculated for PBDTSe-TQx-PBDT-SeQx polymers, and the theoretical results were shown in Figure 3.4d. These estimated Wiberg bond index results indicated that PBDTSe-SeQx and PBDT-SeQx

polymers with selenophene π -bridge displayed higher values than PBDTSe-TQx and PBDT-TQx polymers with thiophene π -bridge. Therefore, these results also concluded that selenophene moiety as π -bridge leads to stronger benzoid to quinoid transition with higher electron delocalization and rigidity.

Table 3.4 Summary of electrochemical properties of polymers

	<i>PBDTSe-TQx</i>	<i>PBDTSe-SeQx</i>	<i>PBDT-TQx</i>	<i>PBDT-SeQx</i>
$E_{p-doping}$ (V)	1.25	1.2	1.23	1.08
$E_{p-dedoping}$ (V)	0.94	1.04	1.05	0.96
$E_{n-doping}$ (V)	-1.30 /-1.84	-1.30 /-1.69	-1.25 /-1.88	-1.32/-1.67
$E_{n-dedoping}$ (V)	-1.18 /-1.44	-0.93 /-1.34	-1.11 /-1.50	-1.25/-1.49
E_{onset}^{ox} (V)	0.81	0.64	0.88	0.51
E_{onset}^{red} (V)	-1	-1.09	-0.97	-1.22
HOMO (eV)	-5.56	-5.39	-5.63	-5.26
LUMO (eV)	-3.75	-3.66	-3.78	-3.53
E_g^{ec} (eV)	1.81	1.73	1.85	1.73

3.2.5 Spectroelectrochemical of BDT and Qx Based Polymers

To investigate the changes in optical characteristics of the polymer film in the neutral state after stepwise increase in potential on the polymer coated ITO electrode, spectroelectrochemical experiments were carried out and responses were collected using UV-Vis-NIR spectroscopy. Figure 3.6 depicts the absorption spectra of polymers under the corresponding potential changes. Moreover, these studies revealed essential characteristics of conjugated polymers such as polaron/bipolaron areas that occur during the doping process, λ_{max} and optical band gap (E_g^{op}).

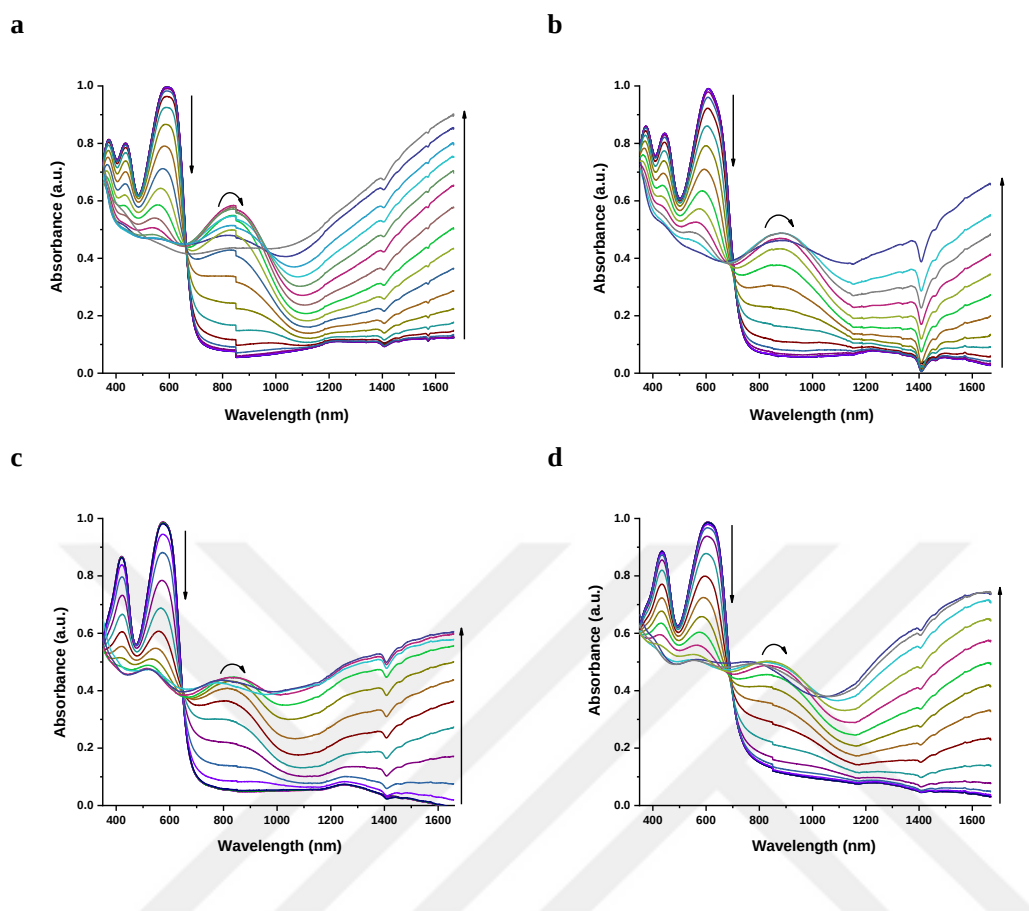


Figure 3.6. Normalized UV-Vis-NIR absorption spectra of thin film of a) PBDTSe-TQx, b) PBDTSe-SeQx, and c) PBDT-TQx and d) PBDT-SeQx upon oxidative doping potentials in 0.1 M TBAPF6/ACN electrolyte solution

The absorption spectra possess three absorption bands for the neutral state of PBDTSe-TQx and PBDTSe-SeQx polymers and two absorption bands for the neutral state of PBDT-TQx and PBDT-SeQx, as shown in Figure 3.6. The bands around 350-500 nm can be allocated to localized π - π^* transitions. The broad band from 500 to 710 nm at the long wavelength was associated with the intramolecular charge transfer (ICT) between acceptor and donor moieties.^{126,127} Selenophene, a thiophene homolog, is frequently employed to improve the optical and electrical characteristics of conjugated polymers. Due to the low aromaticity of selenophene, its ground state quinoid resonance feature enhances, resulting in wide absorption

spectra in Se-containing polymers.⁵⁵ Figure 3.7 shows the UV-Vis absorption spectra of the polymer in CHCl_3 solutions and thin films. As shown in Table 3.5, the PBDTSe-SeQx and PBDT-SeQx thin films' absorption onset was detected at 735 nm and 732 nm, whereas the absorption onset of the PBDTSe-TQx and PBDT-TQx polymers thin films were 691 nm and 681 nm, respectively. When compared to PBDTSe-TQx and PBDT-TQx, the PBDTSe-SeQx and PBDT-SeQx polymers exhibit a noticeable red-shift of the absorption onset (almost 50 nm) as well as the maximum peak value. The optical band gaps of PBDTSe-TQx-PBDT-SeQx were determined to be 1.79 eV, 1.69 eV, 1.82 eV and 1.70 eV from the onset of the maximum absorption peaks of the thin films, correspondingly. PBDTSe-TQx and PBDT-TQx have slightly higher bond length between bridging units than PBDTSe-SeQx and PBDT-SeQx according to theoretical bond lengths calculation of the polymers. The lower experimental and theoretical band gap values of PBDTSe-SeQx and PBDT-SeQx, therefore can be resulted from bond length of the backbone polymer.

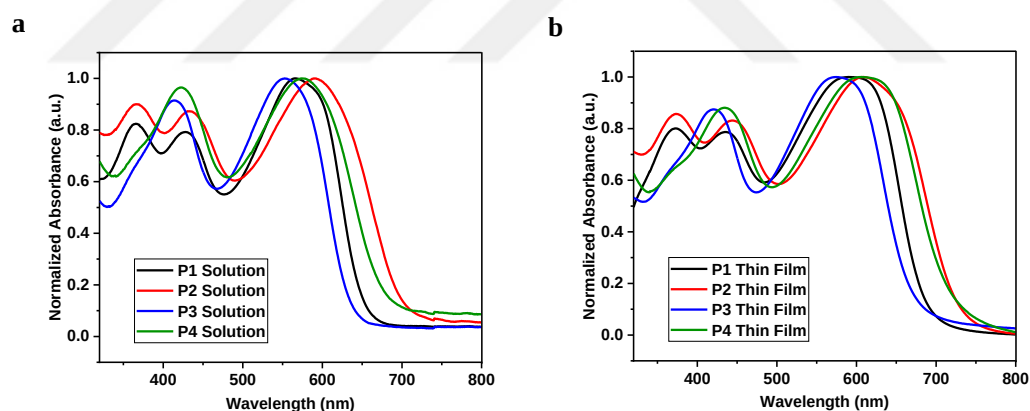


Figure 3.7. UV-Vis absorption spectra of a) PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx in CHCl_3 and b) PBDTSe-TQx-PBDT-SeQx solid state

Table 3.5 Summary of Optical Properties of Polymers.

	λ_{max} (nm) (solution)	λ_{onset} (nm) (solution)	λ_{max} (nm) (thin film)	λ_{onset} (nm) (thin film)	E_g^{op} (eV)
PBDTSe-TQx	565	651	595	691	1.79
PBDTSe-SeQx	591	702	610	735	1.69
PBDT-TQx	552	637	575	681	1.82
PBDT-SeQx	574	679	610	732	1.70

As predicted, the size of the neutral absorption band was decreased during the electrochemical oxidation of polymers, accompanied by the formation of additional bands. This depletion and rise in peak intensity can be explained by the concentration variations of the polymers, where the neutral state concentration of the polymers falls, the polaron/bipolaron concentrations increase during the applied potential.¹²⁸

3.2.6 Kinetic Studies of BDT and Qx Based Polymers

Kinetic experiments were conducted to examine the optical contrast and switching time of the polymers. At a particular wavelength, the optical contrast is defined as the difference in percent transmittance between a material's neutral and completely oxidized states. The switching time is the time needed to transition between these states. Because the human eye is intolerant to color changes of around 5%, the switching time is estimated using 95% of the complete contrast in the literature.¹²⁹ By applying a square-wave potential to the polymer-coated ITO glass substrates at 1 s time intervals, and the measurements were obtained at wavelengths where the maximum absorptions were achieved in spectroelectrochemical studies (Figure 3.8). The change in the percent transmittance ($\Delta T\%$) and switching times (s) for polymers at various wavelengths were summarized in Table 3.6.

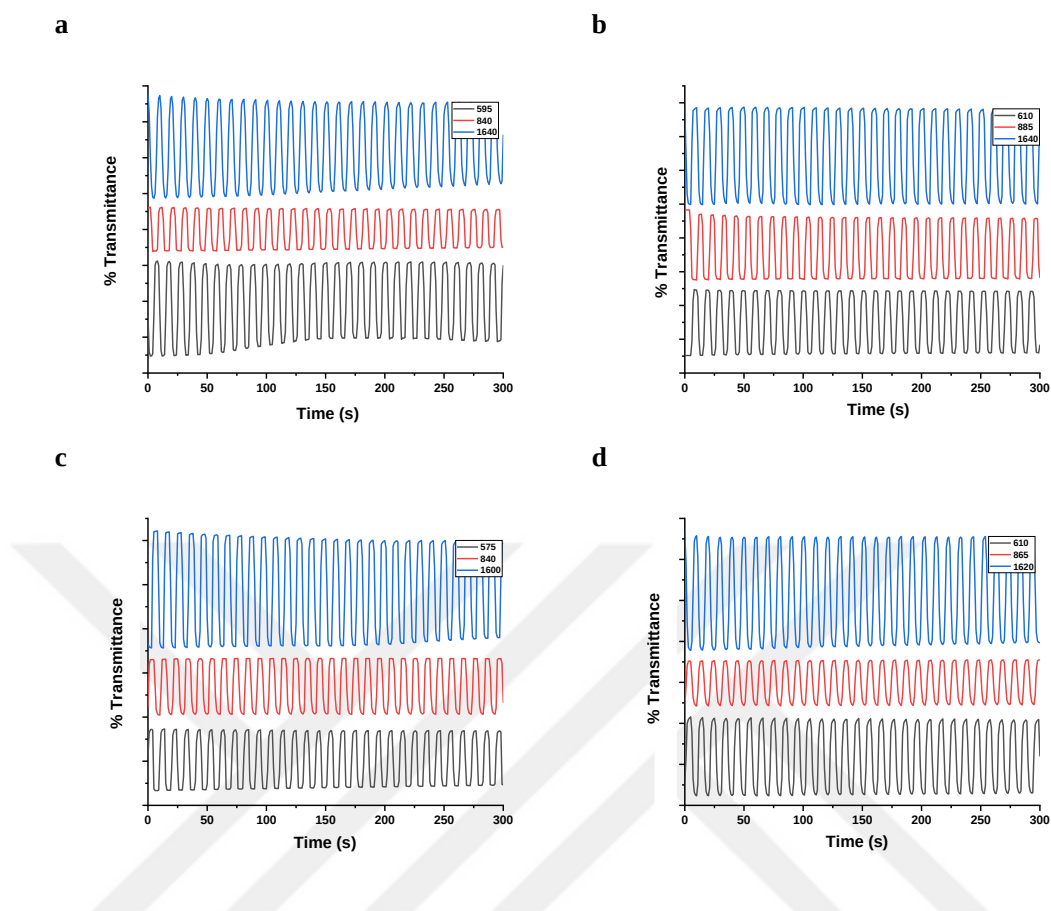


Figure 3.8. Changes in percent transmittance of the thin film of a) PBDTSe-TQx, b) PBDTSe-SeQx, c) PBDT-TQx and d) PBDT-SeQx in 0.1 M TBAPF6/ACN electrolyte/solvent couple

According to kinetic investigations, the optical contrasts of polymers at the bipolaron region around 1600 nm were higher than the optical contrasts in the visible area. With their approximately 60% optical contrast values in the NIR region, these polymers could be excellent candidates for near IR electrochromic smart windows and optical telecommunication.¹³⁰ As summarized in Table 6, PBDTSe-SeQx produced the highest electrochromic properties with 57% optical contrast and 1.9 s of switching time at 1640 nm, among all polymers.

Table 3.6 Summary of Kinetic Studies of Polymers.

	λ (nm)	Optical contrast ($\Delta T\%$)	Switching time (s)
PBDTSe-TQx	595	53	1.9
	840	24	1.8
	1640	57	2.8
PBDTSe-SeQx	610	39	2.8
	885	38	1.9
	1640	57	1.9
PBDT-TQx	575	28	2.0
	840	25	1.9
	1600	52	1.9
PBDT-SeQx	610	38	1.7
	865	22	2.7
	1620	55	2.8

3.2.7 Photovoltaic Performance of BDT and Qx Based Polymers

A set of BHJ solar cells was constructed and evaluated utilizing PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx as donors and PC₇₁BM as an acceptor counterpart to assess the influence of the π -bridge and two-dimensional structure of the polymers on the resultant photovoltaic performance. The devices of the polymers were constructed using a frequently utilized device configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/LiF/Al. *o*-DCB was used as the processing solvent for the active layers of the devices. The device fabrication part contains all of the information for the construction and characterization of the devices. Although enhancing the active layer thickness facilitates the light absorption, the optimal active layer thickness is restricted in organic materials caused by short diffusion length or durability of photo-generated excitons and low charge carrier mobility. The solar cell devices were manufactured with various concentrations and spin coating rates to reach the best thickness for a good comparison between synthesized donor-

acceptor type copolymers in BHJ OSCs. Table 3.7-3.10 summarizes the photovoltaic properties of devices, including open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF), and power conversion efficiency (PCE). Figure 3.9 represents the energy levels of the OSCs based on PBDTSe-TQX-PBDT-SEQX polymers. The results of the most efficient devices based on these polymers were listed in Table 3.11 and the current density–voltage (JV) graphs, obtained under standard illumination (AM 1.5G, 100 mW/cm²), are presented in Figure 3.10a.

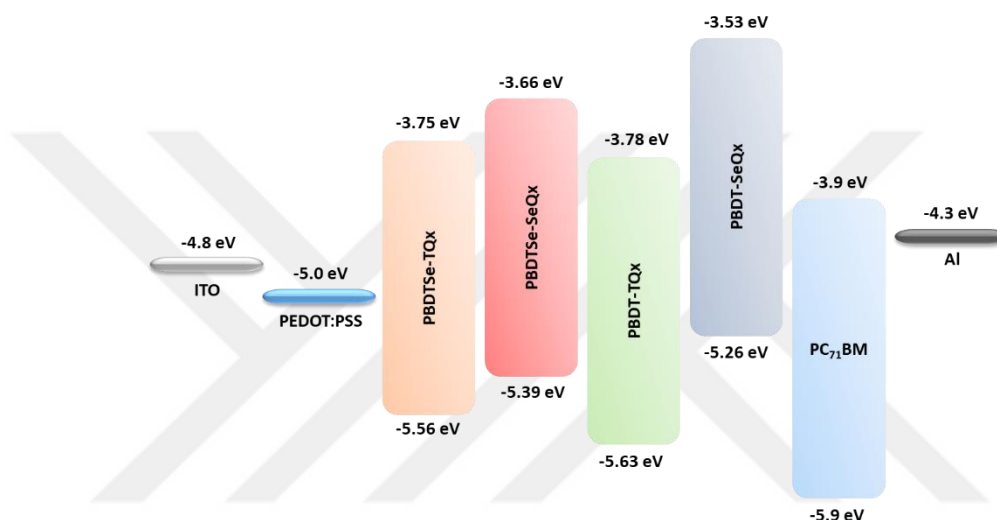


Figure 3.9. Energy level diagram of OSCs based on BDT and Qx polymers

The photovoltaic parameters reduced when the ratio of acceptor material in the BHJ blends was varied. For PBDTSe-TQx, PBDTSe-SeQx and PBDT-SeQx polymers, the increase in the polymer:PCBM ratio from 1:2 (w/w) to 1:3 (w/w) led to reduction of the J_{SC} and FF of the solar cell devices and PCEs were decreased. Therefore, except for PBDT-TQx-based blends, all the polymers had the optimum polymer:PCBM ratio of 1:2 (w/w). The photovoltaic devices fabricated using PBDT-TQx showed the highest J_{SC} and PCE with the polymer:PCBM ratio of 1:1 (w/w) because of its highest light absorption property.

Table 3.7 Photovoltaic Parameters for PBDTSe-TQx

PBDTSe-TQx:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)
1:1 (2%)	4.54	0.79	46.1	1.64	750
1:2 (2%)	6.77	0.76	59.4	3.07	750
1:3 (2%)	4.92	0.76	47.2	1.76	750
1:2 (2.5%)	6.59	0.79	58.7	3.05	750
1:2 (3%)	6.62	0.79	64.4	3.37	750
1:2 (3%)	7.33	0.80	59.7	3.52	500
1:2 (3%)*	8.39	0.80	60.8	4.10	500

*small amount of DIO addition

Table 3.8 Photovoltaic Parameters for PBDTSe-SeQx

PBDTSe-SeQx:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)
1:1 (2%)	6.42	0.74	52.3	2.48	750
1:2 (2%)	7.70	0.76	51.8	3.04	750
1:3 (2%)	5.01	0.72	50.9	1.83	750
1:2 (2.5%)	5.11	0.74	53.0	2.01	750
1:2 (3%)	7.69	0.75	41.2	2.38	750
1:2 (3%)	9.51	0.75	48.3	3.44	500
1:2 (3%)	5.14	0.73	54.6	2.04	1000

By varying the spin coating rates, the active layer thickness of organic solar devices was optimized. The thickness of the active layer increases as the rotation speed diminishes. To achieve higher light absorption, a thicker active layer film is required.¹³¹ Thicker films, on the other hand, might produce undesired recombination processes as a result of the significant distance required for charge carrier transportation.¹³² Therefore, the optimum spin coating rate that produced

maximum PCE was determined to be 500 rpm for PBDTSe-TQx and PBDTSe-SeQx and 750 rpm for PBDT-TQx and PBDT-SeQx. The thickness of the optimum devices was determined from the AFM measurements. The details were discussed in the Morphology Studies section.

As reported in photovoltaic studies, the highest device performance was obtained from PBDT-TQx-based solar cells with 1:1 (w/w) PBDT-TQx:PC₇₁BM blend ratio with 2.5% concentration. This device exhibited the highest PCE of 4.47%, J_{SC} of 10.08 mA/cm², V_{OC} of 0.77 V, and FF of 55%. For selenophene containing analog of this polymer, PBDT-SeQx, the optimum PCE was 3.04% with a J_{SC} of 7.70 mA/cm², a V_{OC} of 0.76 V and a FF of 51.8% using the 2% blend concentration. When the alkoxy side chains of BDT were substituted with 2D conjugated selenophenyl side chains, the resultant polymer PBDTSe-SeQx demonstrated slightly higher PCE than PBDT-SeQx which was 3.44% with 9.51 mA/cm² of J_{SC}, 0.75 V of V_{OC} and 48.3% of FF. However, PBDTSe-TQx:PC₇₁BM (1:2, w/w) based solar device achieved the best PCE of 4.10% after the addition of 2% diiodooctane (DIO). In this work, except for PBDTSe-TQx based solar cell device, solvent additions had no favorable effect on device photovoltaic performances.

Table 3.9 Photovoltaic Parameters for PBDT-TQx

PBDT-TQx:PC ₇₁ BM (w:w)	<i>J_{sc}</i> (mA cm ⁻²)	<i>V_{oc}</i> (V)	<i>FF</i> (%)	<i>PCE</i> %	<i>Spin Coating</i> <i>rate</i> (rpm)
1:1 (2%)	6.15	0.83	52.1	2.66	750
1:2 (2%)	4.93	0.80	48.9	1.94	750
1:3 (2%)	5.22	0.77	44.1	1.77	750
1:1 (3%)	4.64	0.81	37.8	1.42	750
1:1 (2.5%)	10.08	0.80	55.5	4.47	750
1:1 (2.5%)	7.05	0.80	57.3	3.25	500
1:1 (2.5%)	7.59	0.79	58.2	3.50	1000

Table 3.10 Photovoltaic Parameters for PBDT-SeQx

PBDT-SeQx:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)
1:1 (2%)	4.08	0.74	37.0	1.12	750
1:2 (2%)	7.48	0.77	52.3	3.00	750
1:3 (2%)	5.28	0.78	49.2	2.02	750
1:4 (2%)	4.60	0.75	45.4	1.56	750

While numerous researches have shown that V_{OC} is determined by the energy gap between HOMO of the donor and LUMO of the acceptor,^{133–135} J_{SC} is governed by the formation and the subsequent dissociation of excitons at the polymer/acceptor interface, followed by the transition of free charge carriers towards the collecting electrodes in an organic solar cell.¹³⁶ Therefore, deeper HOMO energy levels of PBDTSe-TQx and PBDT-TQx resulted in a high V_{OC} of 0.80 V for the best device performance with respect to PBDTSe-SeQx and PBDT-SeQx based solar cell devices.

Table 3.11 Summary of Photovoltaic Studies for Best Device Performance of Polymers

Polymer:PC ₇₁ BM (w:w)		J_{sc} (mA cm ⁻²)				Thickness (nm)
	V_{oc} (V)	FF (%)	PCE%			
PBDTSe-TQx*	1:2	0.80	8.39 (8.12)	60.8	4.10	86.3
PBDTSe-SeQx	1:2	0.75	9.51 (9.40)	48.3	3.44	103.8
PBDT-TQx	1:1	0.80	10.08 (10.15)	55.5	4.47	102.0
PBDT-SeQx	1:2	0.77	7.48 (7.36)	52.3	3.00	140.3

To get relevant J-V curves with AM 1.5G spectrum from the external quantum efficiency (EQE) analysis, the best-performing devices were fabricated under the same procedures as those used during photovoltaic measurements for each polymer. Figure 3.10.b represents the polymer EQE curves. Notably, all devices showed a photocurrent response between the wavelength region of 300-800 nm. This result was consistent with the absorption spectra of the polymer thin films reported before. The highest EQE values for PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx, and PBDT-SeQx reached 55%, 60%, 74% and 67%, respectively. J_{SC} values from EQE analysis were given in Table 3.11 with parentheses.

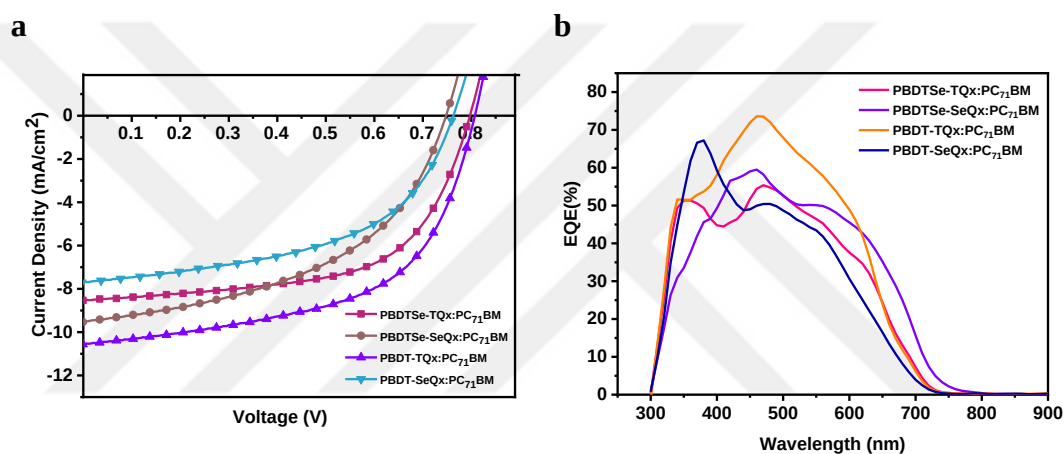


Figure 3.10. a) J-V curves of best performance of polymers based OSCs and b) EQE curves for the best performance OSCs

3.2.8 Morphology Studies of BDT and Qx Based Polymers

To understand the morphology of the active layer, TEM images of the best devices for each polymer were examined. As it could be depicted in Figure 3.11, PBBDTSe-TQx:PC₇₁BM based active layer with 2% DIO solvent addition (Figure 3.11a) possesses the best morphology with continuous channels due to the enhancement of the solubility of PCBM. This notion was validated by the FF result (~61%) given in Table 3.7. For PBBDTSe-SeQx:PC₇₁BM based film, the dark spots that appeared in Figure 3.11.b could be correlated to the precipitated polymers lessening the interpenetrating networks. In addition, the PC₇₁BM aggregation is characterized from the black domains seen in Figure 3.11.c and Figure 3.11.d since its orderly accumulation has a higher electron scattering density than the amorphous polymer aggregation.¹⁰⁹ Although PBBDT-TQx and PBBDT-SeQx based film morphology contain large-scale dark clusters, which cause the exciton diffusion and dissociation inefficiently (Figure 3.11.c and 3.11.d), the best device performance was obtained for PBBDT-TQx-based organic solar cell.

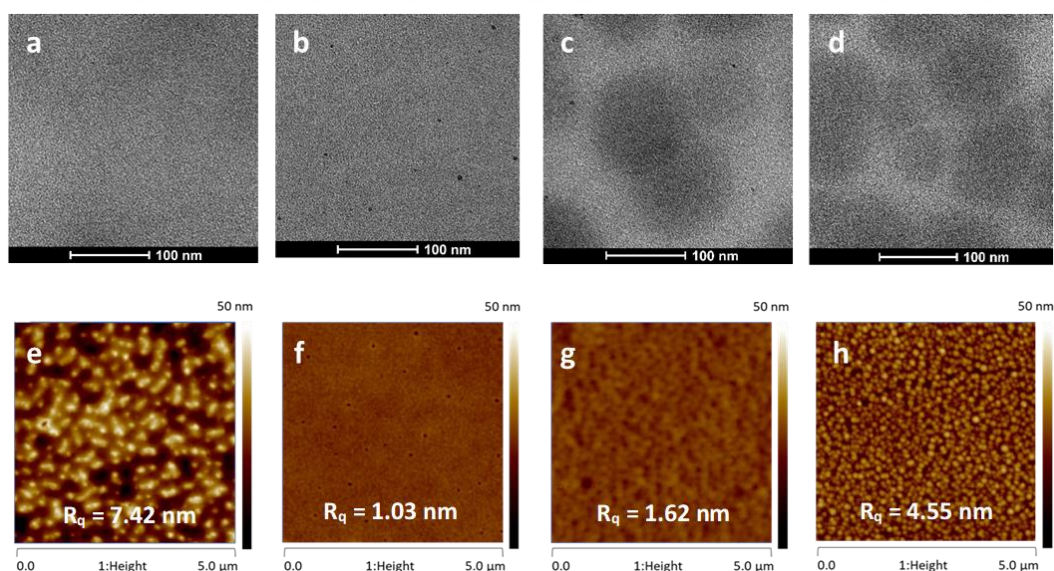


Figure 3.11. TEM images of a) PBBDTSe-TQx:PC₇₁BM with 2% DIO solvent addition, b) PBBDTSe-SeQx:PC₇₁BM, c) PBBDT-TQx:PC₇₁BM and d) PBBDT-

SeQx:PC₇₁BM active layers and e, f, g and h are the corresponding tapping mode AFM images, respectively.

The film topography of the photoactive layers, which were constructed under the same procedures as the best OSC device, was examined using atomic force microscopy (AFM). Figures 3.11e-h depict the AFM height images of the best efficient devices. The root mean square roughness (R_q) of the PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx, and PBDT-SeQx blends with PCBM were measured to be 7.42 nm, 1.03 nm, 1.62 nm and 4.55 nm, respectively. The active layer thicknesses were calculated to be 86.3 nm, 103.8 nm, 102.0 nm and 140.3 nm for PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx blends, respectively, as reported in Table 3.11. The blended film of PBDTSe-TQx and PBDT-SeQx had a higher root mean square roughness than PBDTSe-SeQx and PBDT-TQx-based blends, revealing that the blend films had substantial phase separation. Due to these large phase separations, lower J_{SC} of the PBDTSe-TQx and PBDT-SeQx based devices were obtained. The most uniform and smooth surface with a more favorable morphology for the organic solar cell was observed in PBDT-TQx-based blend film. These results support the significant enhancement in the PCE of PBDT-TQx-based device.

CHAPTER 4

CONJUGATED (D-A1-D-A2) TYPE TERPOLYMERS FOR ORGANIC SOLAR CELL APPLICATIONS

Following the development of the D-A alternating copolymers, a wide range of electron-rich and electron-deficient building blocks for conjugated polymers were produced. These building units have unique characteristics. Particular donors/acceptors, for example, contain chromophores that absorb photons at long wavelengths, while certain units possess deep HOMO levels, and the properties of these components enable the resultant copolymers to be distinctive in various applications. By combining one donor and one acceptor, the D-A alternating copolymers have had a lot of success in developing extremely efficient solar polymers as mentioned earlier. Constructing copolymers with three or more building components is intriguing and promising. Terpolymers with three units in the conjugated polymer backbones are wonderful examples of how to take advantage of the various donors/acceptors' capabilities. Because terpolymers include complex molecular structures while constructing terpolymers for photovoltaic applications, a detailed assessment of factors such as solubility, HOMO-LUMO energy levels, absorbance spectra, and morphology of the blend is required.

In D-A polymers for organic photovoltaics, the thienopyrroledione has been extensively utilized as an electron acceptor component with different donor units. Because of the N atom, this component accommodates high solubility, rigidity and a desirable 3D configuration in the solid-state. The structure of TPD might reduce steric repulsion between nearby backbone units, and feasibly favorable sulfur-oxygen interactions may facilitate planarization of the polymer backbone. Therefore, this chapter depicts the optical and electronic characteristics along with photovoltaic performances of terpolymers based on BDT, thienopyrroldione and benzothiadiazole acceptor units.

4.1 Experimental

4.1.1 Materials

The benzothiadiazole based monomers (Compound 2-7, 2-11 and 2-15) were synthesized before in Chapter 2. (4,8-bis((2-ethylhexyl)oxy) benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-OEH) and 1,3-dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD) were purchased from Sigma Aldrich. The polymerization reactions were performed under N₂ atmosphere and toluene was dried before used in Stille polymerization.

4.1.2 Instrumentation

Thermal characteristics were measured using the thermogravimetric analysis (TGA) (Perkin Elmer Pyris 1) and differential scanning calorimeter (DSC) (Perkin Elmer Diamond) at a heating rate of 10°C/min under N₂. Bruker Spectrospin Avance DPX-400 Spectrometer was used to acquire ¹H and ¹³C Nuclear Magnetic Resonance Spectra with trimethylsilane (TMS) as the internal reference. The average molecular weights of the polymers RP1, RP2 and RP3 in CHCl₃ were determined using gel permeation chromatography (GPC) (polystyrene as the standard reference-Universal Calibration procedure). A Varian Cary 5000 UV–Vis Spectrometer was utilized at room temperature to conduct spectroelectrochemical investigations on RP1, RP2 and RP3. To study the electrochemical properties of these polymers, a Gamry 600 potentiostat was utilized using a three-electrode system with Indium Tin Oxide (ITO) coated glass, platinum wire and Ag wire in 0.1 M tetra-butylammonium hexafluorophosphate/acetonitrile (TBAPF₆/ACN) at 100 mV s⁻¹ scan rate.

4.1.3 Synthesis of Terpolymers

4.1.3.1 Synthesis of RP1

BDT-OEH (0.26 g, 0.336 mmol), compound 2-7 (0.105 g, 0.168 mmol) and TPD (71.2 mg, 0.168 mmol) were dissolved in 10 mL of toluene. N₂ gas was purged through the reaction flask for 40 min. Pd₂(dba)₃ (7.7 mg, 8.4 μmol) catalyst, P(o-tolyl)₃ (20.5 mg, 67.3 μmol) ligand were added and the reaction mixture was heated while stirring at boiling temperature for 23 h. 2-(Tributylstannyl)thiophene (0.118 g, 0.3 mmol) was added and stirred for another 1 h, then 2-bromo thiophene (0.05 g, 0.3 mmol) was added and stirred for a further 1 h. Subsequently, the reaction mixture was cooled to room temperature and the resultant polymer was precipitated with 50 mL of methanol. The polymer was then purified with Soxhlet using methanol, acetone, hexane, and chloroform solvents. The chloroform fraction was recovered under reduced pressure and the solid was precipitated from methanol. The purple solid was then dried under vacuum to obtain RP1 polymer (0.24 g, 86%). ¹H NMR (400 MHz, CDCl₃) δ 8.94 – 6.17 (m, aromatic H), 4.00 (br s, O-CH₂, N-CH₂), 2.42 – 0.42 (m, alkyl H).

4.1.3.2 Synthesis of RP2

BDT-OEH (0.25 g, 0.324 mmol), compound 2-11 (0.104 g, 0.162 mmol) and TPD (68.5 mg, 0.162 mmol) were dissolved in 10 mL of toluene. N₂ gas was purged through the reaction flask for 40 min. Pd₂(dba)₃ (7.4 mg, 8.1 μmol) catalyst, P(o-tolyl)₃ (19.7 mg, 64.7 μmol) ligand were added and the reaction mixture was heated while stirring at boiling temperature for 23 h. 2-(Tributylstannyl)thiophene (0.118 g, 0.3 mmol) was added and stirred for another 1 h, then 2-bromo thiophene (0.05 g, 0.3 mmol) was added and stirred for a further 1 h. Subsequently, the reaction mixture was cooled to room temperature and the resultant polymer was precipitated with 50 mL of methanol. The polymer was then purified with Soxhlet using methanol,

acetone, hexane, and chloroform solvents. The chloroform fraction was recovered under reduced pressure and the solid was precipitated from methanol. The purple solid was then dried under vacuum to obtain RP2 polymer (0.225 g, 84%). ^1H NMR (400 MHz, CDCl_3) δ 8.77 – 7.41 (m, aromatic H), 7.09 – 5.77 (m, aromatic H), 4.84 – 3.19 (m, OCH_2 , N- CH_2), 2.56 – 0.45 (m, alkyl H).

4.1.3.3 Synthesis of RP3

BDT-OEH (0.25 g, 0.324 mmol), compound 2-15 (0.107 g, 0.162 mmol) and TPD (68.5 mg, 0.162 mmol) were dissolved in 10 mL of toluene. N_2 gas was purged through the reaction flask for 40 min. $\text{Pd}_2(\text{dba})_3$ (7.4 mg, 8.1 μmol) catalyst, P(o-tolyl) $_3$ (19.7 mg, 64.7 μmol) ligand were added and the reaction mixture was heated while stirring at boiling temperature for 23 h. 2-(Tributylstannyl)thiophene (0.118 g, 0.3 mmol) was added and stirred for another 1 h, then 2-bromo thiophene (0.05 g, 0.3 mmol) was added and stirred for a further 1 h. Subsequently, the reaction mixture was cooled to room temperature and the resultant polymer was precipitated with 50 mL of methanol. The polymer was then purified with Soxhlet using methanol, acetone, hexane, and chloroform solvents. The chloroform fraction was recovered under reduced pressure and the solid was precipitated from methanol. The purple solid was then dried under vacuum to obtain RP3 polymer (0.217 g, 80%). ^1H NMR (400 MHz, CDCl_3) δ 8.68 – 7.65 (m, aromatic H), 7.16 – 5.82 (m, aromatic H), 3.71 (br s, OCH_2 , N- CH_2), 2.42 – 0.49 (m, alkyl H).

4.1.4 Fabrication of Photovoltaic Devices

The bulk heterojunction organic solar cells were constructed with the device construction of glass/ITO/PEDOT:PSS/active layer/LiF/Al. The glass substrates were ready after the cleaning processes; Hellmanex, water, acetone, and isopropyl alcohol with 15 min ultrasonication for each one, respectively. The substrates were dried with an N_2 gun after that O_2 plasma treatment was used to enhance the work

function of ITO via removing organic impurities as well as to reduce the surface tension of ITO. PEDOT: PSS was filtered through a 0.45 μm PES syringe filter and coated on the ITO surface. Subsequently, the substrates were annealed at 135°C for 15 minutes on the hot plate to evaporate the residual water. In the active layer, the optimizations of donor polymers RP1, RP2 and RP3 were studied with different thicknesses, polymer:PCBM ratios and weight percentages filtered through a 0.22 μm pore-sized PTFE syringe filter and coated on a PEDOT:PSS layer in the nitrogen-filled glove box. LiF was used as a buffer layer with 0.6 nm thickness and finally, Al with 100 nm was used as a cathode. While the hole transport and active layers were spin-coated, LiF and Al were deposited with a vapor deposition under low pressure. All devices were controlled with 16 different devices and the J_{SC} was corrected with IPCE. J-V curves were acquired from Keithley 2400 at AM 1.5G conditions.

4.2 Result and Discussion

4.2.1 Synthesis of Characterization of Terpolymers

All the fluorinated intermediates and monomers were synthesized according to the given references and mentioned in Chapter 2 in the thesis. Benzodithiophene based donor material (BDT-OEH) and thienopyrroledione based acceptor moiety (TPD) were obtained commercially. The routes for the synthesis of three conjugated (D-A1-D-A2) type terpolymers are shown in Figure 4.1. RP1, RP2 and RP3 were prepared via a typical Stille cross-coupling reaction between organotin monomer of alkoxy substituted BDT, brominated TPD and three different benzothiadiazole derivatives (2-7, 2-11 and 2-15) using toluene as solvent and $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-toly})_3$ as the catalyst.¹³⁷ The polymerization reactions were performed under the same conditions in order to compare the properties of the resulted terpolymers. The gel permeation chromatography (GPC) results are shown in Table 4.1. All polymers

show good solubility in chloroform which is favorable for film formation during solar cell device fabrication.

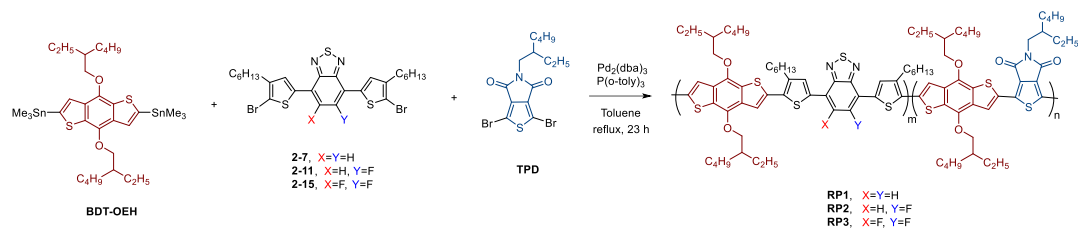


Figure 4.1. Synthesis of terpolymers

Table 4.1 GPC and TGA results of terpolymers

	<i>M_n</i> (kDa)	<i>M_w</i> (kDa)	<i>PDI</i>	<i>T_d</i> (°C)*
RP1	11.0	16.0	1.46	340
RP2	14.3	14.5	1.02	348
RP3	20.7	24.0	1.16	345

*corresponding to 5% weight loss

4.2.2 Thermal Studies of Terpolymers

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were utilized to determine the thermal properties of the polymers. The TGA measurements showed that 5% weight loss degradation temperatures (*T_d*) of RP1, RP2 and RP3 were 340°C, 348°C and 345°C, respectively. The terpolymers did not display any phase transition in temperature vs. heat flow graph measured up to 300°C. According to the measurements, RP1, RP2 and RP3 have good thermal stability.

4.2.3 Electrochemical Studies of Terpolymers

The cyclic voltammetry (CV) measurements were performed for RP1, RP2 and RP3 between the appropriate potentials with a constant 100 mV s⁻¹ scan rate at room

temperature. CV experiments were carried out using a three-electrode setup with indium tin oxide (ITO), Ag wire and Pt wire as the working electrode, the reference electrode and the counter electrode, respectively. The measurement was performed in ACN solvent using TBAPF₆ as the supporting electrolyte. As depicted in Figure 4.2, all polymers showed both p-dopable and n-dopable characters. The summary of all the electrochemical properties is listed in Table 4.2 and Table 4.3. When the p-doping/dedoping peaks for RP1, RP2 and RP3 were measured as 0.98 V/0.86 V, 1.13 V/0.87 V and 1.60 V/0.67 V, the n-doping/dedoping peaks were calculated as -1.67 V/-1.15 V, -1.62 V/-1.12 V and -1.77 V/-1.11 V, respectively. The literature studies have shown that the effective conjugation length can be affected by the molecular weight of the polymers resulting in a variation in their optical and electronic properties.¹⁰⁵

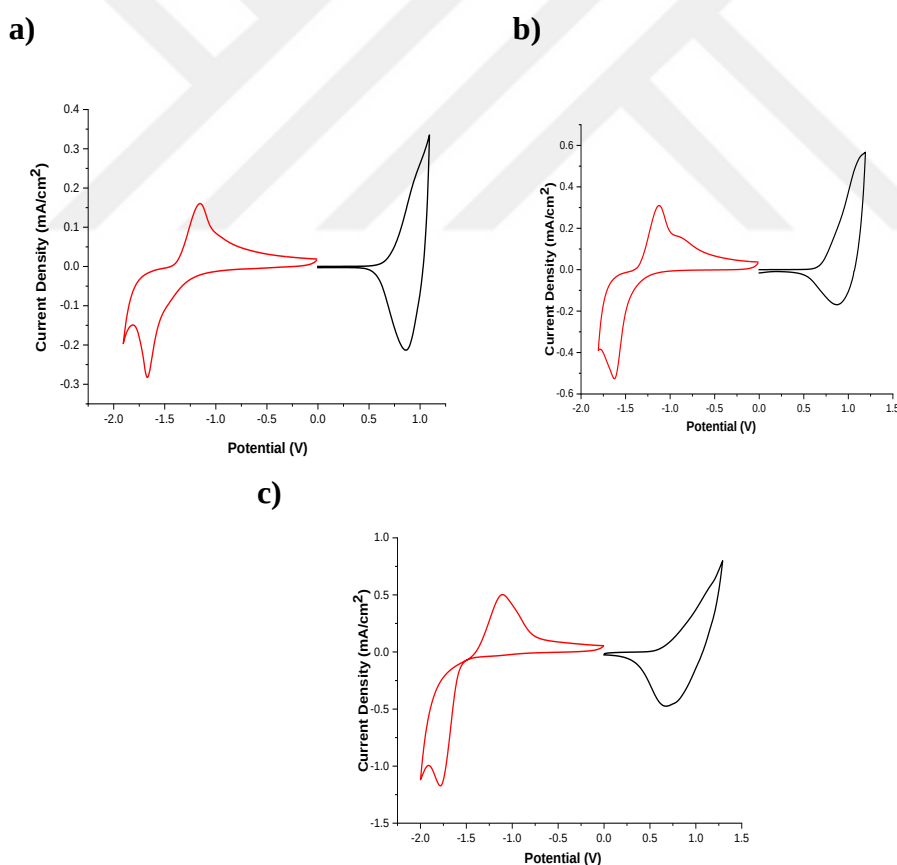


Figure 4.2. Single-scan cyclic voltammogram of a) RP1, b) RP2 and c) RP3 in 0.1 M TBAPF₆/ACN solution at a scan rate of 100 mV/s

HOMO and LUMO energy levels of the polymers were determined using their onset oxidation and reduction potentials due to the ambipolar nature of the polymers. HOMO energy levels for RP1, RP2 and RP3 were found as -5.45 eV, -5.50 eV and -5.42 eV, whereas LUMO energy levels were calculated as -3.32 eV for RP1 and RP2, -3.19 eV for RP3. The electron-withdrawing property of the fluorine atom results in a lower electron density on benzothiadiazole moiety in the polymer backbone and an increased intermolecular interaction of RP1, RP2 and RP3 terpolymer chains. Therefore, the electron density distribution along the polymer chain backbone results in lower energy levels while increasing the number of fluorine atom substitutions.⁶³ As a consequence, RP2 had the lowest HOMO and LUMO energy levels, while the highest HOMO and LUMO energy levels were obtained for RP3.

Table 4.2 Summary of electrochemical properties of RP1-RP3

	$E_{p-doping}$	$E_{p-dedoping}$	$E_{n-doping}$	$E_{n-dedoping}$	E_{onset}^{ox}	E_{onset}^{red}
	(V)	(V)	(V)	(V)	(V)	(V)
RP1	0.98	0.86	-1.67	-1.15	0.70	-1.43
RP2	1.13	0.87	-1.62	-1.12	0.75	-1.43
RP3	1.60	0.67	-1.77	-1.11	0.67	-1.56

Table 4.3 Summary of electrochemical properties of RP1-RP3 (continued)

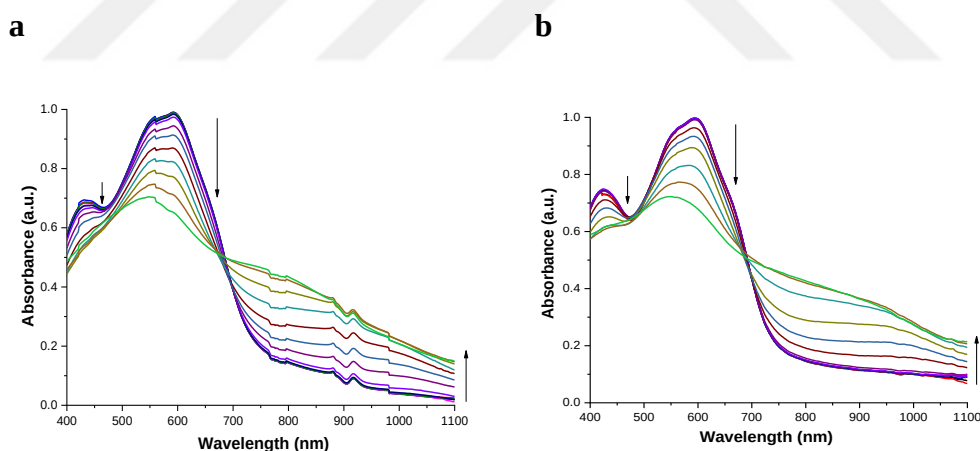
	HOMO (eV)	LUMO (eV)	E_g^{el} (eV)
RP1	-5.45	-3.32	2.13
RP2	-5.50	-3.32	2.18
RP3	-5.42	-3.19	2.23

The E_g^{el} of the terpolymers was calculated from the differences between HOMO and LUMO energy levels of the corresponding polymers and reported as 2.13 eV, 2.18 eV and 2.23 eV for RP1, RP2 and RP3, respectively. The randomly distributed

fluorinated acceptor monomers along the polymer backbone may lead to the destruction of the planarization of the polymer's chains via non-covalent bond interactions.¹³⁸ This destruction may result in twisting of the polymer chains, which causes a decrease in effective conjugation length. Therefore, higher bandgaps were obtained for RP2 and RP3 terpolymers.¹³⁹

4.2.4 Spectroelectrochemical Studies of Terpolymers

The UV-Vis-NIR spectra of the terpolymers were obtained to examine the optical and electrochemical changes upon the doping process. The absorption spectra are shown in Figure 4.3, and the measurements were taken in 0.1 M TBAPF₆/ACN solution. The optical properties comprising E_g , maximum absorption wavelength and states of spectroelectrochemical analysis while applying potential were found in Figure 4.3. The rise in the NIR absorbance region of terpolymers indicates the formation of polaron and bipolaron states after applying stepwise oxidation.



c

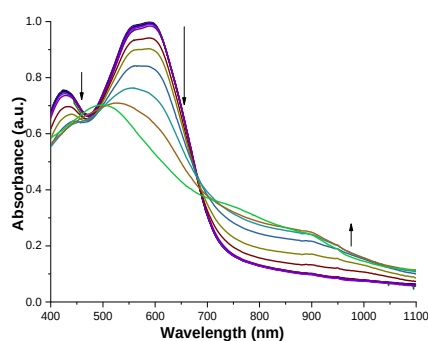


Figure 4.3. UV–Vis-NIR absorption spectra of thin film of a) RP1, b) RP2 and c) RP3 in 0.1 M TBAPF6/ACN solution

$\lambda_{\max}$ and λ_{onset} of the polymers were calculated from the neutral states of the terpolymers in Figure 4.3. The summary of the optical studies obtained from absorption spectra is given in Table 4.4. For RP1, RP2 and RP3, the optical band gaps were determined as 1.62 eV, 1.63 eV, and 1.68 eV, respectively. The fluorination of the backbone raised the optical band gaps moderately, and the variations in the onset of maximum absorption peak clearly show the influence of the fluorine atom substitution. The results of the spectroelectrochemical analysis were similar to PBDT-BT, PBDT-FBT and PBDT-FFBT alternating polymers mentioned in Chapter 2. However, there is a more pronounced peak shoulder for RP2 terpolymers, which contains one F atom substituted on benzothiodiazole unit. The reason could be significant crystal formations between polymer chains resulted from π - π interactions.¹⁴⁰

Table 4.4 Summary of spectroelectrochemical properties of RP1-RP3

	$\lambda_{\max}$ (nm)	λ_{onset} (nm)	E_g^{op} (eV)
RP1	595	765	1.62
RP2	595	762	1.63
RP3	592	740	1.68

4.2.5 Organic Solar Cell Applications of Terpolymers

A set of BHJ solar cells was constructed and evaluated utilizing RP1, RP2 and RP3 as donors and PC₇₁BM as an acceptor component to assess the influence of incorporation of the third component and fluorine atom substitution on the resultant photovoltaic performance. The devices of the polymers were constructed using a frequently utilized device configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/LiF/Al. *o*-DCB was used as the processing solvent for the active layers of the devices. The solar cell devices were manufactured with various concentrations and spin coating rates to reach the best thickness for a good comparison between synthesized donor-acceptor type copolymers in BHJ OSCs. Moreover, a small amount of 1,8-diiodooctane (DIO) and diphenyl ether (DFE) was used to optimize the photovoltaic performance of the devices. The thicknesses of the active layers were optimized by altering the spin coating rate which was found as 500 rpm for RP1 and 350 rpm for RP2 and RP3.

While determining the effect of the molecular properties of polymers on photovoltaic performance, the weight ratio and the concentration of the polymer blends in the active layer were altered during the construction of the solar cells. As summarized in Table 4.6, the weight ratio of 1:3 for RP1:PCBM resulted the higher PCE of 2.36%. The best concentration was determined as 3% which resulted in better photovoltaic parameters. Therefore, the best device performance was obtained with 1:3 RP1:PCBM with 3% concentration and 500 rpm spin coating rate without any additional treatment. A J_{sc} of 6.13 mA/cm², V_{oc} of 0.79 V, FF of 65% and PCE of 3.16% were recorded for this device configuration. The spin coating rate of 350 and 750 produced lower photovoltaic parameters than 500 rpm.

Table 4.5 Summary of photovoltaic parameters of RP1 utilized bulk heterojunction solar cells

RP1:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)	Treatment
1:1 (2%)	3.57	0.75	57	1.54	500	-
1:2 (2%)	5.32	0.78	55	2.30	500	-
1:3 (2%)	4.92	0.78	62	2.36	500	-
1:4 (2%)	4.66	0.74	39	1.32	500	-
1:3 (2.5%)	5.82	0.79	62	2.86	500	-
1:3 (3%)	6.13	0.79	65	3.16	500	-
1:3 (3.5%)	5.55	0.80	44	1.95	500	-
1:3 (3%)	6.33	0.79	57	2.88	350	-
1:3 (3%)	5.52	0.79	66	2.86	750	-
1:3 (3%)	5.50	0.74	62	2.51	500	2% DIO
1:3 (3%)	4.73	0.75	64	2.26	500	3% DPE

Table 4.7 summarizes the photovoltaic parameters for RP2. The best weight ratio of RP2:PCBM and the active layer concentration were determined as 1:2 and 2.5%, respectively while using 500 rpm of spin coating process. While increasing the concentration of the blend solution led to an improvement on J_{sc} and PCE due to the combined absorption range of the PCBM and polymer, the thickness of the active layer should be also studied. The decrease in the spin coating rate from 500 rpm to 350 rpm generates thicker active layer. Therefore, enhancing the active layer thickness facilitates higher light absorption which was supported by further gain in the J_{sc} value.¹⁴¹ Based on these fabrication parameters, the highest device performance was obtained for RP2 -based solar cells with 1:2 (w/w) RP2:PC₇₁BM blend ratio with 2.5% concentration at 350 rpm spin coating rate. This device exhibited the highest PCE of 3.38%, J_{sc} of 7.79 mA/cm², V_{oc} of 0.77 V, and FF of 56%.

Addition of small amount of DIO or DFE additives can enhance the active layer by optimizing the domain size and polymer PCBM interface. However, for RP1 and RP2, there was any improvement on PCE while processing the device with 2% DIO and 3% DFE addition.

Table 4.6 Summary of photovoltaic parameters of RP2 utilized bulk heterojunction solar cells

RP2:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)	Treatment
1:1 (2%)	6.20	0.76	48	2.27	500	-
1:2 (2%)	6.11	0.76	56	2.62	500	-
1:3 (2%)	5.49	0.76	60	2.49	500	-
1:4 (2%)	3.97	0.78	60	1.86	500	-
1:2 (2.5%)	7.43	0.77	54	3.09	500	-
1:2 (2.5%)	6.66	0.76	51	2.58	500	-
1:2 (2.5%)	7.79	0.77	56	3.38	350	-
1:2 (2.5%)	5.50	0.77	60	2.56	750	-
1:2 (2.5%)	6.46	0.74	38	1.83	350	2% DIO
1:2 (2.5%)	6.99	0.75	43	2.26	350	3% DPE

Table 4.7 Summary of photovoltaic parameters of RP3 utilized bulk heterojunction solar cells

RP3:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)	Treatment
1:1 (2%)	4.36	0.67	40	1.18	500	-
1:2 (2%)	3.76	0.66	47	1.18	500	-
1:3 (2%)	4.12	0.66	51	1.39	500	-
1:4 (2%)	3.62	0.69	52	1.31	500	-
1:2 (2%)	5.83	0.74	43	1.84	500	NF

1:3 (2%)	5.63	0.74	44	1.85	500	NF
1:4 (2%)	4.72	0.72	51	1.73	500	NF
1:3 (2.5%)	5.88	0.77	45	2.05	500	NF
1:3 (3%)	5.51	0.77	44	1.88	500	NF
1:3 (2.5%)	6.36	0.77	45	2.21	350	NF
1:3 (2.5%)	5.56	0.75	49	2.03	750	NF
1:3 (2.5%)	6.85	0.75	45	2.33	350	NF+2% DIO
1:3 (2.5%)	7.35	0.74	48	2.60	350	NF+3% DPE
1:3 (2.5%)	4.71	0.75	41	1.45	350	NF+3% DIO
1:3 (2.5%)	6.88	0.74	45	2.28	350	NF+6% DPE

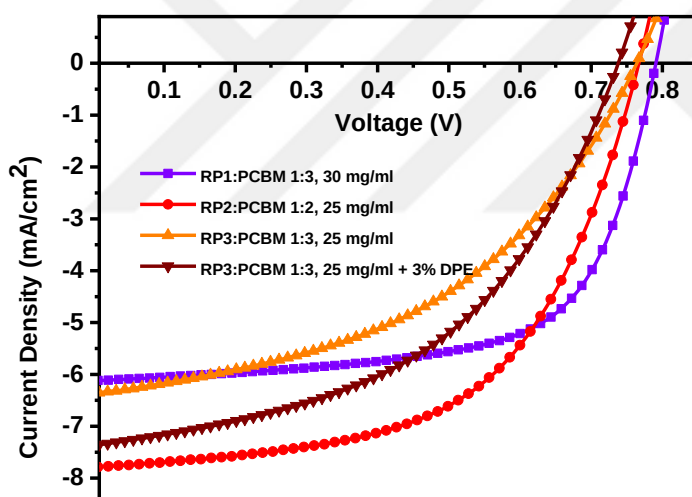


Figure 4.4. Current density-voltage curves of solar cells based on RP1-RP3

External quantum efficiency (EQE) curves of the devices based on RP1, RP2 and RP3 via using the optimum conditions were shown in Figure 4.5. The conversion efficiencies measured for the best device performances were observed over the wavelength range of 350–800 nm which are in agreement with the absorption spectra of the polymers. The highest EQE% values were found as 31%, 38% and 34% for RP1, RP2 and RP3, respectively.

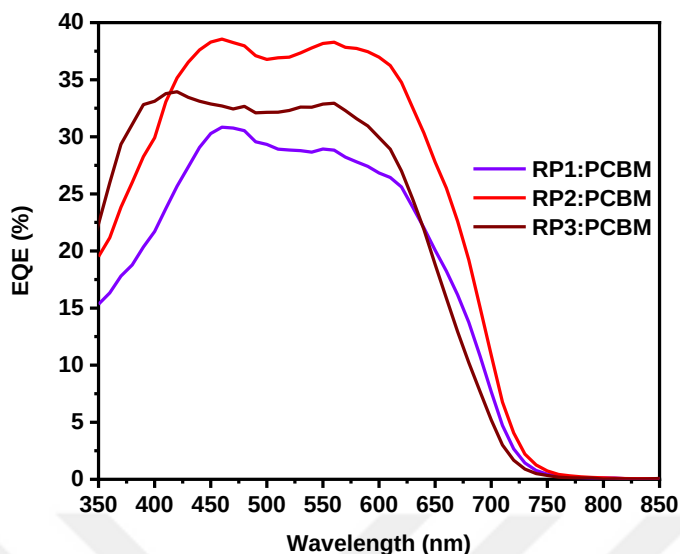


Figure 4.5. EQE curves of solar cells based on RP1-RP3

4.2.6 Morphology Studies of Terpolymers

To understand the morphology of the active layer, TEM images of the best devices for each polymer were examined. As seen from Figure 4.6a-b, RP1 and RP2 based solar cells display homogenous and nanoscale phase separation. However, RP2:PC₇₁BM based active layer (Figure 4.6a) possesses the best morphology with continuous channels due to the more orderly accumulation of donor and acceptor materials. This outcome was validated by the J_{SC} and FF results obtained from the best device performance of RP2. The dark spots that appeared in Figure 4.6c-d is characterized as PCBM domains. The more separated polymer and PCBM domains lessens the interpenetrating networks.²⁶ Therefore, the addition of 3% DPE to the active layer solution provides continuous and well distributed polymer networks which leads to development of the J_{SC} , FF and PCE values.⁷⁹

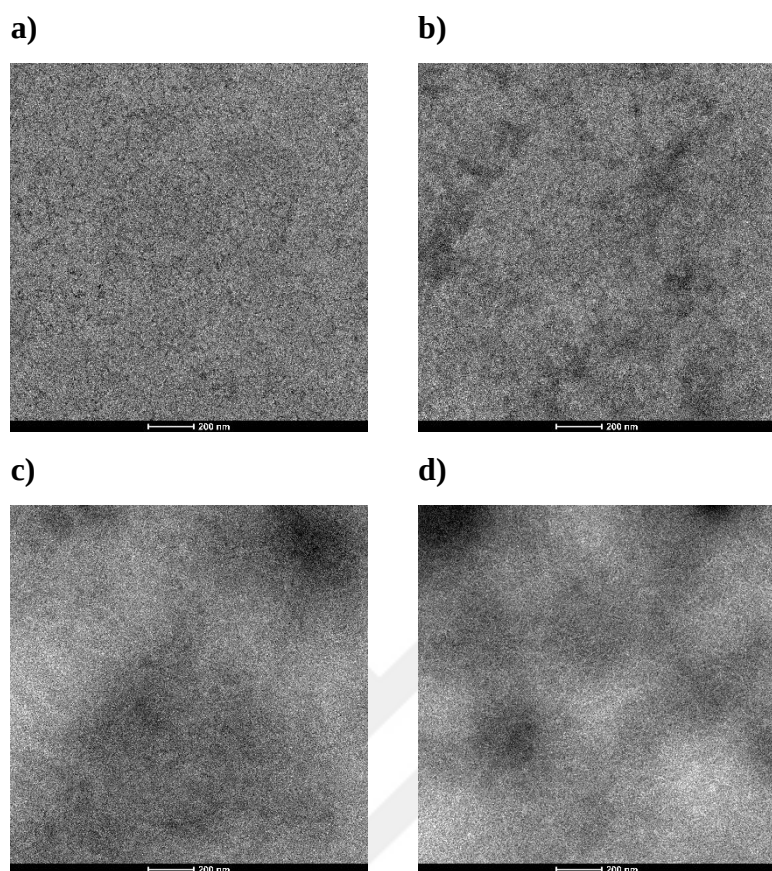


Figure 4.6. TEM images of a) RP1:PC71BM, b) RP2PC71BM, c) RP3:PC71BM and d) RP3:PC71BM with 3% DPE solvent addition active layers

The film topography of the photoactive layers, which were constructed under the same procedures as the best OSC device, was examined using atomic force microscopy (AFM). Figures 4.7a-d depict the AFM height images of the best efficient devices. The root mean square roughness (R_q) and the active layer thicknesses of the terpolymers were measured and the results were given in Table 4.9.

Table 4.8 Summary of the AFM studies

	R_q (nm)	Thickness (nm)
RP1	0.91	136.5
RP2	1.35	128.9
RP3	10.1	126.2
RP3 with additive	13.2	123.3

The blended film of RP3 and RP3 with 3% DPE additive had approximately ten times higher root mean square roughness than RP1 and RP2 -based blends, revealing that the blend films had extremely large phase separation. These extensive phase separations produced lower FF of the RP3 based devices (48%). The active layer thickness of the best devices were calculated as similar and the most uniform and smooth surface with a more favorable morphology for the organic solar cell was observed in RP2 -based blend film. These results support the significant enhancement in the PCE of RP2-based device.

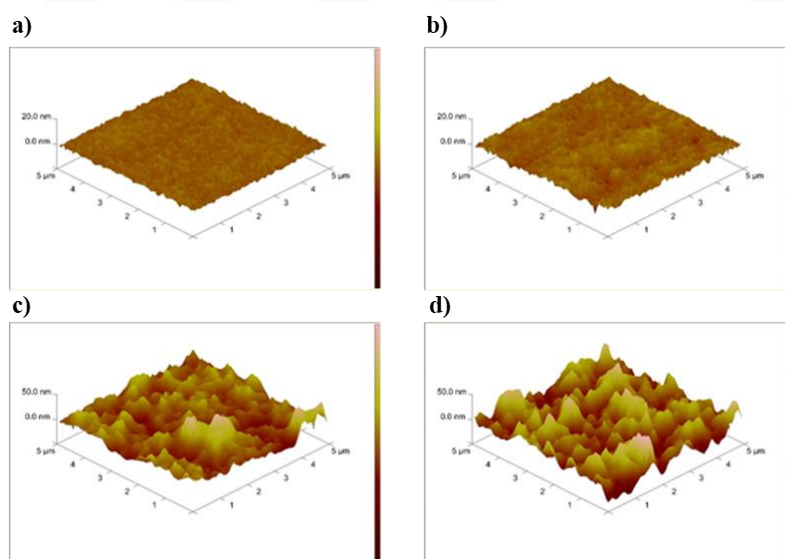


Figure 4.7. AFM images of a) RP1:PC71BM, b) RP2:PC71BM, c) RP3:PC71BM and d) RP3:PC71BM with 3% DPE solvent addition active layers



CHAPTER 5

THE STUDY OF THE EFFECT OF DIFFERENT SIDE GROUPS ON BENZODITHIOPHENE AND BENZOTRIAZOLE BASED POLYMERS FOR SOLAR CELLS

In general, incorporating two dimensional (2D) conjugated side chains to BDT units affected not only the absorption values of the resultant polymers, but also their molecular energy levels, crystalline characteristics, and charge carrier mobilities, leading to a broad impact on the photovoltaic properties of the PSC devices. Employing 2D conjugated side chains to tune the optical and electronic characteristics of synthesized polymers is a simple and appealing strategy.

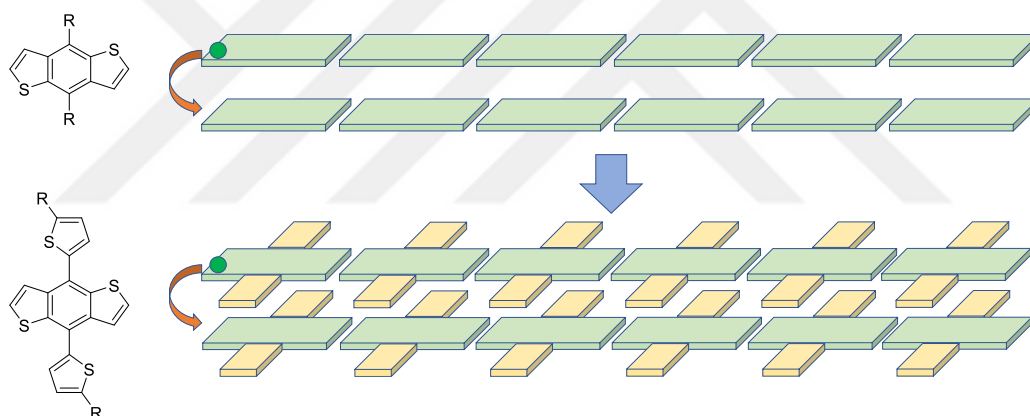


Figure 5.1. Schematic representation of 2D conjugated BDT units

Several researchers have developed and synthesized various conjugated molecules that are employed as side chains in 2D-BDT polymers throughout the last several years.^{142–144} Thienyl-substituted BDT was the first 2D conjugated BDT unit, and thienyl-substituted BDT units were found in numerous extensively reported excellent conjugated polymers.^{145,146} Furan and selenophene are also widely utilized to change the physicochemical characteristics of thienyl-BDT incorporating polymers as a comparable series of thiophene. To change the composition of the BDT-based polymer, a phenyl-substituted BDT was produced by researchers due to

its weak electron-donating characteristics, broad π -conjugated area, and excellent planarity of the benzene ring. Many conjugated side chains having higher π -conjugated areas and extended conjugated lengths, such as thienothiophene, oligothiophene and thianaphthene were also created to prolong the impacts of the 2D conjugated side chain.^{144,147}

In this study, the aim was the synthesis of novel conjugated polymers with BDT and benzotriazole (BTz) units and to present a comprehensive study on how benzotriazole-containing polymers will affect photovoltaic performance when used together with 2D-BDT structures with phenyl, thienyl and thienothiophenyl side chains.

5.1 Experimental

5.1.1 Materials

4-Bromophenol, 3-bromophenol, benzo[1,2-b:4,5-b']dithiophene-4,8-dione, (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-T) and 4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (compound 5-5) were purchased commercially. 4,7-bis(5-bromoselenophen-2-yl)-2-(2-octyldodecyl)-2H-benzo[d][1,2,3]triazole (BTz) was synthesized in Çirpan's Research Laboratory, earlier. The polymerization reactions were performed under N₂ atmosphere and toluene was dried before used in Stille polymerization.

5.1.2 Synthesis of Monomers

5.1.2.1 Synthesis of 5-1

4-Bromophenol (8.6 g, 50 mmol), K₂CO₃ (8.3 g, 60 mmol) was placed in a three-necked, round-bottomed flask and then 200 mL of DMF was added. Under an

nitrogen atmosphere, 1-bromo-2-ethylhexane (9.5 g, 50 mmol) was added dropwise via a syringe. The mixture was heated at reflux overnight in the dark. It was then cooled to room temperature and the reaction mixture was poured into 300 mL of water and extracted three times with CHCl_3 . The organic extract was successively washed twice with saturated KOH and water. The combined organic phases were dried with MgSO_4 . After filtration the solvents were evaporated under vacuum and the crude product was purified on a silica gel column eluting with hexane. A colorless liquid was obtained (10.3 g, 73%). ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 9.0$ Hz, 2H), 6.67 (d, $J = 9.0$ Hz, 2H), 3.69 (d, $J = 6.0$ Hz, 2H), 1.61 (dt, $J = 12.2, 6.0$ Hz, 1H), 1.46 – 1.13 (m, 8H), 0.86 – 0.78 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 132.2, 116.3, 112.5, 70.7, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1.

5.1.2.2 Synthesis of 5-2

Magnesium particles (0.797 g, 33.2 mmol) in anhydrous THF (35 mL) were placed in the reaction flask under nitrogen atmosphere, then Compound 5-1 (7.87 g, 27.6 mmol) was added dropwise with vigorous stirring. I_2 (10 mg) was added as catalyst for the reaction during the process. The solution was stirred at boiling temperature using reflux for 5 hours until the magnesium was consumed and then cooled. The solution system was slowly added to a solution of benzo[1,2-b:4,5-b']dithiophene-4,8-dione (2.03 g, 9.22 mmol) dispersed in 40 mL of THF via a syringe. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (13.3 g) was dissolved in 10% aqueous HCl (18.6 mL) and then added dropwise to the above reaction mixture. The solution was stirred for another 20 hours at 50°C . After cooling to room temperature, the mixture was poured into water and extracted with DCM. The organic phase was successively washed twice with water and sodium bicarbonate solution, and the combined organic phase was dried with MgSO_4 and evaporated to give the crude product. The crude product was purified on a silica gel column eluting with pure hexane. White powder solid was obtained (1.7 g, 31%). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.7$ Hz, 2H), 7.29 (dd, $J = 17.8, 5.7$ Hz, 2H), 7.02 (d, $J = 8.7$ Hz, 2H), 3.88 (d, $J = 5.5$ Hz, 2H), 1.73 (dt, $J = 12.1, 6.0$ Hz, 1H),

1.56 – 1.24 (m, 8H), 0.96 – 0.84 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 138.3, 136.2, 131.4, 130.5, 130.0, 127.0, 123.1, 114.7, 70.5, 39.5, 30.6, 29.2, 23.9, 23.1, 14.1, 11.2.

5.1.2.3 Synthesis of BDT-Ph

A solution of compound 5-2 (0.9 g, 1.5 mmol) in dry THF (30 mL) was deoxygenated with nitrogen for 30 min and then a 2.5 M solution of n-BuLi in n-hexane (1.8 mL, 4.62 mmol) at 0°C was added dropwise. The solution was then allowed to warm to room temperature for 30 min and a 1.0 M solution of trimethyltin chloride in THF (4.9 mL, 4.9 mmol) was added and stirred overnight. The mixture was then poured into water and extracted with DCM. The organic phase was evaporated and the residue recrystallized from acetone to give a pale yellow solid (0.75 g, 54%). ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 8.6 Hz, 2H), 7.31 (s, 1H), 7.03 (d, J = 8.7 Hz, 2H), 3.89 (d, J = 5.7 Hz, 2H), 1.72 (dt, J = 12.1, 6.0 Hz, 1H), 1.56 – 1.24 (m, 8H), 0.89 (dt, J = 13.9, 7.2 Hz, 6H), 0.28 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 141.6, 137.1, 132.1, 130.9, 130.6, 128.5, 114.6, 70.5, 39.5, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2, -8.3.

5.1.2.4 Synthesis of 5-3

3-bromophenol (5.0 g, 28.9 mmol) was taken into a 100 mL reaction flask and stirred at 60°C for half an hour in anhydrous DMF (35 mL) solvent under N_2 atmosphere. The compound 2-ethylhexyl bromide (6.14 g, 31.8 mmol) was added to the reaction mixture and the reaction was spun at 150°C until the next day. The next day, the reaction was brought to room temperature and stopped by adding distilled water. Afterwards, it was extracted using a mixture of chloroform and brine, and the obtained organic phase was dried with MgSO_4 , filtered with filter paper, and then concentrated. Purification of the material was done by silica gel column chromatography method using hexane and the material was obtained cleanly (3.96

g, 80%). ^1H NMR (400 MHz, CDCl_3) δ 7.08 – 6.96 (m, 3H), 6.75 (ddd, J = 8.2, 2.2, 1.1 Hz, 1H), 3.74 (dd, J = 5.7, 1.3 Hz, 2H), 1.68 – 1.58 (m, 1H), 1.47 – 1.16 (m, 8H), 0.92 – 0.77 (m, 6H).

5.1.2.5 Synthesis of 5-4

Under N_2 atmosphere and in a 100 mL reaction flask, Compound 5-3 (2.50 g, 8.77 mmol) was added dropwise onto magnesium (0.355 g, 14.61 mmol) and mixed in anhydrous THF (35 mL) solvent. At this time, I_2 (10 mg, 0.04 mmol) was added to the reaction as catalyst. The reaction mixture was refluxed for 5 hours until the magnesium was consumed. After the reaction mixture refluxed for another 1 hour, it was cooled to room temperature. This reaction mixture was then superimposed on benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.644 g, 2.92 mmol) dissolved in 40 mL of THF solvent in another 100 mL reaction flask. added slowly. Then, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (4.22 g, 18.70 mmol) was dissolved in 10% HCl solution and added to the reaction mixture dropwise. The reaction was stirred for an additional hour at 50°C and then brought to room temperature. Then the reaction mixture was added to brine and extracted with DCM. The organic phase was dried with MgSO_4 , filtered through filter paper, and then concentrated. Purification of the obtained material could not be performed due to low yield.

5.1.2.6 Synthesis of BDT-TT

Commercially available compound 5-5 (2.0 g, 2.9 mmol) was dissolved in dry THF, then a solution of $n\text{-BuLi}$ (3.47 mL, 8.7 mmol, 2.5 M in hexane) was added dropwise to the reaction medium at -78°C under N_2 atmosphere. was done. The reaction medium was stirred at -78°C for 1 hour, then warmed to room temperature and stirred for 1 hour. The reaction medium was cooled back to -78°C and trimethyltin chloride (10.1 mL, 10.1 mmol, 1.0 M in THF) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. Water was added to the mixture

to quench the reaction and the aqueous phase was extracted with EtOAc. The organic phases were collected and dried using MgSO_4 . The organic phases were evaporated under reduced pressure. The residue was recrystallized from acetone to give a yellow solid (2.9 g, 98%). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 2H), 7.59 (s, 2H), 7.03 (s, 2H), 2.89 (d, $J = 6.7$ Hz, 4H), 1.74 – 1.64 (m, 4H), 1.48 – 1.27 (m, 12H), 1.02 – 0.87 (m, 18H), 0.39 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.5, 143.8, 143.1, 140.2, 139.3, 137.6, 131.0, 122.6, 120.3, 117.4, 41.5, 35.3, 32.4, 29.0, 25.5, 23.1, 14.3, 10.9, -8.2.

5.1.3 Synthesis of Polymers

5.1.3.1 Synthesis of PBDTPh-BTz

BDT-Ph (0.2 g, 0.22 mmol), BTz (0.180 g, 0.22 mmol) and 12 mL of dry toluene were placed in a two-neck flask. The solution was flushed with nitrogen for 1 hour, then $\text{Pd}_2(\text{dba})_3$ (10 mg, 11.0 μmol) and $\text{P}(o\text{-tolyl})_3$ (27.0 mg, 88.0 μmol) were added to the reaction medium. The oil bath was carefully heated to 110°C and the reaction was stirred at this temperature for 17 hours under an argon atmosphere. The reaction mixture was then cooled to room temperature and poured slowly into methanol (100 mL). The resulting precipitate was purified with methanol, hexane, chloroform and chlorobenzene solutions, respectively, with the aid of a Soxhlet apparatus. Finally, the polymer was recovered as a solid from the chlorobenzene fraction by rotary evaporation. A purple solid was obtained (0.19 g, 68%). ^1H NMR (400 MHz, CDCl_3) δ 7.95 – 6.67 (m, aromatic H), 4.97 – 4.51 (m, aromatic H), 4.44 – 3.69 (m, OCH_2 , NCH_2), 2.49 – 2.07 (m, alkyl H), 1.88 – 0.64 (m, alkyl H).

5.1.3.2 Synthesis of PBDTT-BTz

BDT-T (0.186 g, 0.205 mmol), BTz (0.167 g, 0.205 mmol) and 10 mL of dry toluene were placed in a two-neck flask. The solution was gassed with nitrogen gas for 1

hour, then $\text{Pd}_2(\text{dba})_3$ (9.4 mg, 10.0 μmol) and $\text{P}(\text{o-tolyl})_3$ (25.0 mg, 82.0 μmol) were added to the reaction medium. The oil bath was carefully heated to 110°C and the reaction was stirred at this temperature for 17 hours under an argon atmosphere. The reaction mixture was then cooled to room temperature and poured slowly into methanol (100 mL). The resulting precipitate was purified with methanol, hexane, chloroform and chlorobenzene solutions, respectively, with the aid of a Soxhlet apparatus. Finally, the polymer was recovered as a solid from the chlorobenzene fraction by rotary evaporation. A blue solid was obtained (0.21 g, 81%). ^1H NMR (400 MHz, CDCl_3) δ 8.54 – 6.59 (m, aromatic H), 4.95 – 4.27 (m, NCH_2), 2.93 (br s, $-\text{CH}_2-$), 2.31 (br s, $-\text{CH}_2-$), 2.00 – 0.52 (m, alkyl H).

5.1.3.3 Synthesis of PBDTTT-BTz

BDT-TT (0.172 g, 0.169 mmol), BTz (0.138 g, 0.169 mmol) and 10 mL of dry toluene were placed in a two-neck flask. The solution was gassed with nitrogen gas for 1 hour, then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (9.5 mg, 13.5 μmol) was added to the reaction medium. The oil bath was carefully heated to 110°C and the reaction was stirred at this temperature under an argon atmosphere for 23 hours. The reaction mixture was then cooled to room temperature and poured slowly into methanol (100 mL). The resulting precipitate was purified using a Soxhlet apparatus using methanol, hexane and chloroform solvents, respectively. Finally, the polymer was recovered as a solid from the chloroform fraction by rotary evaporation. A purple solid was obtained (0.21 g, 77%). ^1H NMR (400 MHz, CDCl_3) δ 8.05 – 6.36 (m, aromatic H), 5.05 – 4.25 (m, $-\text{NCH}_2$), 2.93 (br s, $-\text{CH}_2-$), 2.40 – 0.59 (m, alkyl H).

5.1.4 Fabrication of Photovoltaic Devices

PSCs were constructed utilizing the conventional device architecture of ITO/PEDOT:PSS/active layer/LiF/Al. The active layer contains PBDT-PhBTz, PBDT-TBTz and PBDT-TTBDT as donor polymers and PC_{71}BM as an acceptor in

the mixture, which is used to create an active layer in a bulk heterojunction solar cell. For 15 minutes, ITO-coated glasses were ultrasonicated with Hellmanex, distilled water, acetone, and isopropyl alcohol, within the order. The oxygen plasma was then used to clear the organic contaminants and regulate the work function. PEDOT: PSS was coated and annealed at 135°C for 15 minutes after cleaning operations. The optimal weight concentration for polymer PBDT-TBTz was 30 mg/ml, while it was optimized as 20 mg/ml for PBDT-TTBTz with 1,2-dichlorobenzene (*o*-dcb) as the solvent. Although solvent additives (DIO, CN, and DPE) were used to increase the PCE value in this study, they did not lead an increase in the performance of the solar cell. At the top of the device, LiF and Al were deposited under low pressure. The JV characterizations of generated PSCs were carried out with a Keithley 2400 under simulated AM 1.5G solar irradiation (100 mW cm⁻²).

5.2 Result and Discussion

5.2.1 Synthesis and Characterization of BDT and BTz Based Polymers

The pathway determined for the synthesis of the p-alkoxyphenyl substituted 2D-BDT donor material is given in Figure 5.2. The reaction of the commercially purchased 4-bromophenol compound with the 2-ethylhexyl bromide in the presence of K₂CO₃ was carried out in DMF solvent and Compound 5-1 was successfully obtained. Then, the reaction of Compound 5-1 with commercially available benzo[1,2-b:4,5-b']dithiophene-4,8-dione was carried out firstly in the presence of Mg metal and the following with Sn₂Cl.2H₂O resulted Compound 5-2. After the cleavage of the proton at near the sulfur atom of benzodithiophene using nBuLi solution, BDT-Ph was synthesized with SnClMe₃ solution successfully.^{49,142}

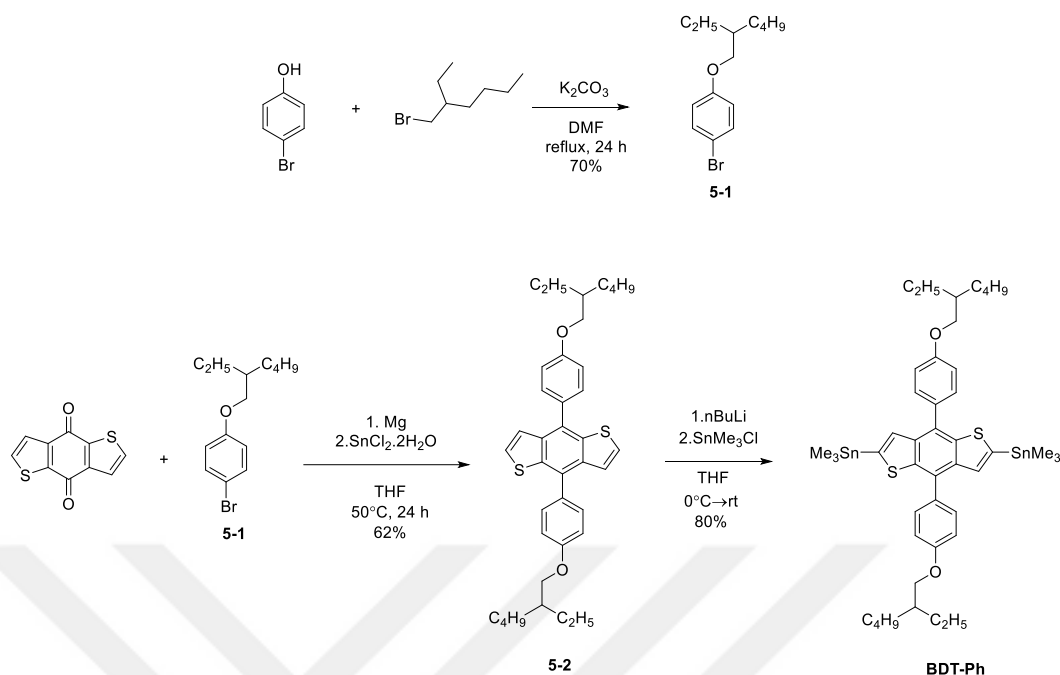


Figure 5.2. Synthetic pathway for p-alkoxy phenyl substituted BDT donor

When the recent studies are examined, it is seen that the energy levels of conjugated polymers containing BDT can be controlled by playing with side units. In addition to the side group used, it was observed that the position of the alkyl unit attached to the aromatic ring used also affects the molecular energy level. Based on these results, another 2D-BDT donor moiety was decided to synthesize using the alkoxy group attached to the meta position. For this purpose, Compound 5-3 was synthesized using commercially purchased 3-bromophenol and 2-ethylhexyl bromide with the same synthetic procedure. The synthesis pathway is shown in Figure 5.3. The frequently used procedure for the synthesis of BDT donors in the literature which is using the $\text{nBuLi/Sn}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ compounds was employed. However, the desired attachment of m-alkoxyphenyl group was not occurred after the optimization reactions. Therefore, this reaction was repeated in the presence of Mg metal leading very low product yield and the reaction performed under these conditions was also considered unsuccessful as a result of column chromatography to obtain BDT-mPh.

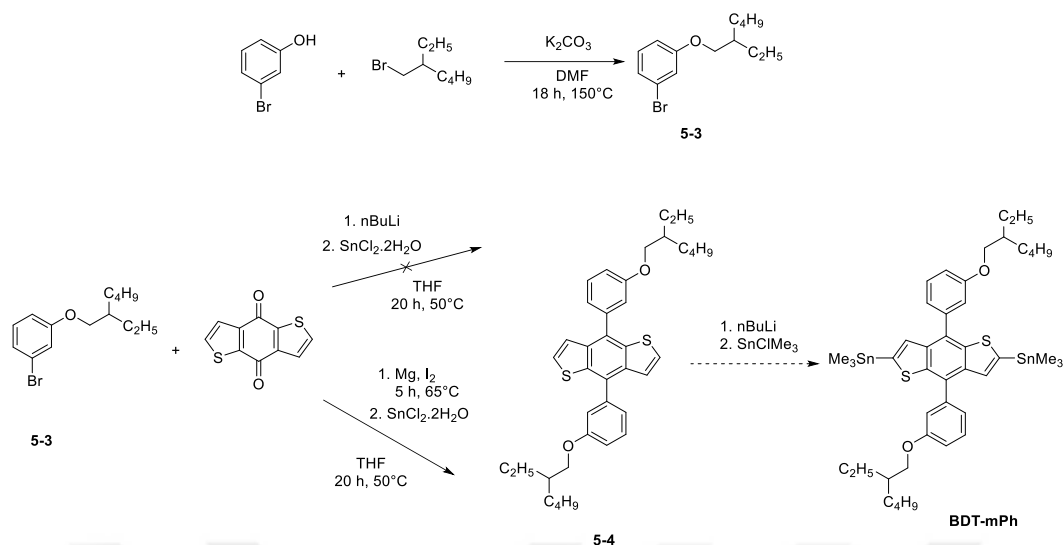


Figure 5.3. Synthetic pathway for m-alkoxy phenyl substituted BDT donor

Alkoxy group (-OR) has a property of ‘ortho and para directors’. In electrophilic substitution reactions, ortho- and para- products dominate, and the meta- product is an highly minor byproduct. Therefore, the reaction of m-alkoxyphenyl with BDT was failed. Eventhough the synthesis of BDT-mPh was not accomplished, the thienothiophene containing the BDT was successfully synthesized and shown in Figure 5.4.

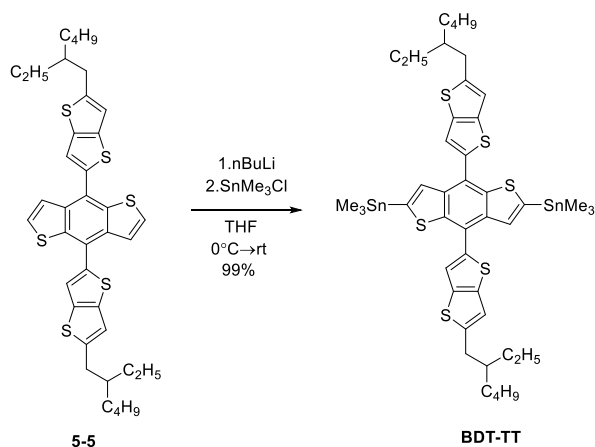


Figure 5.4. Synthesis of thienothiophene substituted BDT donor

PBDT-PhBTz and PBDT-TBTz polymers were synthesized by the Stille coupling reaction in the presence of $\text{Pd}_2(\text{dba})_3$ and *o*-tolyl-phosphine in toluene solvent (Figure 5.5). However, when this catalyst pair was used for the synthesis of PBDT-TTBTz polymer, the resultant polymer was insoluble in CHCl_3 and chlorobenzene solvents. Therefore, the less reactive catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ was used for PBDT-TTBTz. The polymers were purified by Soxhlet extraction with methanol, acetone, hexane, chloroform and chlorobenzene. Oligomers and Pd catalyst were removed by Soxlet extraction method and the purity and molecular weight of the polymers were determined by GPC.

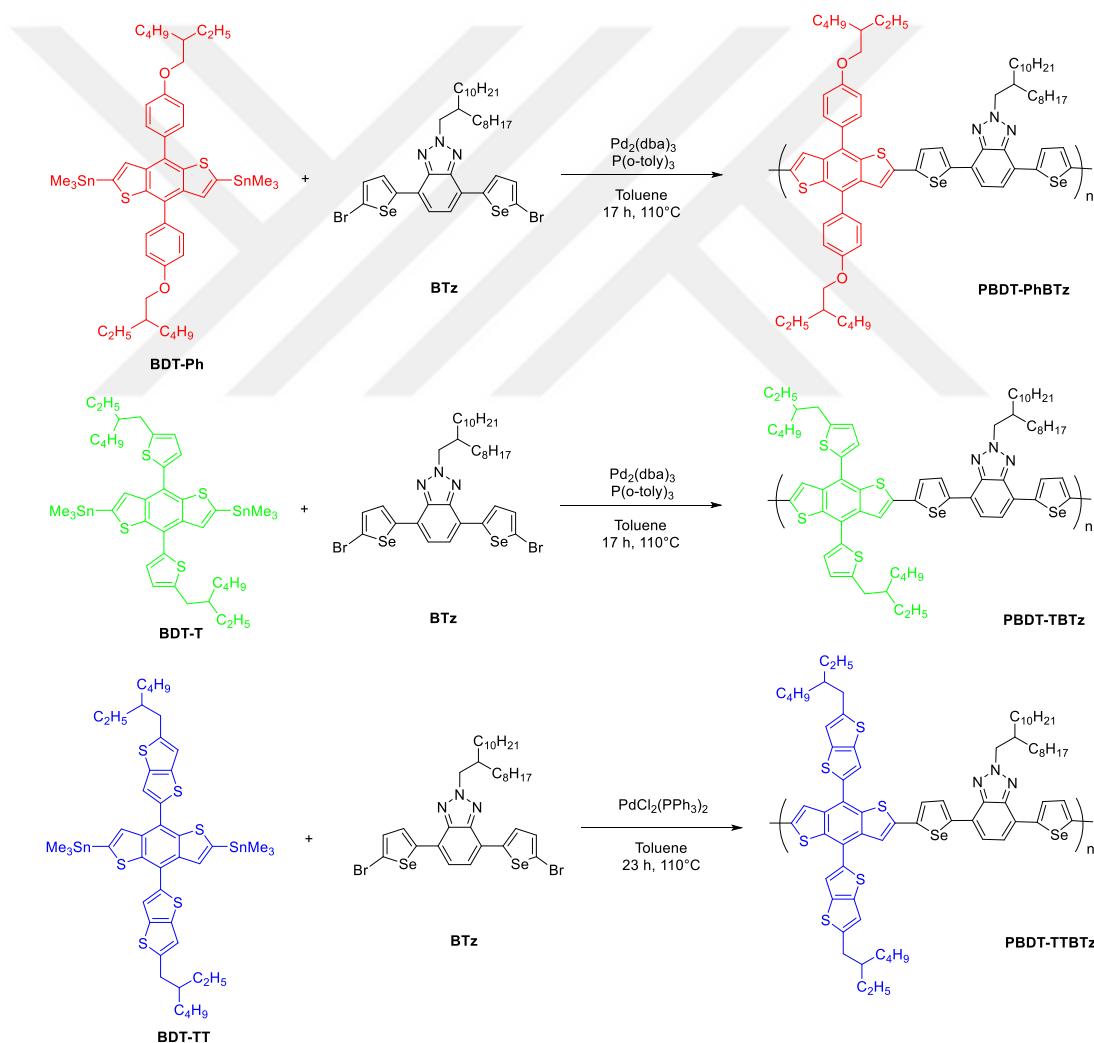


Figure 5.5. Synthesis of BDT and BTz based polymers

Table 5.1 GPC and TGA results of BDT and BTz based polymers

	<i>M_n</i> (kDa)	<i>M_w</i> (kDa)	<i>PDI</i>	<i>T_d</i> (°C)*
PBDTPh-BTz	13.3	34.2	2.57	450
PBDTT-BTz	11.6	22.0	1.89	452
PBDTTT-BTz	34.4	39.4	1.15	435

5.2.2 Thermal Studies of BDT and BTz Based Polymers

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were utilized to determine the thermal properties of the polymers. The TGA measurements showed that 5% weight loss degradation temperatures (*T_d*) of PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz were 450°C, 452°C and 435°C, respectively. The polymers did not display any phase transition in temperature vs heat flow graph measured up to 350°C. According to the measurements, PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz have good thermal stability.

5.2.3 Electrochemical Studies of BDT and BTz Based Polymers

Single scan CV studies were used to determine the redox behaviors, oxidation/reduction potentials, HOMO/LUMO energy levels, and polymers' electronic band gap values. For electrochemical investigations, the synthesized polymers PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz were dissolved in chloroform (5 mg/mL) and spray-coated onto ITO-coated glass slides. Table 5.2 summarizes the electrochemical properties of these polymers. As depicted in Figure 5.6, all polymers showed both p-dopable and n-dopable character.

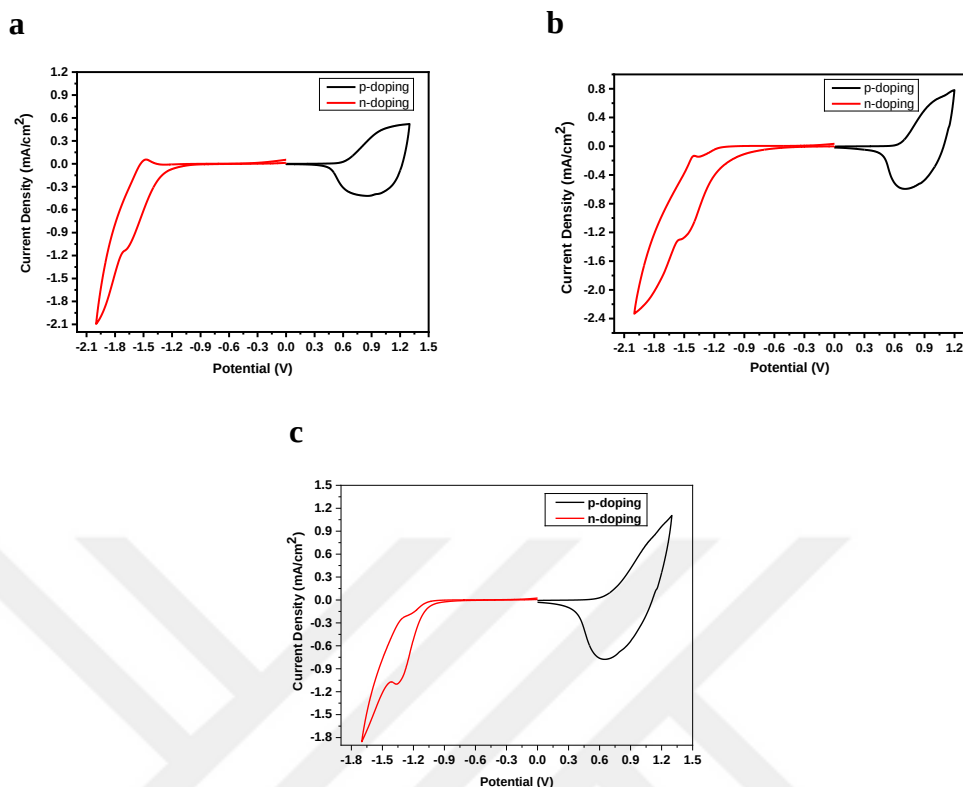


Figure 5.6. Single-scan cyclic voltammogram of a) PBDTPh-BTz, b) PBDTT-BTz and c) PBDTTT-BTz in 0.1 M TBAPF₆/ACN solution at a scan rate of 100 mV/s

Incorporation of the 2D conhgated side groups is used to tune the eletronic features of the conjugated polymers. Due to the differences between planarity, delocalization, aromaticity and electron donating strenght of the side groups, the oxidation and reduction behaviour of the polymers may differ.⁶⁰ The oxidation onset potential, HOMO and LUMO energy levels of PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz have an increased order of thienothieryl>thienyl>phenyl side group substitution. According to the literature, the resonance energy of the phenyl side groups is greater than thiophene and thienothiophene, resulting more aromatic behaviour.¹⁴⁸ Therefore, the highest electron donating character can result in lowest oxidation potential, HOMO and LUMO energy levels.

Table 5.2 Summary of electrochemical studies of BDT and BTz based polymers

	PBDTPh-BTz	PBDTT-BTz	PBDTTT-BTz
$E_{p-doping}$ (V)	1.02	1.01	1.08
$E_{p-dedoping}$ (V)	0.86	0.71	0.65
$E_{n-doping}$ (V)	-1.69	-1.52	-1.36
$E_{n-dedoping}$ (V)	-1.48	-1.4	-1.30
E_{ox}^{onset} (V)	0.61	0.66	0.69
E_{red}^{onset} (V)	-1.31	-1.13	-1.08
HOMO (eV)	-5.36	-5.41	-5.44
LUMO (eV)	-3.44	-3.62	-3.67
E_g^{el} (eV)	1.92	1.79	1.77

Since the electron delocalization throughout the conjugation backbone of the polymers can be further extended via conjugated side chains, the increase in probability of transitions between the ground state and excitation state can occur.¹⁴⁹ As a consequence, enlarging the surface area of the conjugated polymers could improve the intermolecular π - π interaction which generates smaller band gap.^{150,151} The electronic band gaps (E_g^{el}) of PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz were calculated from the energy level difference between HOMO and LUMO and found as 1.92 eV, 1.79 eV and 1.77 eV for PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz, respectively. The E_g^{el} of PBDTTT-BTz was found as the smallest value.

5.2.4 Optical Studies of BDT and BTz Based Polymers

The UV-Vis spectra of the conjugated polymers were obtained to examine the optical properties. The absorption spectra were shown in Figure 5.7 and the measurements were taken both in chloroform solution and thin film.

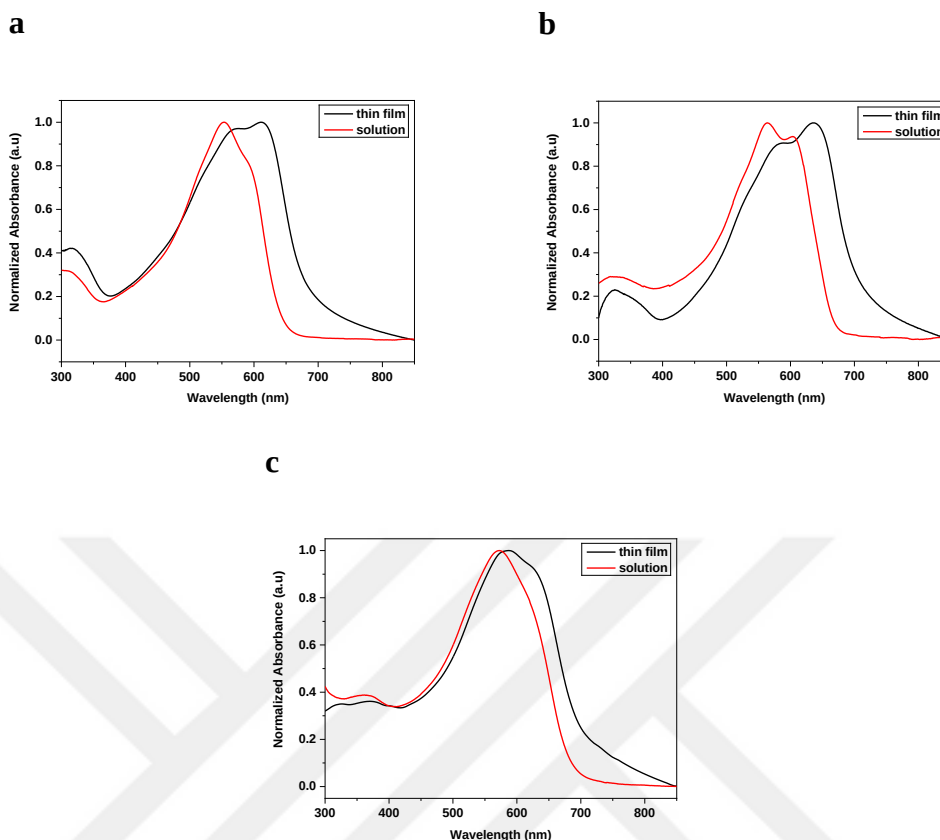


Figure 5.7. UV–Vis absorption spectra of a) PBDTPh-BTz b) PBDTT-BTz c) PBDTTT-BTz thin film in 0.1 M TBAPF₆/ACN solution and in CHCl₃ solvent

Table 5.2 summarizes the optical properties of the polymers in CHCl₃ solution and thin film. As shown in Table 5.2, the maximum absorption values in solution for polymers PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz were found to be 553 nm, 564 nm and 572 nm, correspondingly. The maximum absorption values of thin films of PBDTPh-BTz and PBDTT-BTz polymers were determined at 606 nm and 632 nm, while the maximum absorption values of thin films of PBDTTT-BTz polymer was 585 nm. When the solution maximum absorption and thin film maximum absorption values were compared, the PBDTPh-BTz and PBDTT-BTz exhibited a noticeable red shift in the maximum absorption values (almost 50 nm) compared to the PBDTTT-BTz polymer. In the literature, the best device performance was obtained with highest chain packing of the polymers in the active layer with BDT and thiophene side group.¹⁵² The optical band gaps were determined as 1.79 eV, 1.73

eV, and 1.74 eV for PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz, respectively. Due to the smaller λ_{onset} value of the PBDTPh-BTz, the optical bandgap was obtained higher than PBDTT-BTz and PBDTTT-BTz.

Table 5.3 Summary of optical properties of polymers

	λ_{max} (nm) (solution)	λ_{max} (nm) (thin film)	λ_{onset} (nm) (thin film)	E_g^{op} (eV)
PBD-PhBTz	553	606	692	1.79
PBDT-TBTz	564	632	715	1.73
PBDT-TTBTz	572	585	710	1.74

5.2.5 Photovoltaic Studies of BDT and BTz Based Polymers

BHJ-OSCs were constructed by blending PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz as donor material and PC₇₁BM as an acceptor material in the active layer. In order to investigate the effect of the side conjugated group on BDT moiety on the photovoltaic performances of BDT and BTz based polymers, the device configuration ITO/PEDOT:PSS/polymer:PC₇₁BM/LiF/Al in o-DCB processing solvent was constructed. Various polymer:PC₇₁BM (w:w) ratios, active layer concentrations and spin coating rates were conducted to reach the best device performance in BHJ-OSCs. Table 5.4-5.6 summarizes the photovoltaic properties of PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz based solar devices and the current density–voltage (JV) graphs, obtained under standard illumination (AM 1.5G, 100 mW/cm²), are presented in Figure 5.8.

Table 5.4 Summary of photovoltaic studies of PBDT-PhBTz utilized bulk heterojunction solar cells

PBDTPh- BTz:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)
1:1 (2%)	4.46	0.63	51.58	1.45	750
1:2 (2%)	5.33	0.61	60.26	1.96	750
1:3 (2%)	3.47	0.62	58.03	1.25	750
1:4 (2%)	4.20	0.60	47.41	1.22	750
1:2 (2.5%)	5.96	0.60	60.79	2.17	750
1:2 (3%)	7.92	0.62	58.25	2.85	750
1:2 (3.5%)	9.89	0.62	46.77	2.92	750
1:2 (4%)	9.22	0.62	41.02	2.35	750
1:2 (3.5%)	10.17	0.60	40.02	2.46	500
1:2 (3.5%)	10.87	0.63	50.66	3.49	1000
1:2 (3.5%)*	5.50	0.59	49.06	1.60	1000
1:2 (3.5%)**	8.69	0.60	48.10	2.49	1000
1:2 (3.5%)***	9.83	0.59	54.01	3.13	1000

*thermal annealing **2% DIO addition ***3% DPE addition

Table 5.5 Summary of photovoltaic studies of PBDTT-BTz utilized bulk heterojunction solar cells

PBDTT-BTz:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)
1:0.8 (2.0%)	6.69	0.63	53	2.24	750
1:1 (2.0%)	7.93	0.65	55	2.82	750
1:2 (2.0%)	6.37	0.62	63	2.51	750
1:1 (2.5%)	9.49	0.66	62	3.83	750
1:1 (3.0%)	10.08	0.67	64	4.34	750
1:1 (3.0%)	10.45	0.64	56	3.75	500
1:1 (3.0%)	7.47	0.67	62	3.10	1000
1:1 (3.0%)*	10.26	0.64	57	3.72	750
1:1 (3.0%)**	10.04	0.57	52	2.95	750

*2% DIO addition **3% DPE addition

The best performance was obtained 1:2 (w:w) of PBDTPh-BTz:PC₇₁BM, 1:1 (w:w) of PBDTT-BTz: PC₇₁BM and 1:0.8 (w:w) of PBDTTT-BTz:PC₇₁BM devices after the optimizations. Further optimization for photovoltaic parameters revealed that the concentrations of best devices constructed with PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz polymers was 3.5%, 3% and 2%, respectively. Therefore, after the spin coating rate optimizations, the active layer obtained by PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz polymers was obtained by the most suitable device optimization parameters. The spin coating rates were decided 1000 rpm for PBDTPh-BTz, and 750 rpm for PBDTT-BTz and PBDTTT-BTz. When examined the photovoltaic parameters for the best devices, a PCE of 3.49% with a J_{sc} of 10.87 mA/cm², a V_{oc} of 0.63 V and a FF of 50.66% were recorded for PBDTPh-BTz: PC₇₁BM based solar cell. Photovoltaic parameters with J_{sc} of 10.08 mA/cm², a V_{oc} of 0.67 V and a FF of 64% resulted 4.34% of PCE for PBDTT-BTz:PC₇₁BM while PBDTTT-BTz:PC₇₁BM blend in the active layer resulted in a J_{sc} of 8.50 mA/cm², a

V_{OC} of 0.66 V with a FF of 48% yielding a PCE of 2.70%. Addition of 2% DIO and 3% DPE solvents in the active layer of each polymers had no favorable effect on the photovoltaic performances.

Table 5.6 Summary of photovoltaic studies of PBDTTT-BTz utilized bulk heterojunction solar cells

PBDTTT-BTz:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin Coating rate (rpm)
1:0.7 (2.0%)	9.01	0.65	45	2.62	750
1:0.8 (2.0%)	8.50	0.66	48	2.70	750
1:1 (2.0%)	6.79	0.65	49	2.15	750
1:0.8 (2.5%)	8.72	0.65	45	2.54	750
1:0.8 (2.0%)	9.45	0.61	40	2.27	500
1:0.8 (2.0%)	7.47	0.65	47	2.27	1000
1:0.8 (2.0%)*	6.83	0.59	53	2.12	750
1:0.8 (2.0%)**	6.57	0.57	53	2.01	750

*2% DIO addition **3% DPE addition

As is widely established in the literature, a deeper HOMO level is favorable to get an increased open voltage (V_{oc}) in BHJ-OSCs.^{101,153} Since PBDTT-BTz and PBDTTT-BTz had more deeper HOMO energy levels, the V_{OC} of the best devices for these polymers was higher than PBDTPh-BTz. Since their HOMO surfaces may be effectively delocalized along their backbones, the 2D-conjugated BDT-based polymers can be applicable to prolong the conjugation of the backbones and so enhance the potential of developing efficient interchain overlaps.

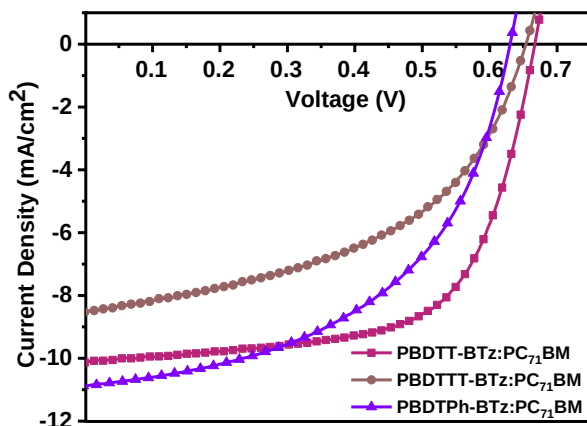


Figure 5.8. Current density-voltage curves of best solar cells based on PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz

The J_{SC} of organic solar cells is primarily related to the active layer's absorption property and the charge transport within the active layer. As mentioned before, the λ_{max} values of PBDPh-BTz and PBDTT-BTz were recorded as approximately 20 nm and 50 nm higher than λ_{max} of PBDTTT-BTz in the thin film. Therefore, the measured J_{SC} of 10.87 mA/cm², 10.08 mA/cm² and 8.5 mA/cm² for PBDPh-BTz, PBDTT-BTz and PBDTTT-BTz are in agreement with the recorded absorption features of these polymers.

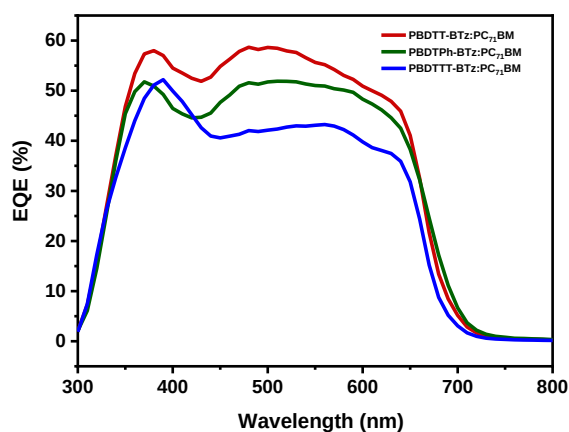


Figure 5.9. EQE curves of best solar cells based on PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz

The EQE measurements of the best OSCs based on PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz were investigated to determine the efficiency of the solar cells in converting the sunlight into electricity. The EQE curves were shown in Figure 5.9. The max EQE value of 58% was obtained for PBDTT-BTz:PCBM blend while 52% and 43% of EQE values were found for PBDTPh-BTz and PBDTTT-BTz with PCBM blends over the visible wavelength range. Therefore, the performance of solar cells constructed with BDT and BTz based polymers was also supported by outcomes of the EQE measurements.

5.2.6 Morphology Studies of BDT and BTz Based Polymers

The microstructures of the best OSC based on PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz and PCBM blend films were characterized using TEM to observe the effect of the difference in side-chain groups on the active layer morphology. Compared with phenyl and thienothienyl substituted BDT on the polymer backbone, PBDTPh-BTz and PBDTTT-BTz, a better interpenetrating bicontinuous network was observed for PBDTT-BTz:PCBM blended film. The improved J_{SC} and FF value of PBDTT-BTz based solar cell supports this observations.

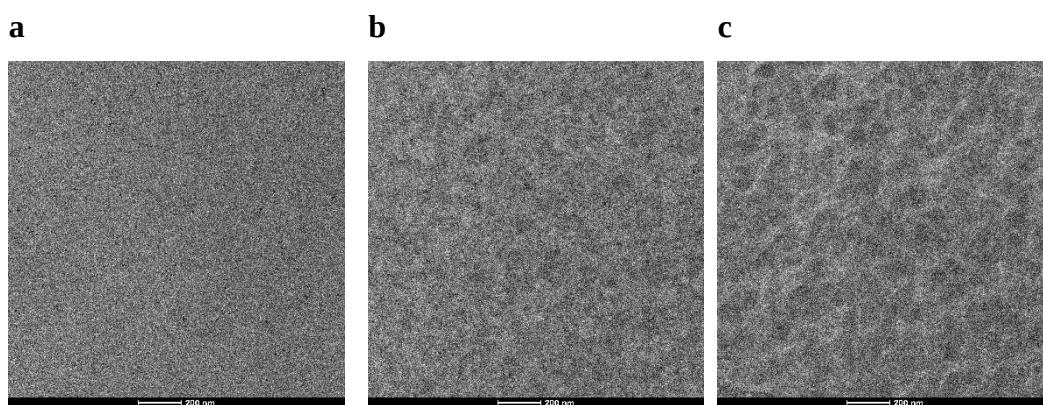


Figure 5.10. TEM images of best devices constructed with a) PBDTPh-BTz:PCBM b) PBDTT-BTz:PCBM and c) PBDTTT-BTz:PCBM

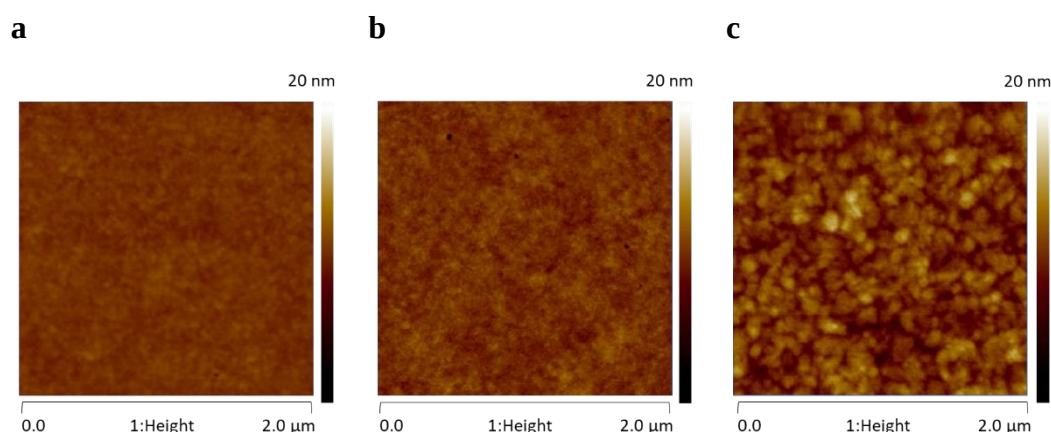


Figure 5.11. AFM images of best devices constructed with a) PBDTPh-BTz:PCBM b) PBDTT-BTz:PCBM and c) PBDTTT-BTz:PCBM

The AFM images of the most efficient devices are shown in Figure 5.11 to investigate the surface topography and the thickness of the active layer of the solar cells. The root mean square roughness of the blend of PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz with PCBM were calculated as 0.58 nm, 0.67 nm and 1.53 nm, respectively. The active layer thickness values were found as 136 nm, 109 nm and 138 nm, correspondingly. As can be seen from Figure 5.11a, the blend of the PBDTPh-BTz:PCBM had the lowest roughnesses. The dark areas show the deep regions of the film surface; therefore, PBDTTT-BTz based blend film possesses a rough surface topography. With a thin active layer, conjugated polymers can absorb light at the maximum of their absorption spectrum.^{154,155} Therefore, the combination of a thin active layer and proper surface topography results in an increased efficiency of the PBDTT-BTz based solar cell.

CHAPTER 6

ISOINDIGO AND BENZODITHIOPHENE BASED POLYMERS FOR ORGANIC SOLAR CELLS

Isoindigo which has a strong electron deficient property, is an isomer of the common natural dye indigo. The benefits of isoindigo as a key element for conjugated polymers result from a number of significant properties, including backbone planarity, low-lying frontier orbital energy levels, extended conjugation, good solubility due to alkylation, and simplicity of synthesis.^{156,157} Currently, OSCs and OFETs are two potential applications for which conjugated polymers based on isoindigo moiety are designed and synthesized. The study of isoindigo based BHJ-OSC application was firstly reported by Reynolds et al. in 2010.¹⁵⁸

The aim was to find the connection between the chemical structures of the isoindigo-based polymers and their PV capabilities since the PV performances of isoindigo-based polymers varied substantially in the literature. Four D-A type conjugated polymers were designed and synthesized using isoindigo as the common electron-deficient unit and BDT with thiophene and thienothiophene units as the electron-rich moieties, respectively. Their electrochemical, optical and photovoltaic characteristics were examined.

6.1 Experimental

6.1.1 Synthesis of Monomers

6.1.1.1 Synthesis of 6-1

Commercially purchased IID (0.52 g, 0.81 mmol) and compound 3-4 (0.78 g, 1.86 mmol) were dissolved in 10 ml of anhydrous toluene, nitrogen gas was passed

through the reaction medium for 40 min. $\text{Pd}_2(\text{dba})_3$ (37 mg, 0.04 mmol) and $\text{P}(\text{o-tolyl})_3$ (49 mg, 0.08 mmol) were added at room temperature. The reaction mixture was allowed to react at 110°C for 20 h under N_2 atmosphere. After the reaction was finished, the mixture was poured into 150 mL of 1.0 M HCl solution. The organic phase was extracted with chloroform, dried over anhydrous MgSO_4 . After evaporation of the solvent, the residue was separated by column chromatography using a hexane to give a red solid (0.56 g, 93%). ^1H NMR (400 MHz, CDCl_3) δ 9.10 (dd, $J = 8.4, 0.9$ Hz, 1H), 8.04 (dd, $J = 5.5, 0.9$ Hz, 1H), 7.58 (dd, $J = 3.8, 0.9$ Hz, 1H), 7.37 (dd, $J = 5.5, 3.8$ Hz, 1H), 7.24 (dd, $J = 8.4, 1.7$ Hz, 1H), 6.88 (s, 1H), 3.74 – 3.54 (m, 2H), 1.88 – 1.77 (m, 1H), 1.44 – 1.21 (m, 10H), 0.96 – 0.78 (m, 7H).

6.1.1.2 Synthesis of 6-2

Compound 6-1 (0.497 g, 0.67 mmol) was dissolved in 30 mL of chloroform and N-bromosuccinimide (NBS) (0.24 g, 0.133 mmol) was added. After stirring the mixture for 18 h at room temperature in the dark, it was poured into 150 mL of water. The organic phase was extracted with chloroform, dried over anhydrous MgSO_4 and then concentrated. The residue was precipitated with methanol to give a red solid (0.51 g, 85%). ^1H NMR (400 MHz, CDCl_3) δ 9.10 (d, $J = 8.4$ Hz, 1H), 7.31 – 7.22 (m, 3H), 7.10 (dd, $J = 8.4, 1.7$ Hz, 1H), 6.77 (s, 1H), 3.75 – 3.53 (m, 3H), 1.91 – 1.75 (m, 1H), 1.46 – 1.26 (m, 11H), 1.00 – 0.82 (m, 8H).

6.1.2 Synthesis of Polymers

6.1.2.1 Synthesis of PDBTTT-IID

Compound BDT-TT (0.2 g, 0.20 mmol) and IID (0.13 g, 0.20 mmol) were dissolved with 7 mL of THF and 40 minutes of N_2 gas passed and $\text{Pd}(\text{PPh}_3)_4$ (11.4 mg, 9.9 μmol) catalyst was added. The reaction mixture was heated to reflux and stirred for 17 h. Tributyl (thiophen-2-yl) stannane (0.22g, 0.4 mmol) was added and stirred for

a further 2 hours, followed by the addition of 2-bromo thiophene (0.07 g, 0.4 mmol) for 2 hours. The reaction mixture was then brought to room temperature and the polymer was precipitated by the addition of 50 mL of methanol. The precipitate was then extracted with Soxhlet with methanol, hexane, and chloroform. The polymer in the chloroform fraction was recovered as a green solid by precipitation from methanol. The solid was dried under vacuum (0.228 g, 96%).

6.1.2.2 Synthesis of PDBTT-IID

Compound BDT-T (0.183 g, 0.2 mmol) and IID (0.13 g, 0.2 mmol) were dissolved with 7 mL of THF and 40 minutes of N₂ gas passed and Pd(PPh₃)₄ (11.7 mg, 10.1 μmol) catalyst was added. The reaction mixture was heated to reflux and stirred for 17 h. Tributyl (thiophen-2-yl) stannane (0.22 g, 0.6 mmol) was added and stirred for a further 2 hours, followed by the addition of 2-bromo thiophene (0.07 g, 0.4 mmol) for 2 hours. The reaction mixture was then brought to room temperature and the polymer was precipitated by the addition of 50 mL of methanol. The precipitate was then extracted with Soxhlet with methanol, hexane, and chloroform. The polymer in the chloroform fraction was recovered as a green solid by precipitation from methanol. The solid was dried under vacuum (0.210 g, 95%).

6.1.2.3 Synthesis of PDBTTT-SeIID

Compound BDT-TT (0.157 g, 0.16 mmol) and compound 6-2 (0.14 g, 0.16 mmol) were dissolved with 7 mL of THF and 40 minutes of N₂ gas passed and Pd(PPh₃)₄ (9.0 mg, 7.8 μmol) catalyst was added. The reaction mixture was heated to reflux and stirred for 17 h. Tributyl (thiophen-2-yl) stannane (0.22 g, 0.4 mmol) was added and stirred for a further 2 hours, followed by the addition of 2-bromo thiophene (0.07 g, 0.4 mmol) for 2 hours. The reaction mixture was then brought to room temperature and the polymer was precipitated by the addition of 50 mL of methanol. The precipitate was then extracted with Soxhlet with methanol, hexane, and chloroform.

The polymer in the chloroform fraction was recovered as a green solid by precipitation from methanol. The solid was dried under vacuum (0.15 g, 66%).

6.2 Result and Discussion

6.2.1 Synthesis and Characterization of BDT and IID

The synthetic pathway for the preparation of the IID compound using selenophene as π -bridge is shown in Figure 6.1.

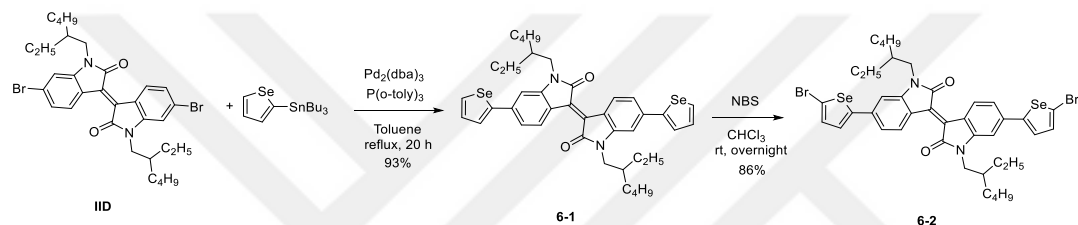


Figure 6.1. Synthesis of IID based novel acceptor

The reaction of the commercially purchased IID compound with the 2-tributylselenophene in the presence of $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-tolyl})_3$ was carried out in toluene solvent and compound 6-1 was successfully obtained. The bromination reaction was carried out under dark conditions with NBS to obtain compound 6-2 which was utilized as acceptor for the synthesis of D-A type conjugated polymers.

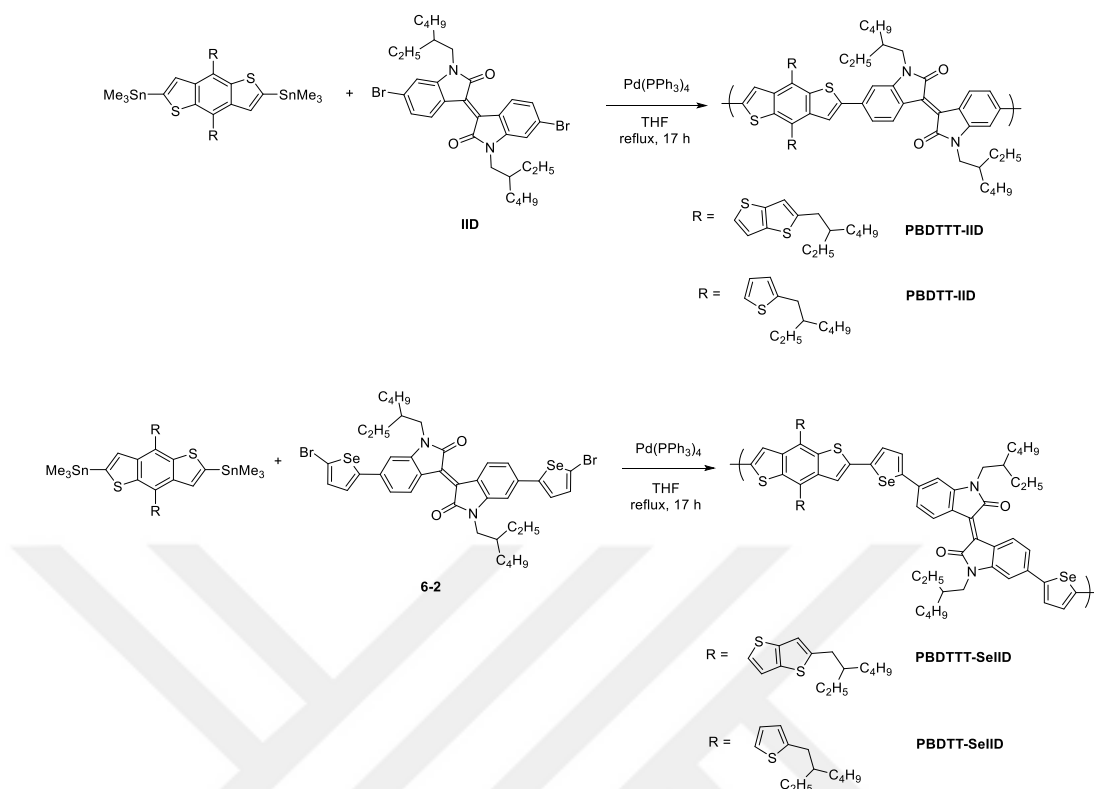


Figure 6.2. Synthesis of BDT and IID based polymers

The synthesis of the polymers with BDT and IID derivatives was presented in Figure 6.2. BDT-T and BDT-TT were used as donor while commercially purchased IID and compound 6-2 were reacted as the acceptor for chemical polymerization. Stille coupling reaction conditions were carried out to synthesize the desired BDT and IID based polymers successfully. However, PBDTT-SeIID could not be purified from Soxhlet apparatus due to the solubility issues, therefore, except PBDTT-SeIID, other BDT and IID based polymers were further investigated.

6.2.2 Electrochemical Studies of BDT and IID

CV experiments were carried out with a constant 100 mV s^{-1} scan rate at room temperature using a three-electrode setup with indium tin oxide (ITO), Ag wire and Pt wire as the working electrode, the reference electrode and the counter electrode, respectively. Acetonitrile (ACN) was used as the solvent during the experiments, and

tetrabutylammoniumhexafluorophosphate (TBAPF₆) was used as the supporting electrolyte. Single scan CV studies were used to determine the redox behaviors, oxidation/reduction potentials, HOMO/LUMO energy levels, and polymers' electronic band gap values. For electrochemical investigations, the synthesized polymers were dissolved in chloroform (5 mg/mL) and spray-coated onto ITO-coated glass slides. As depicted in Figure 6.3, PBDTT-IID and PBDTTT-SeIID polymers showed both p-dopable and n-dopable character while PBDTTT-IID resulted p-doped character. All the electrochemical properties were summarized in Table 6.3. Since the onset reduction potential calculated from n-doping curve yielded the LUMO energy level of the polymers, the energy level could not be determined for PBDTTT-IID polymer.

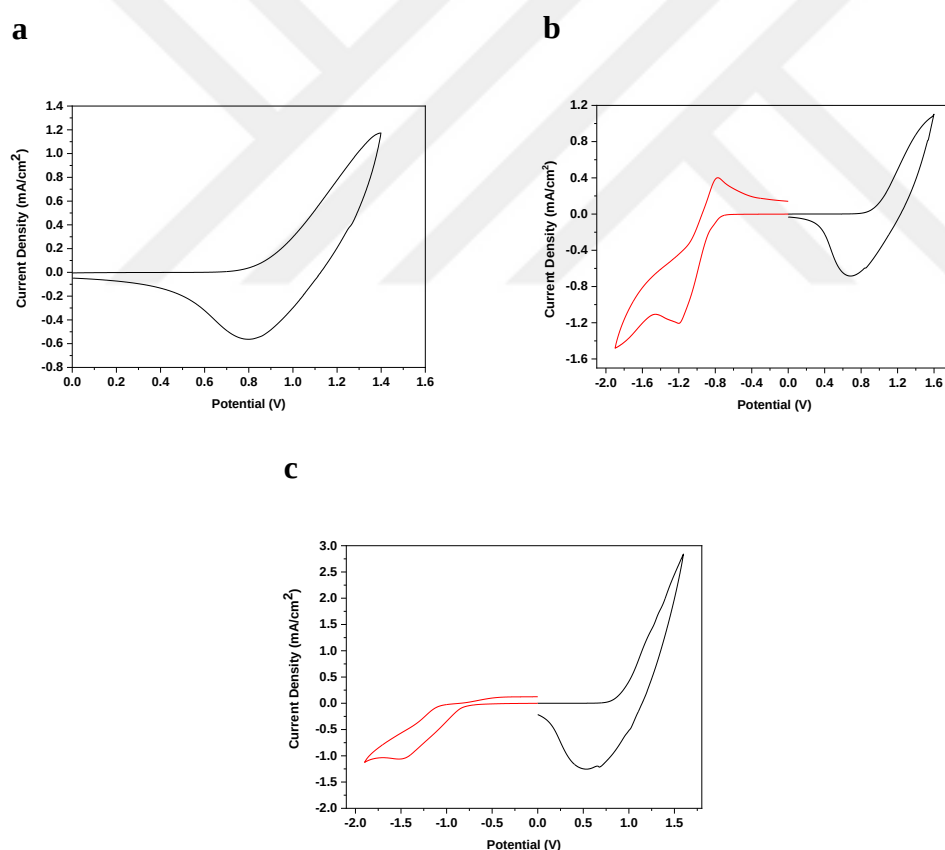


Figure 6.3. Single-scan cyclic voltammogram of a) PBDTTT-IID, b) PBDTT-IID and c) PBDTTT-SeIID in 0.1 M TBAPF₆/ACN solution at a scan rate of 100 mV/s

Table 6.1 Summary of electrochemical studies of BDT and IID based polymers

	PBDTTT-IID	PBDTT-IID	PBDTTT-SeIID
$E_{p\text{-doping}}$ (V)	1.35	1.46	1.39
$E_{p\text{-dedoping}}$ (V)	0.8	0.67	0.54
$E_{n\text{-doping}}$ (V)	-	-1.19	-1.45
$E_{n\text{-dedoping}}$ (V)	-	-0.8	-1.08
E_{ox}^{onset} (V)	0.88	0.96	0.91
E_{red}^{onset} (V)	-	-0.83	-0.80
HOMO (eV)	-5.63	-5.71	-5.66
LUMO (eV)	-	-3.92	-3.95
E_g^{el} (eV)	-	1.79	1.71

*If it is assumed that $E_g^{op} = E_g^{el}$, LUMO = -4.02 eV.

The onset oxidation potentials for PBDTTT-IID, PBDTT-IID and PBDTTT-SeIID were measured as 0.88 V, 0.96 V and 0.91 V, respectively. The incorporation of selenophene as π -bridge on the polymer backbone resulted an increase in the onset oxidation potential leading deeper HOMO energy level for PBDTTT-SeIID. A spacer between BDT donor and IID acceptor can generate a reduction in the E_g^{el} . The reduction of steric hindrance and the elongation of π -conjugation reduce E_g , and the amount of the reduced E_g is strongly associated with the quinoidal nature of the π -bridge along with the donor-acceptor copolymer backbone.^{101,159} Moreover, the replacement of thiophene side group on BDT donor with thienothiophene side group may cause an enlargement on the surface area of conjugated polymer. The efficient intermolecular π - π interaction was produced and, therefore, the smaller band gap may be obtained.

6.2.3 Optical Studies of BDT and IID

Figure 6.4 displays the normalized UV-Vis absorption spectra in both solid state and in chloroform solution for PBDTTT-IID, PBDTT-IID and PBDTTT-SeIID. Table

6.2 contains the corresponding spectroscopic properties. An absorption bands with vibrational shoulders are present in all polymers. The low-energy bands result from intramolecular charge transfer (ICT) from the donor to the acceptor units, while the high-energy bands can be attributed to the π - π^* transition. Therefore, for PBDTTT-IID, PBDTT-IID and PBDTTT-SeIID polymers, λ_{max} values were measured at 622 nm, 632 nm and 620 nm in solution state whereas λ_{max} values were 630 nm, 692 nm and 710 nm in the solid state, correspondingly. The strong electron-withdrawing properties of isoindigo moieties and the efficient ICT cause the low-energy absorption bands to possess an increased intensity. It should be highlighted that all of the absorption spectra of the polymers significantly vary when progressing from the solution to the solid state. This means that a strong aggregation and π - π stacking of the polymer chains occur in the solid state.^{101,120}

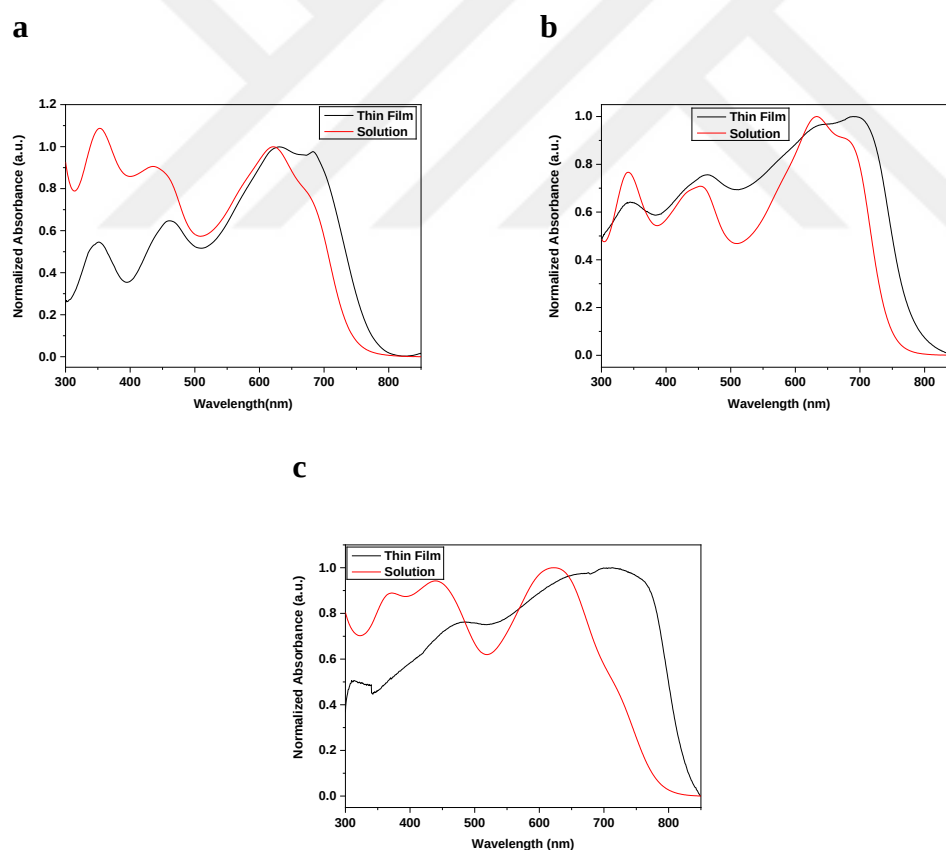


Figure 6.4. UV–Vis absorption spectra of a) PBDTTT-IID b) PBDTT-IID c) PBDTTT-SeIID thin film in 0.1 M TBAPF₆/ACN solution and in CHCl₃ solvent

The optical band gaps estimated from the onset of their absorption spectra in the solid state were 1.61 eV, 1.58 eV, and 1.50 eV for PBDTTT-IID, PBDTT-IID and PBDTTT-SeIID, respectively, which are ideal band gaps for donor polymer in the solar cell. The significant decrease in the optical band gap of the polymers were attributed to the incorporating the selenophene as π -bridge when the polymer compositions examined.^{160,161}

Table 6.2 Summary of Optical Properties of BDT and IID Polymers

	λ_{max} (nm) (solution)	λ_{max} (nm) (thin film)	λ_{onset} (nm) (thin film)	E_g^{op} (eV)
PBDTTT-IID	622	630	770	1.61
PBDTT-IID	632	692	783	1.58
PBDTTT-SeIID	620	710	827	1.50

6.2.4 Photovoltaic Studies of BDT and IID

The solar devices of the polymers were constructed using a frequently utilized configuration of ITO/PEDOT:PSS/ polymer:PC₇₁BM/LiF/Al. *o*-DCB was used as the processing solvent for PBDTTT-IID and dichlorobenzene (dcb) was used in the active layers of PBDTT-IID and PBDTTT-SeIID. The photovoltaic parameters were measured to assess the influence of the π -bridge and different two-dimensional structure of the donor moiety on the resultant device performance. Due to the incomplete photovoltaic results for PBDTTT-IID, PBDTT-IID and PBDTTT-SeIID based polymers, the discussion can be performed only parameters given in Table 6.3, Table 6.4 and Table 6.5. Only polymer:PCBM weight ratio investigations were performed with 2% blend concentration and 750 rpm spin coating rate for all the polymers. Figure 6.5 depicts the J-V curves of the solar cells for the corresponding polymers. The PCBM in the blend film function as enhancing the balance between the hole and electron charge transportation. Therefore, the optimization of polymer:PCBM weight ratio is crucial to obtain efficient solar cells. For all polymers,

1:3 (w:w) Polymer:PCBM ratio resulted higher photovoltaic parameters. A PCE of 0.77% with a J_{SC} of 4.09 mA/cm², a V_{OC} of 0.57 V and a FF of 32.6% were recorded for PBDTPh-BTz: PC₇₁BM based solar cell.

Table 6.3 Summary of photovoltaic studies of PBDTTT-IID utilized bulk heterojunction solar cells

PBDTTT-					
IID:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin coating rate (rpm)
1:2 (2%)	2.09	0.57	30.8	0.37	750
1:3 (2%)	4.09	0.57	32.6	0.77	750
1:4 (2%)	3.71	0.57	32.4	0.69	750

Table 6.4 Summary of photovoltaic studies of PBDTT-IID utilized bulk heterojunction solar cells

PBDTT-					
IID:PC ₇₁ BM (w:w)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	Spin coating rate (rpm)
1:2 (2%)	6.57	0.75	39.6	1.94	750
1:3 (2%)	6.49	0.75	41.6	2.03	750
1:4 (2%)	4.06	0.76	46.0	1.44	750
1:3 (2%)*	5.81	0.75	43.6	1.90	750

*3% DPE addition

A small amount of DPE (3%) processing solvent was included to the active layer of during the fabrication process of PBDTT-IID of solar cell. However, any improvement was recorded. Among the resultant measurements, the best device for PBDTT-IID had a PCE of 2.03% with a J_{SC} of 6.49 mA/cm², a V_{OC} of 0.75 V and a FF of 41.6%. On the other hand, 3% DPE treatment in the active layer of PBDTTT-SeIID produced a slight increase in FF value resulting 1.52% of PCE. This result

may arise from the modest improvement of the thin film morphology. The optimization studies are ongoing.

Table 6.5 Summary of photovoltaic studies of PBDTTT-SeIID utilized bulk heterojunction solar cells

PBDTTT-					
SeIID:PC ₇₁ BM	J_{sc}	<i>Spin coating</i>			
(w:w)	(mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE%	rate (rpm)
1:2 (2%)	4.05	0.68	34.0	0.94	750
1:3 (2%)	5.87	0.68	35.5	1.41	750
1:4 (2%)	4.64	0.70	38.8	1.26	750
1:3 (2%)*	5.76	0.69	38.2	1.52	750

*3% DPE addition

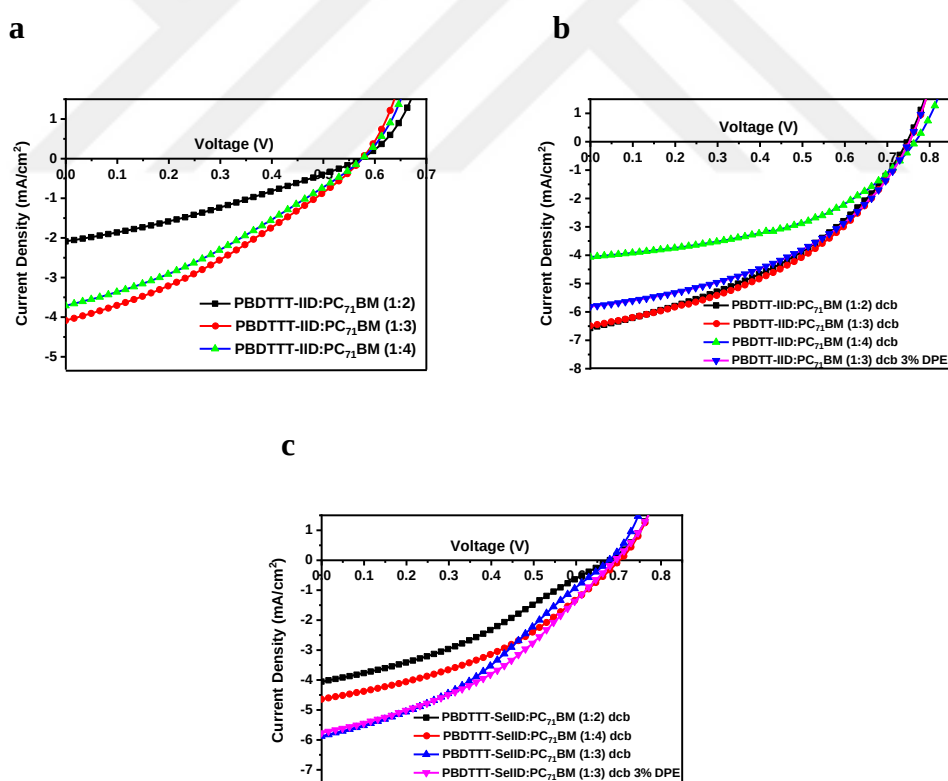


Figure 6.5. Current density-voltage curves of solar cells based on PBDTTT-IID, PBDTT-IID and PBDTT-SeIID



CHAPTER 7

CONCLUSION AND OUTLOOK

As a consequence, in Chapter 2, to investigate the effect of the number of fluorine atoms substituted to the benzothiadiazole, 2-ethylhexyl selenophene substituted benzodithiophene monomer (BDTSe) and benzothiadiazole monomer with the fluorine substitution were used as the electron rich and the electron deficient units during Stille coupling polymerization, respectively. As a result, a series of new conjugated polymers PBDTSe-BT, PBDTSe-FBT and PBDTSe-FFBT were developed and examined explicitly for their photovoltaic properties. The resulting polymers showed good thermal stability with T_d higher than 400°C. With the incorporation of fluorine atom, the HOMO energy level of the PBDTSe-FBT and PBDTSe-FFBT were decreased compared to the polymer PBDTSe-BT. DFT studies were conducted for these polymers to get more information about the electronic and optical parameters. According to the computational studies, fluorine atom substituted benzothiadiazole moiety improved the electron accepting ability of the acceptor unit in the polymer backbone. Hole reorganization energies, delocalization energies and average torsional angles were also affected by fluorine substitution, which may result in the promoted PCEs. The optimization of the photovoltaic properties of the polymers was conducted with different weight ratios of polymer:PC₇₁BM, the concentration of the active layer, additive volume ratio and thickness. For the optimized active layer of PBDTSe-FFBT, J_{SC} of 7.24 mA cm⁻², V_{OC} of 0.72 V and FF of 50.6% was found, resulting in a PCE of 2.63%. The fluorine substitution on the benzothiadiazole unit was shown to influence the thin-film morphology of the organic solar cell with PC₇₁BM, and therefore an optimized phase separation was achieved with the assistance of a small molecule processing additive, DIO. It should be noted that PBDTSe-FBT had one fluorine atom substituted to the polymer backbone resulting asymmetrical structure that may influence the photovoltaic

performance of the solar cell. It is concluded that conjugated polymers with fluorine substituent on the acceptor moiety have an impact on the solar cell performances.

In Chapter 3, four new conjugated polymers were successfully designed and synthesized by Pd catalyzed Stille cross-coupling reaction using quinoxaline derivatives with different π -bridges and BDT containing 2-ethylhexylselenophene and alkoxy side group. Computational studies revealed the explanation of the experimental performances of the PBDTSe-TQx, PBDTSe-SeQx, PBDT-TQx and PBDT-SeQx polymers at electronic and molecular level. According to ESP map, all copolymers had the extension and the overlapping of both HOMO and LUMO frontier orbitals. From the cyclic voltammograms, all polymers were observed to have ambipolar characters. The lower oxidation onset potentials were calculated for PBDTSe-SeQx and PBDT-SeQx due to the incorporation of the selenophene bridge into the polymer backbone. According to the results obtained from the optical studies, maximum absorption peaks were observed at 595 nm and 610 nm for PBDTSe-TQx and PBDTSe-SeQx containing 2D-benzodithiophene, while maximum absorption peaks were observed at 575 nm and 610 nm for PBDT-TQx and PBDT-SeQx polymers. It was observed that the absorption onsets of PBDTSe-SeQx and PBDT-SeQx polymers containing selenophene π bridge were relatively red-shifted to 735 nm and 732 nm, respectively. Kinetic studies were also carried out to investigate the switching times and optical contrast values of the synthesized polymers. Electrochemical, optical and spectroelectrochemical experiments showed that the synthesized polymers are viable for solar cell applications due to favorable HOMO-LUMO energy levels, broad absorption spectra in the UV-Vis region, and low band gaps that is an important parameter for photovoltaic applications to harvest as much as the solar spectrum. The photovoltaic characterization of polymers demonstrated that the best performing device achieved 4.47% PCE from PBDT-TQx-based solar cell thanks to the improved photovoltaic parameters and active layer morphology. In particular, these results enlightened the effects of π -bridge and different substituents along the backbone on the solar cell performances of alternating conjugated polymers.

In Chapter 4, a series of terpolymers based on BDT, BT and TPD were successfully synthesized in which the effect of the number of fluorine atoms on the properties of the terpolymers was investigated. As the content of the fluorine atom was raised, the angle between donor and acceptor may be further twisted, which results in a decrease in the effective conjugation length and planarity. As a result, the UV-Vis absorption of fluorine substituted polymers, RP2 and RP3, was blue-shifted and the optical band gap of the polymers was slightly increased. The HOMO energy levels of RP1, RP2 and RP3 were varied with the addition of fluorine atom substitution. The highest PCE of 3.38% was obtained by using RP2 as the donor and PCBM as the acceptor in the organic solar cell. Due to the higher molecular weight of RP3, the filtration process while fabricating the solar device was unsuccessful in obtaining proper film formation. Therefore, the fabrication of RP3:PCBM based solar cells was performed via any filtration of the polymer solution. Moreover, the 3% DPE treatment resulted in an increase in the photovoltaic parameters of RP3:PCBM based solar cells. Compared to alternating conjugated polymers in this study, random polymers had higher electronic bandgaps due to incorporating the third component into the polymer backbone.

In Chapter 5, three different conjugated side chains (phenyl, thienyl and thienothienyl) were employed for synthesizing substitution to BDT donor to investigate the effect of the difference in conjugation strength of the side groups on the photovoltaic properties of solar cells. Stille coupling polymerization between BDT and BTz resulted in PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz polymers. The electrochemical studies showed that the oxidation onset potential, HOMO and LUMO energy levels of PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz have an increased order of thienothienyl>thienyl>phenyl side group substitution. The best device efficiency was obtained with thienyl side group. The optical band gaps were determined as 1.79 eV, 1.73 eV, and 1.74 eV for PBDTPh-BTz, PBDTT-BTz and PBDTTT-BTz, respectively. Due to the smaller λ_{onset} value of the PBDTPh-BTz, the optical bandgap was obtained higher than PBDTT-BTz and PBDTTT-BTz. Photovoltaic parameters with J_{SC} of 10.08 mA/cm², a V_{OC} of 0.67 V and a FF of 64%

resulted in 4.34% of PCE for PBDTT-BTz:PC₇₁BM. Among the other polymers in this chapter, the best device efficiency was found for thienyl substituted BDT and BTz.

In Chapter 6, isoindigo and BDT based polymers were used to construct the photovoltaic devices. According to preliminary studies, the incorporation of the selenophene π -bridge leads to an increase in the J_{SC} for PBDTTT-SeIID polymer. The solar cell studies are ongoing.

Overall, with a molecular design strategy, some series of conjugated polymers were synthesized via Stille coupling polymerization reaction. Using the terpolymer configuration increased the PCE as expected. 2D BDT based polymers showed more deeper HOMO energy levels, and fluorine substitution on the acceptor moiety led to a decrease in HOMO and LUMO energy levels of polymers due to the electron-withdrawing property. Side chain group alternation (selenophenyl, thienyl, phenyl etc.) resulted from modification of the maximum absorption for all the polymers. The higher λ_{max} was obtained with thienyl side chain when compared to other aromatic side groups and the alkoxy group. The photovoltaic and morphology studies showed that polymer:PCBM weight ratio, concentration, spin coating rate and additive treatment had an impact on the PCE of the polymers.

By adjusting the structural design, polymer properties such energy levels, absorption spectra and morphologies of BDT-based polymers can be efficiently tuned. The BDT-based conjugated polymers are interesting materials for use in PSCs because of their practical production process and adjustable characteristics. For the design of organic photovoltaic materials, the molecular structural evolutions with different acceptor groups can be considered as great references.

The collaborative efforts in material synthesis/design and device processing/optimization will result in the development of more innovative BDT-based photovoltaic materials and devices.

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APPENDICES

A. NMR Spectra of Compounds

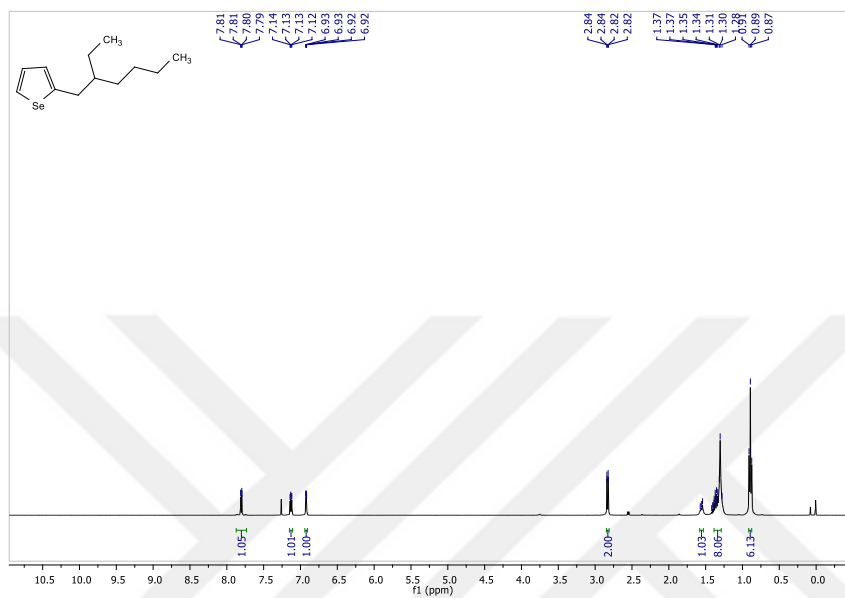


Figure 7.1. ¹H NMR of Compound 2-1

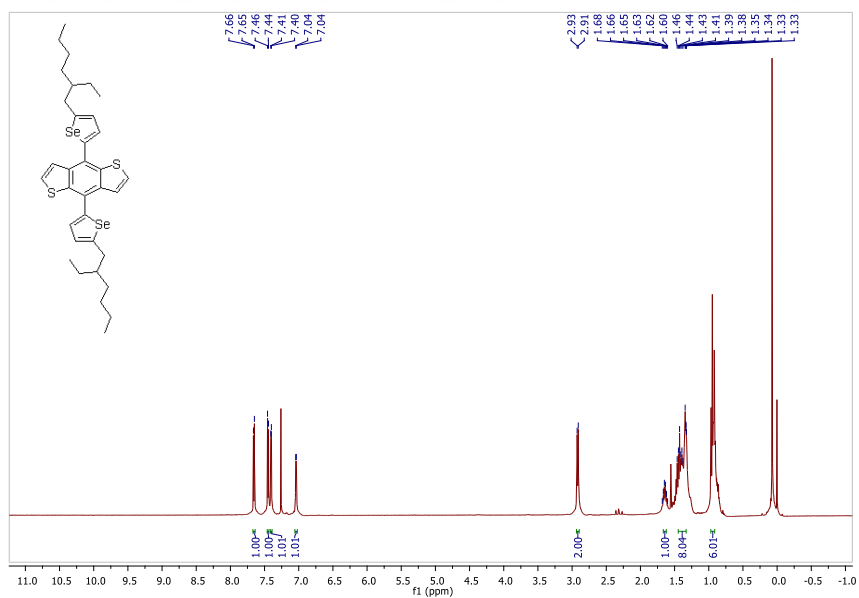


Figure 7.2. ¹H NMR of Compound 2-2

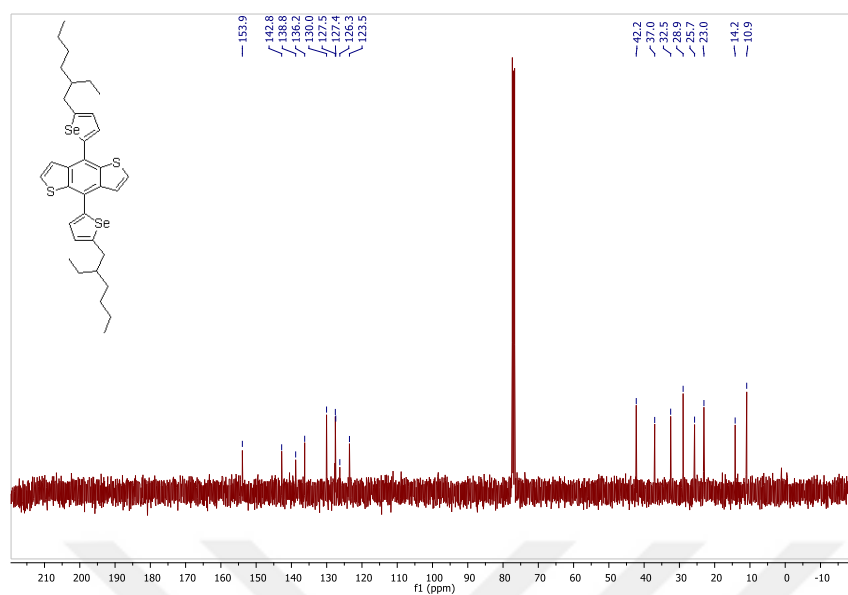


Figure 7.3. ^{13}C NMR of Compound 2-2

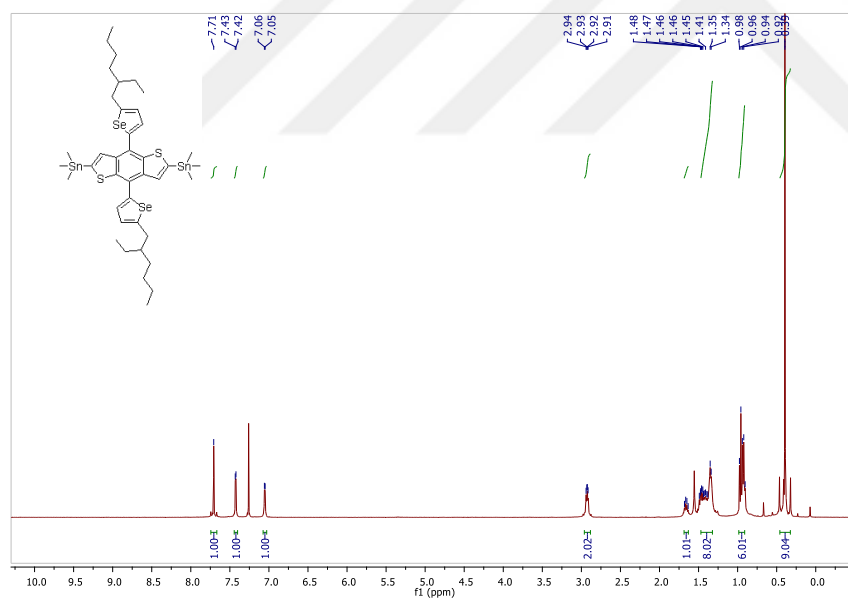


Figure 7.4. ^1H NMR of Compound 2-3

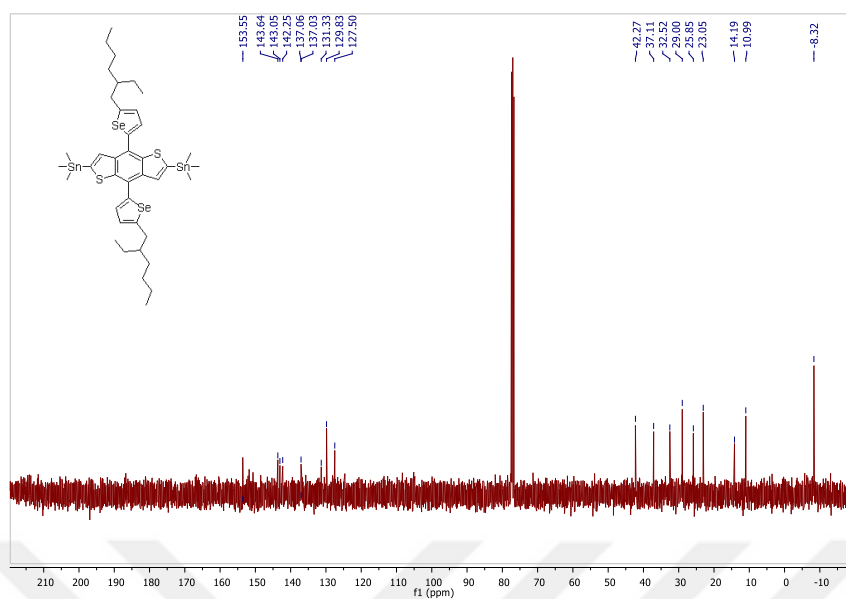


Figure 7.5. ^{13}C NMR of Compound 2-3

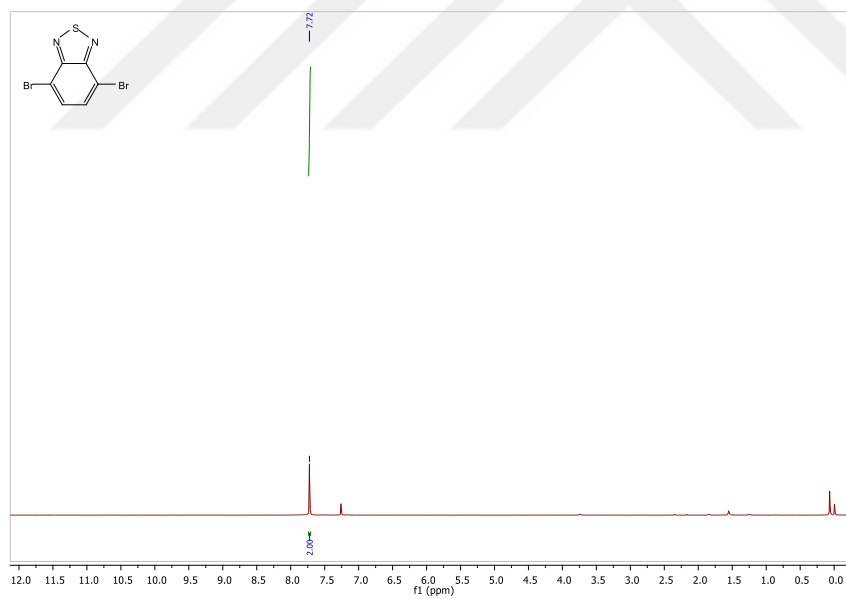


Figure 7.6. ^1H NMR of Compound 2-4

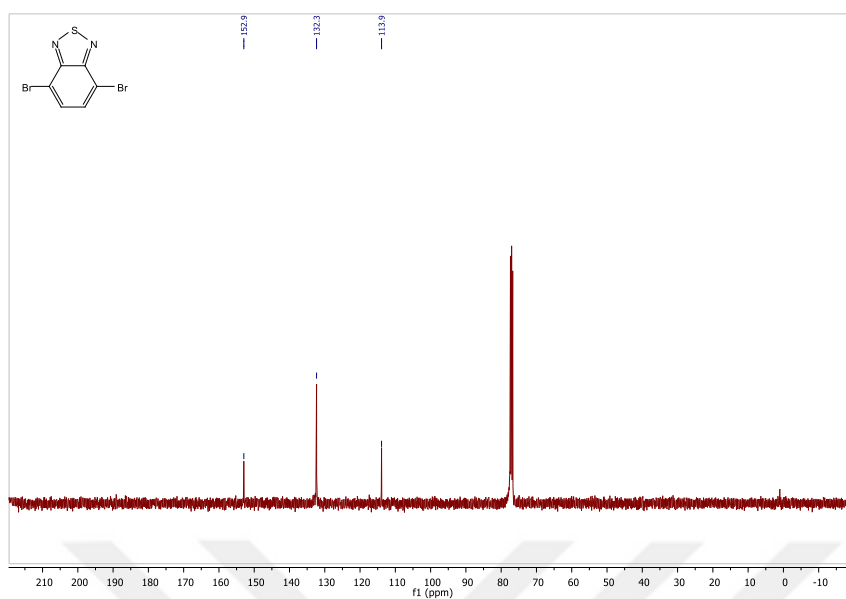


Figure 7.7. ^{13}C NMR of Compound 2-4

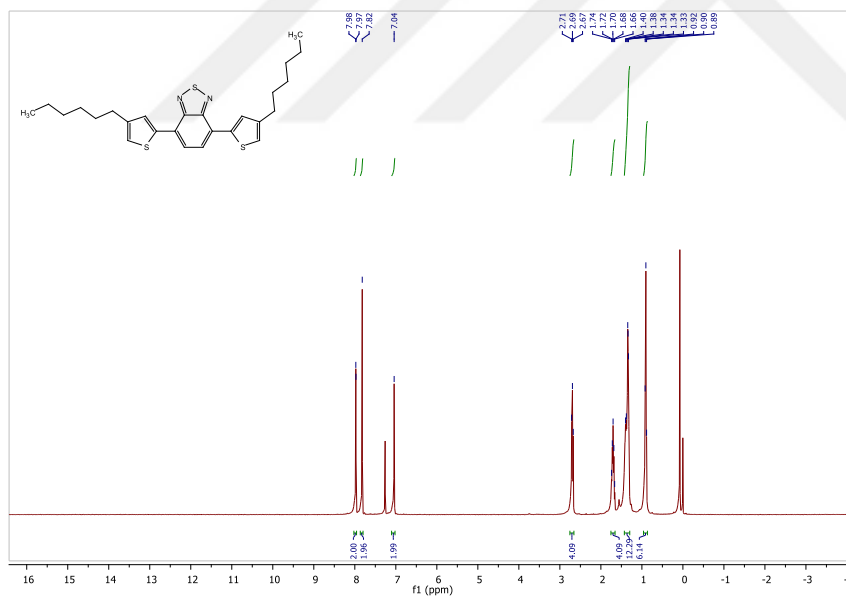


Figure 7.8. ^1H NMR of Compound 2-6

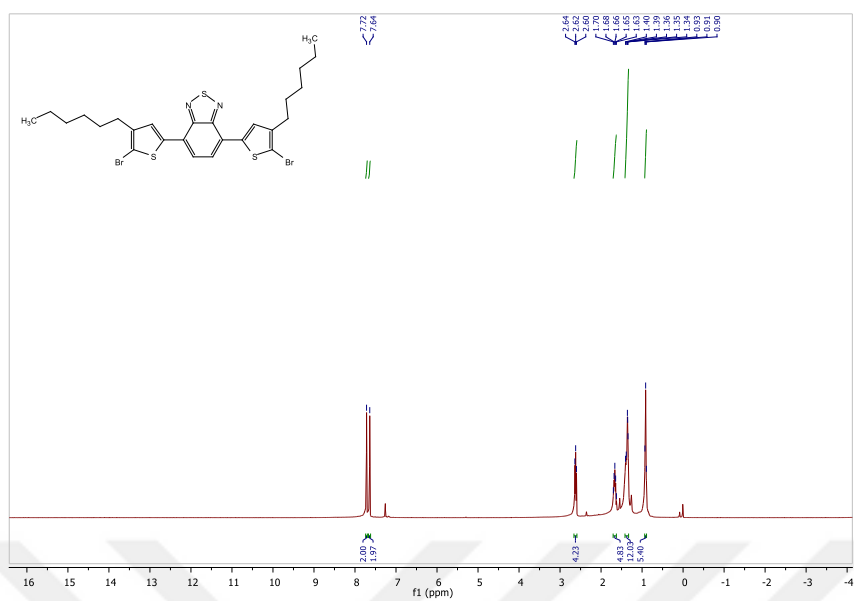


Figure 7.9. ¹H NMR of Compound 2-7

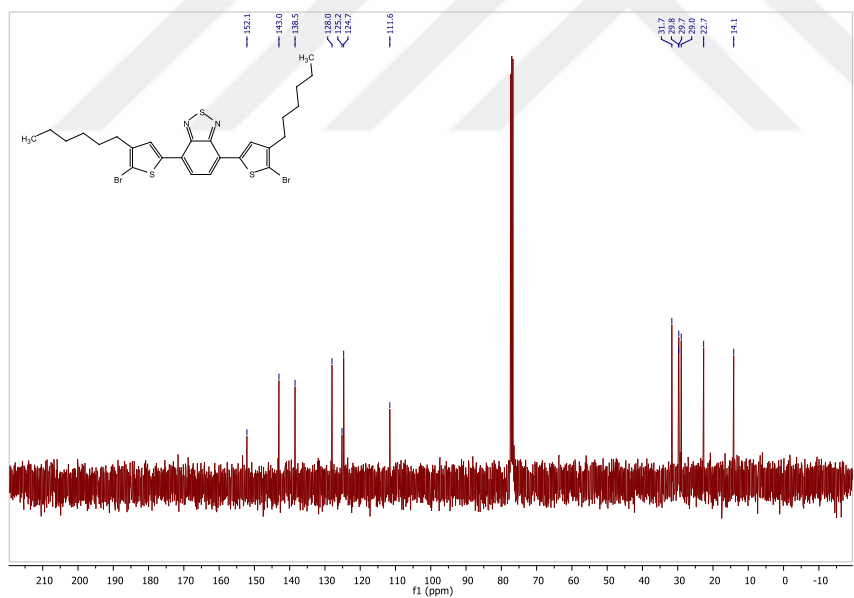


Figure 7.10. ¹³C NMR of Compound 2-7

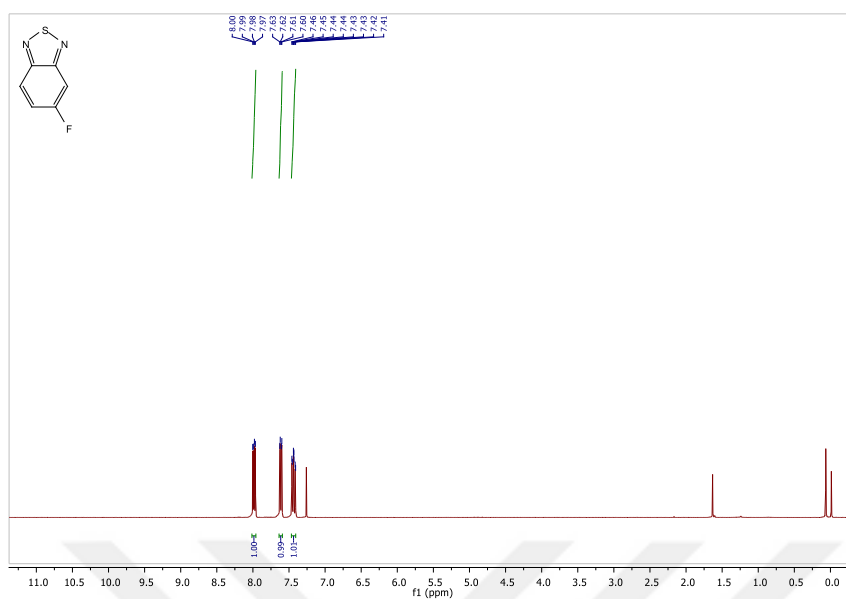


Figure 7.11. ¹H NMR of Compound 2-8

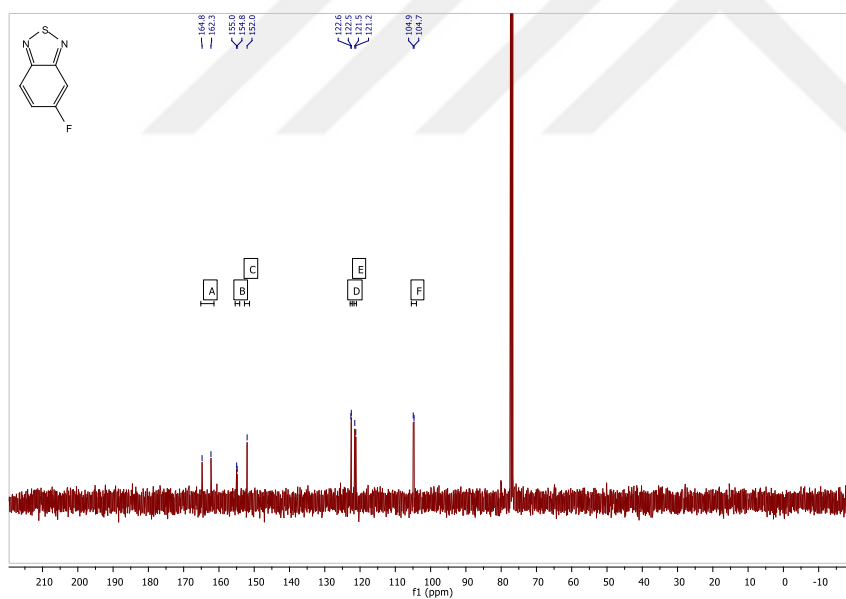


Figure 7.12. ¹³C NMR of Compound 2-8

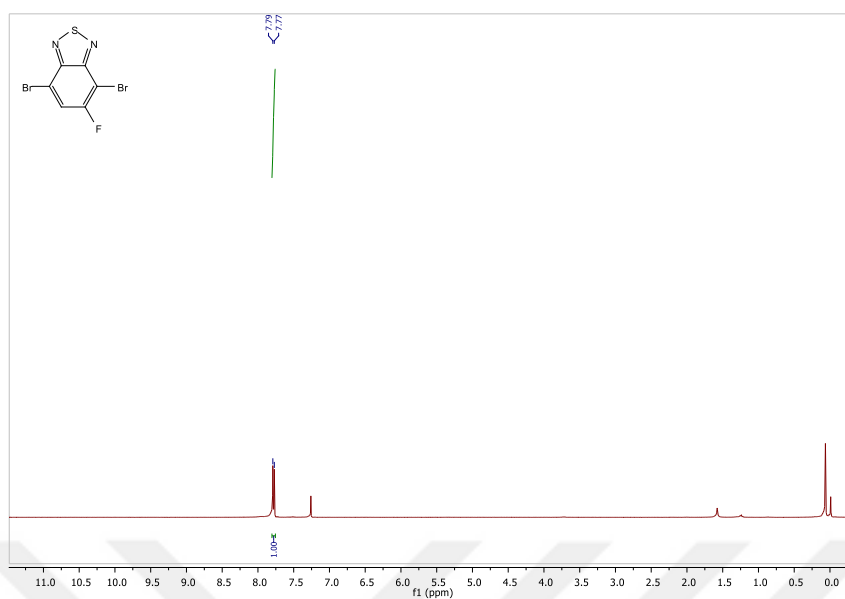


Figure 7.13. ¹H NMR of Compound 2-9

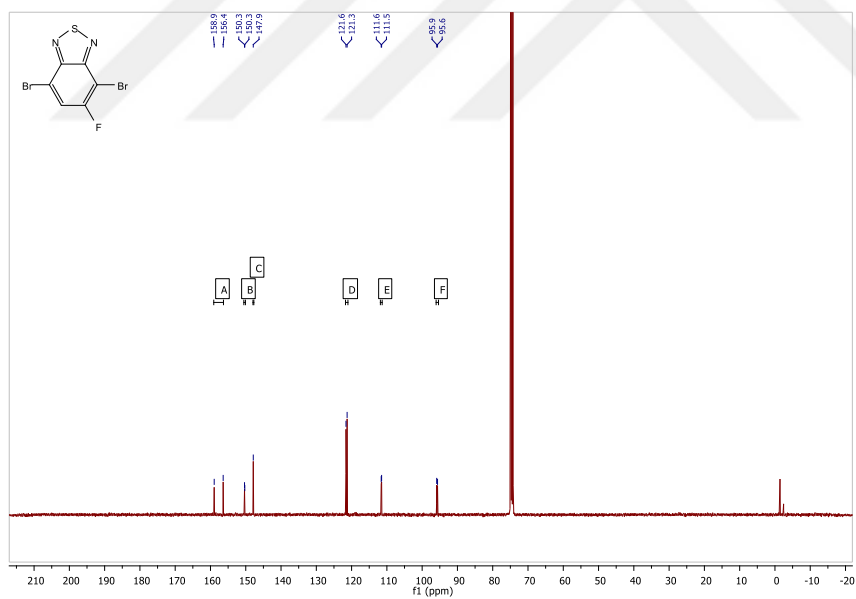


Figure 7.14. ¹³C NMR of Compound 2-9

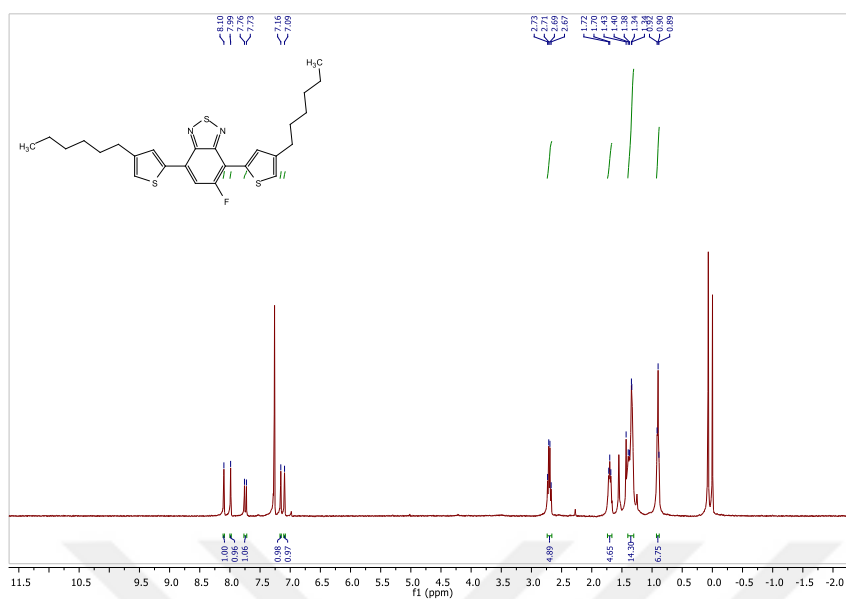


Figure 7.15. ¹H NMR of Compound 2-10

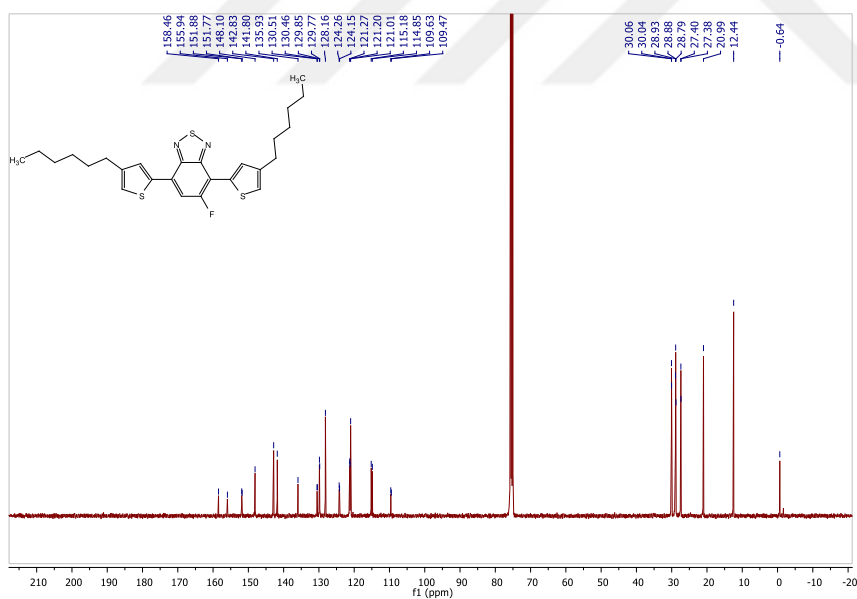


Figure 7.16. ¹³C NMR of Compound 2-10

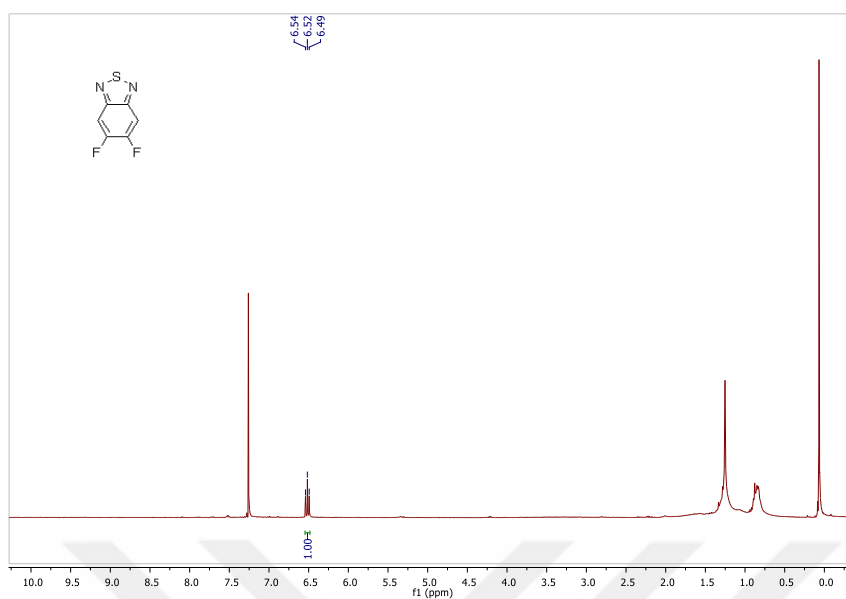


Figure 7.19. ¹H NMR of Compound 2-12

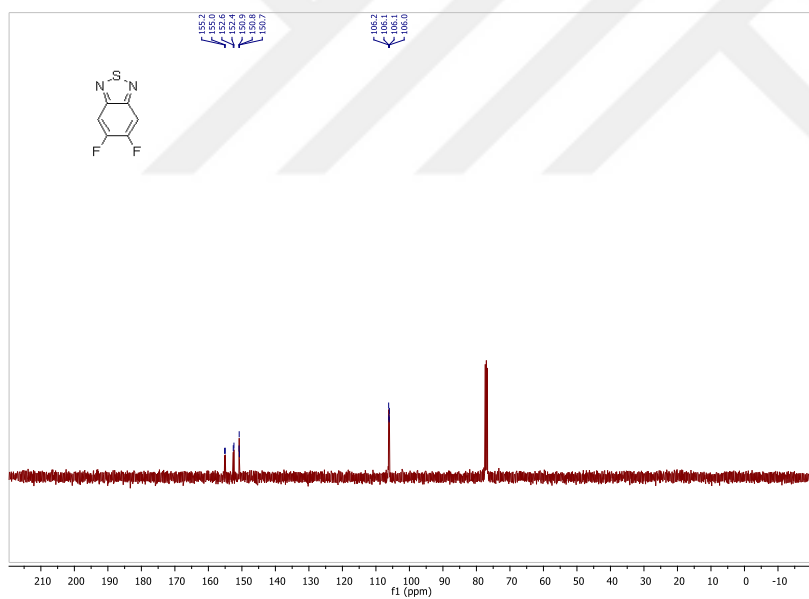


Figure 7.20. ¹³C NMR of Compound 2-12

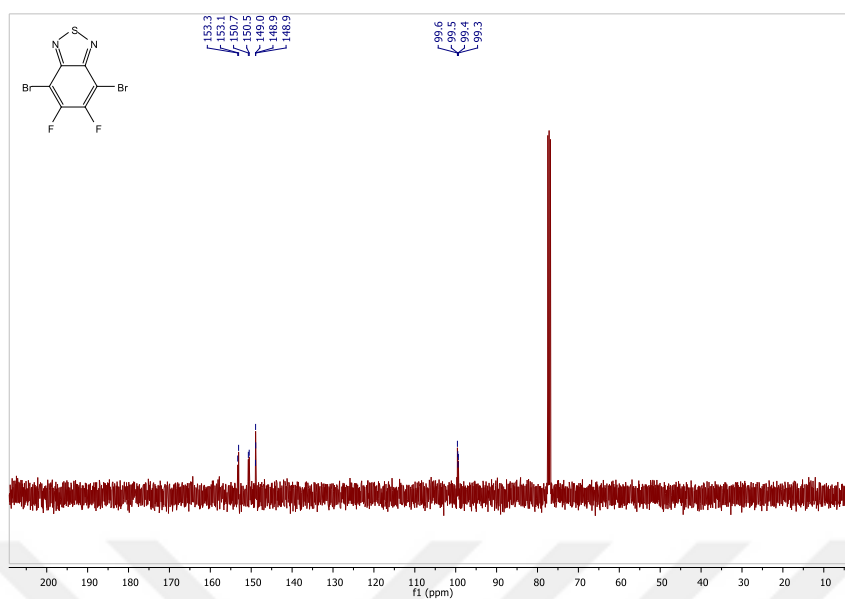


Figure 7.21. ¹³C NMR of Compound 2-13

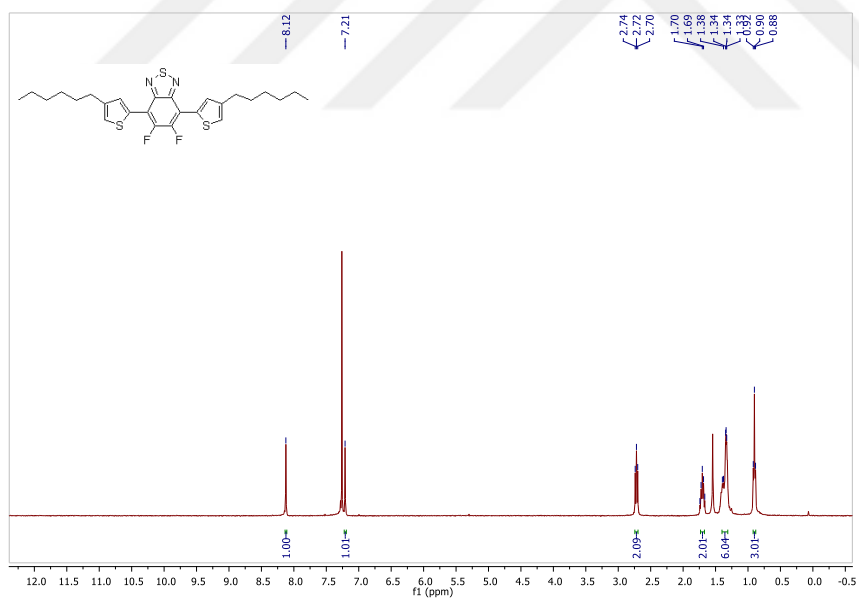


Figure 7.22. ¹H NMR of Compound 2-14

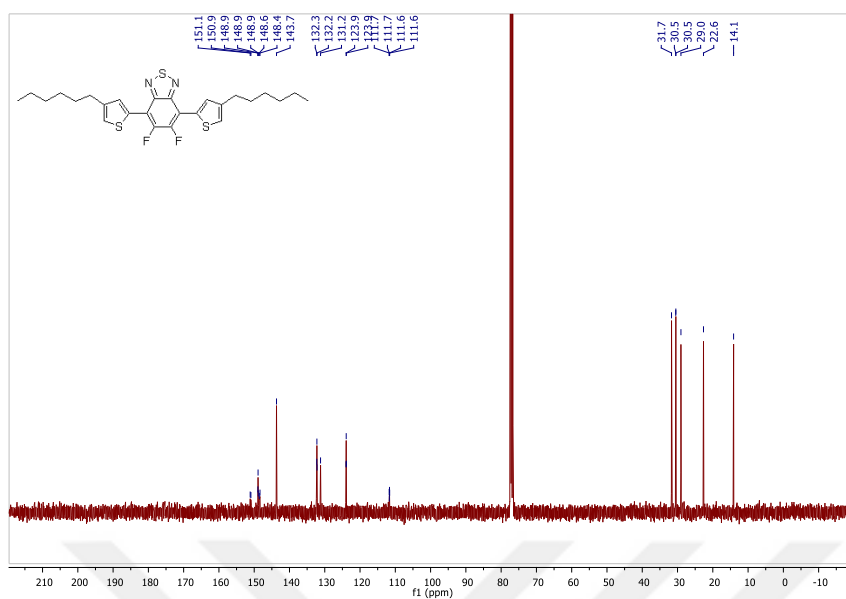


Figure 7.23. ¹³C NMR of Compound 2-14

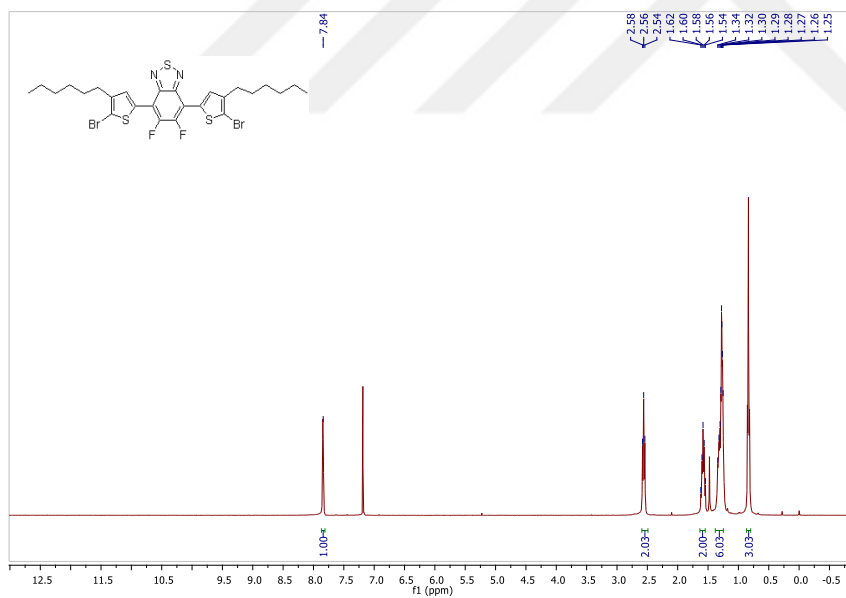


Figure 7.24. ¹H NMR of Compound 2-15

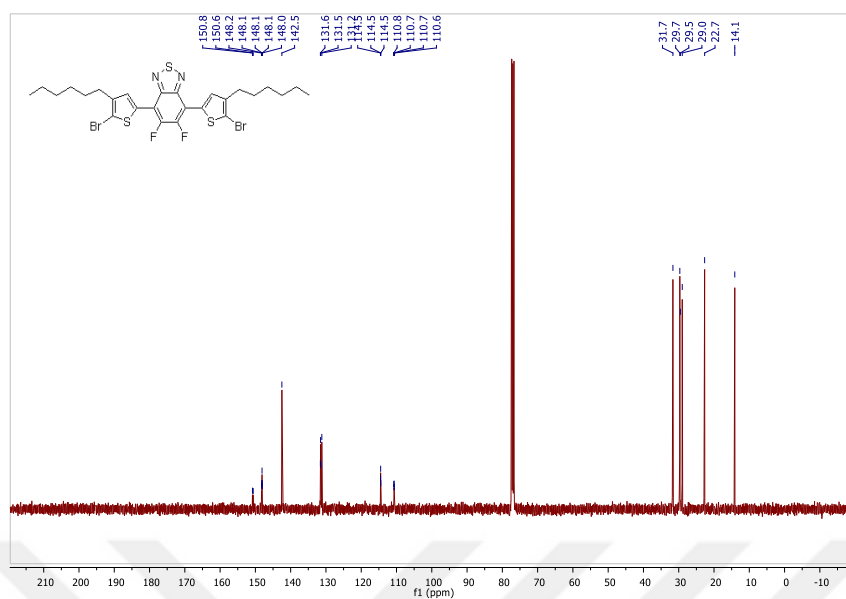


Figure 7.25. ¹³C NMR of Compound 2-15

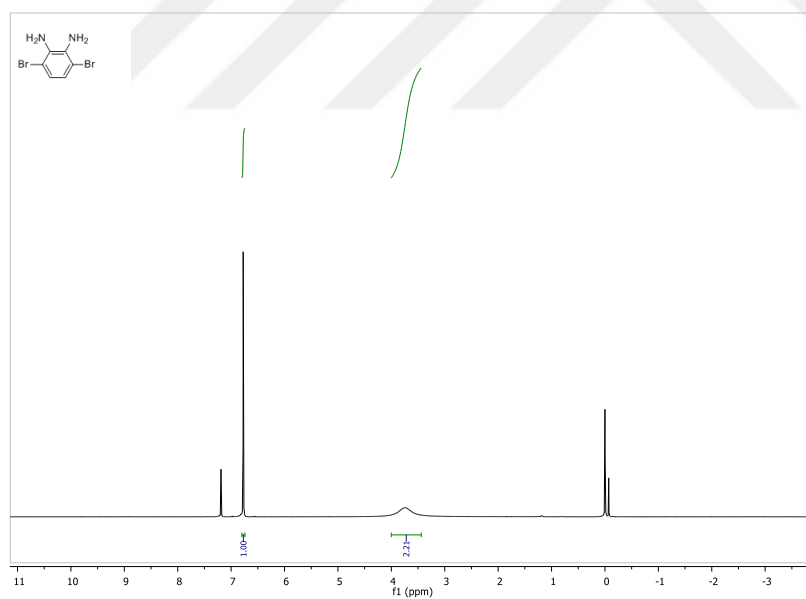


Figure 7.26. ¹H NMR of Compound 3-2

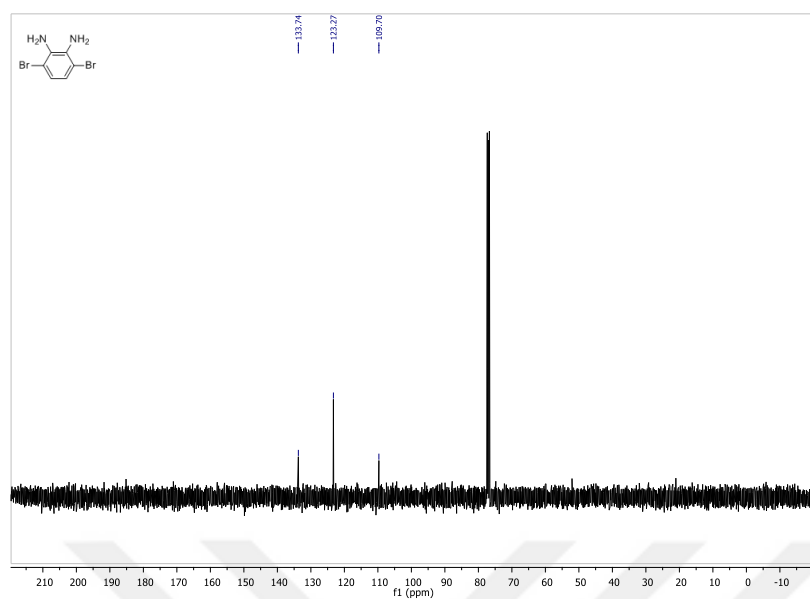


Figure 7.27. ¹³C NMR of Compound 3-2

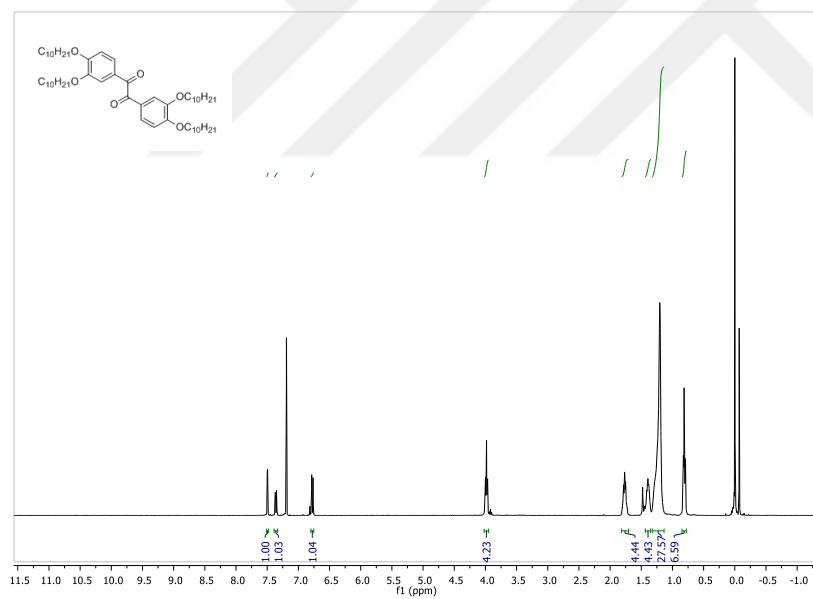


Figure 7.28. ¹H NMR of Compound 3-5

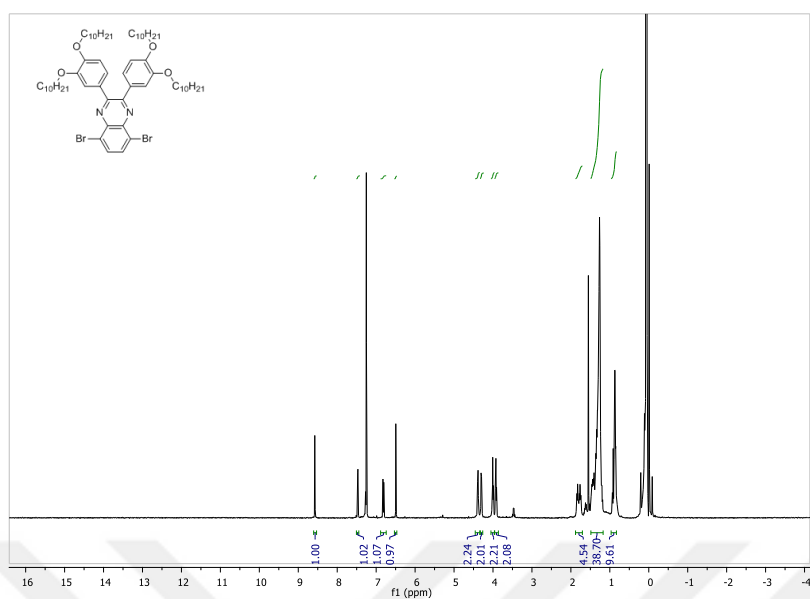


Figure 7.29. ¹H NMR of Compound 3-6

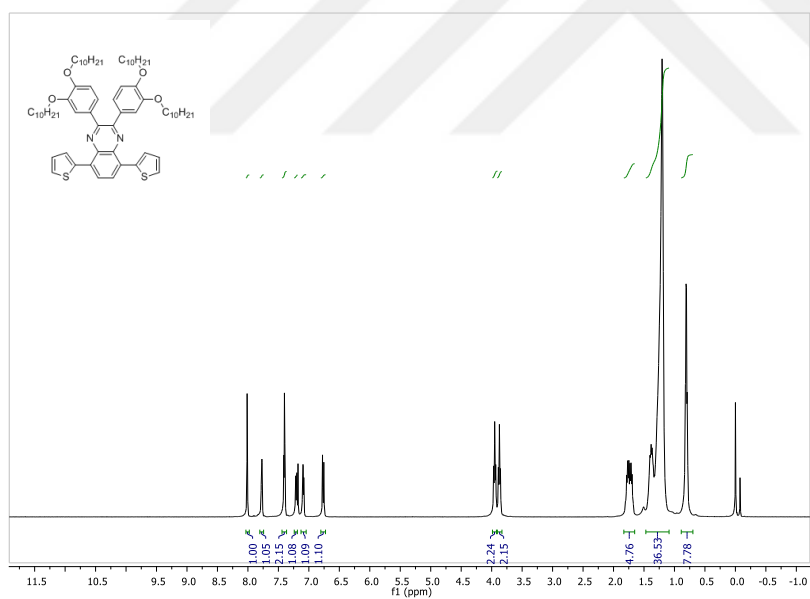


Figure 7.30. ¹H NMR of Compound 3-7

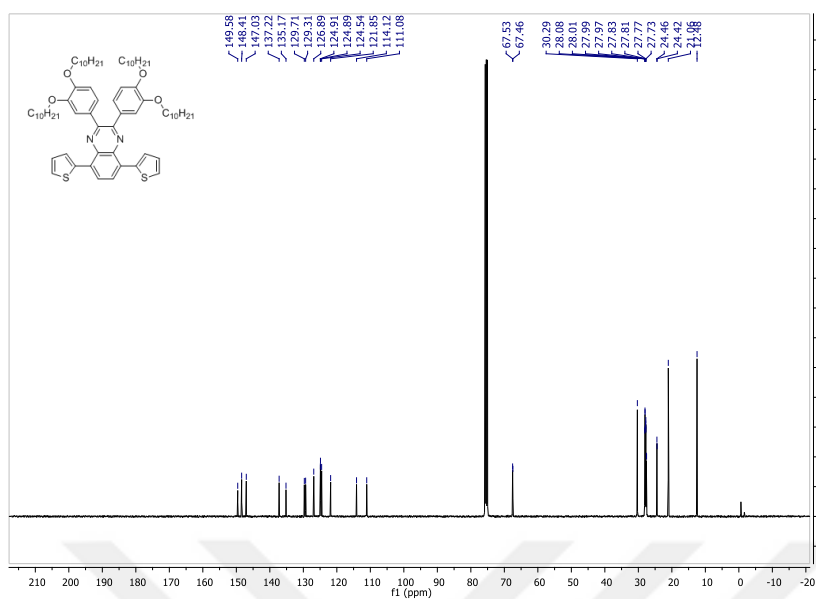


Figure 7.31. ^{13}C NMR of Compound 3-7

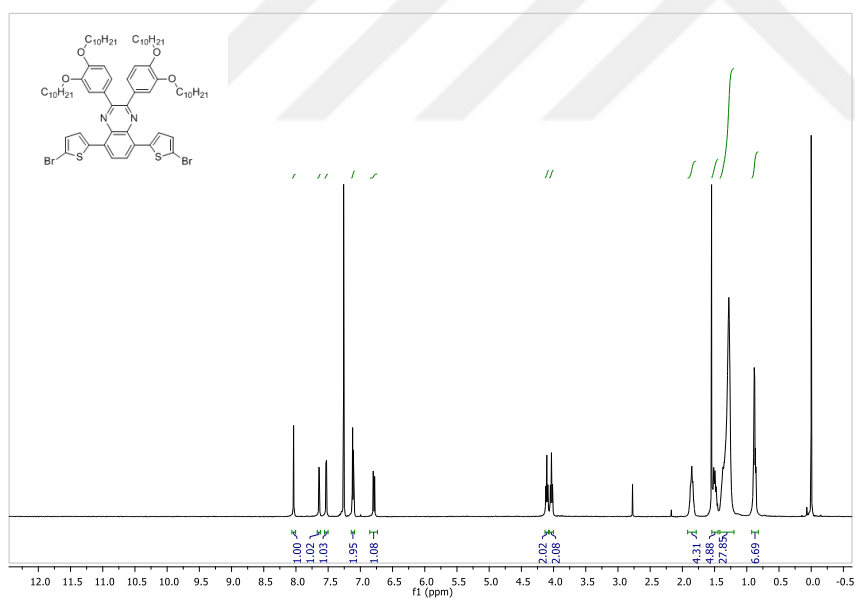


Figure 7.32. ^1H NMR of Compound 3-9

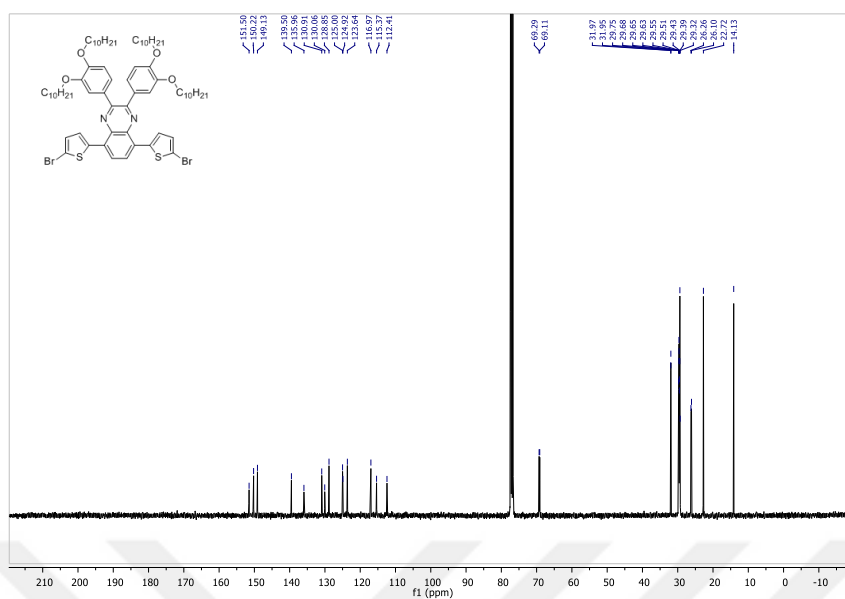


Figure 7.33. ¹³C NMR of Compound 3-9

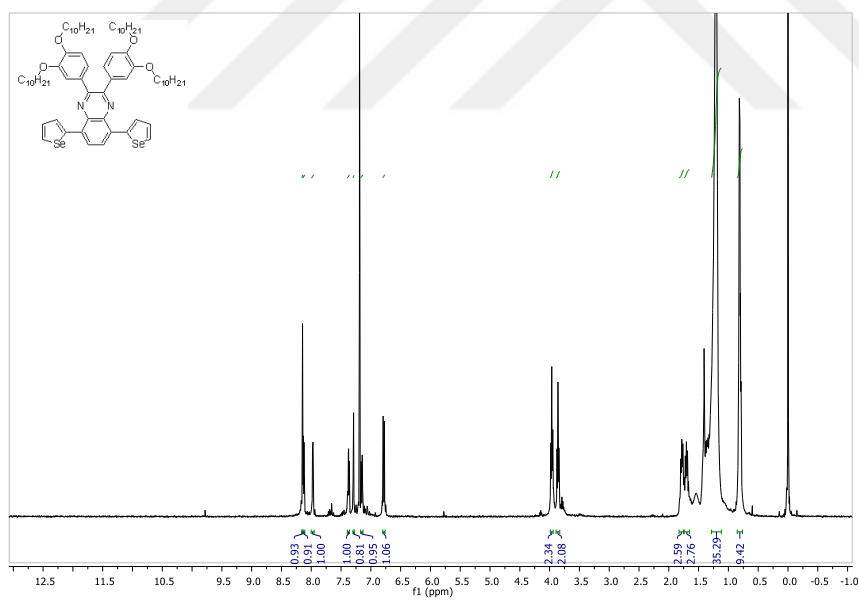


Figure 7.34. ¹H NMR of Compound 3-8



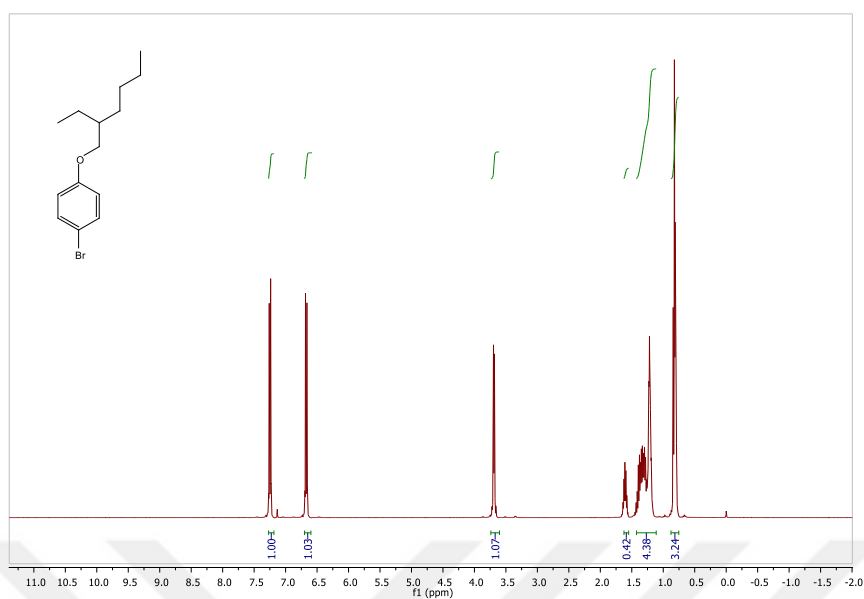


Figure 7.37. ^1H NMR of Compound 5-1

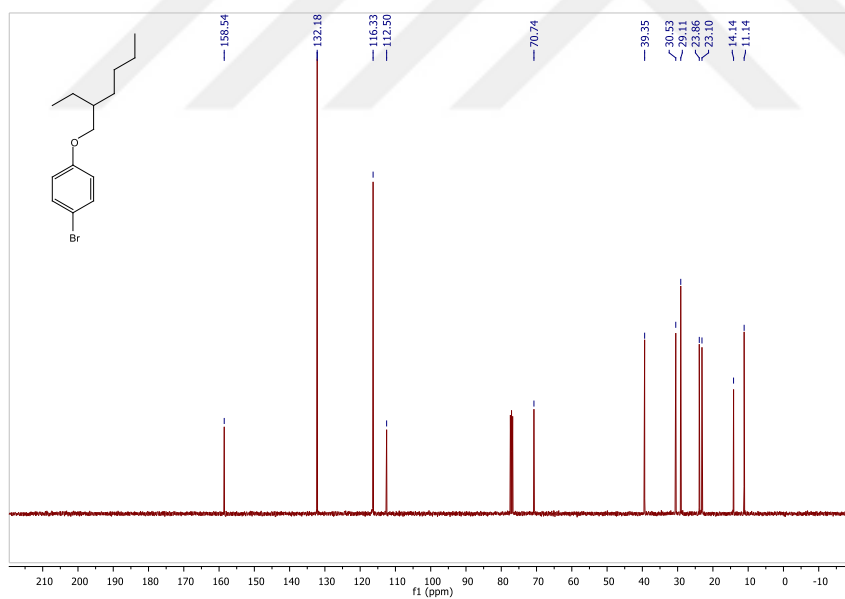


Figure 7.38. ^{13}C NMR of Compound 5-1

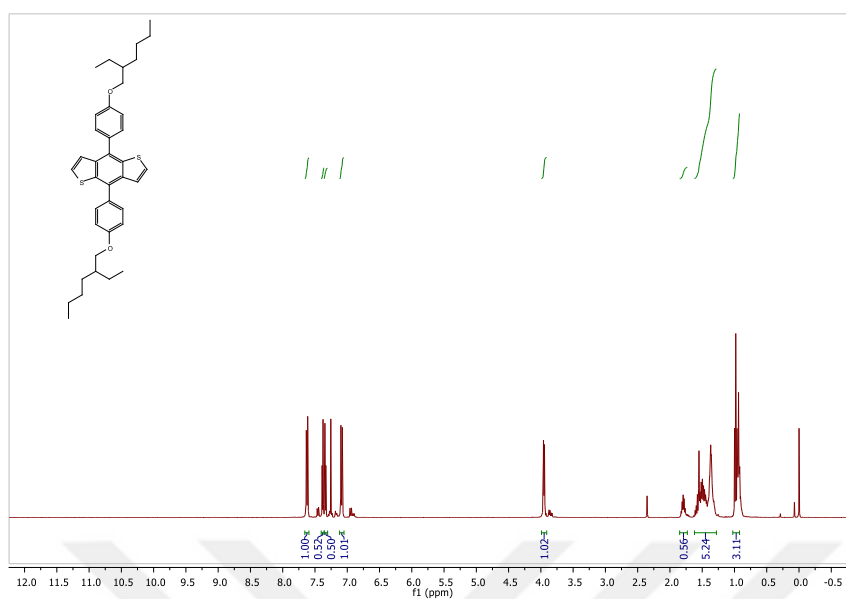


Figure 7.39. ¹H NMR of Compound 5-2

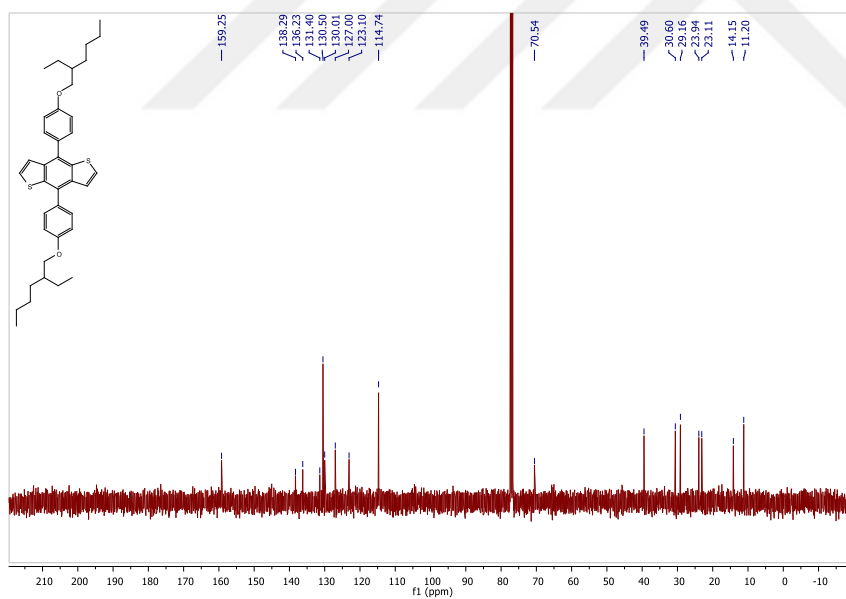


Figure 7.40. ¹³C NMR of Compound 5-2

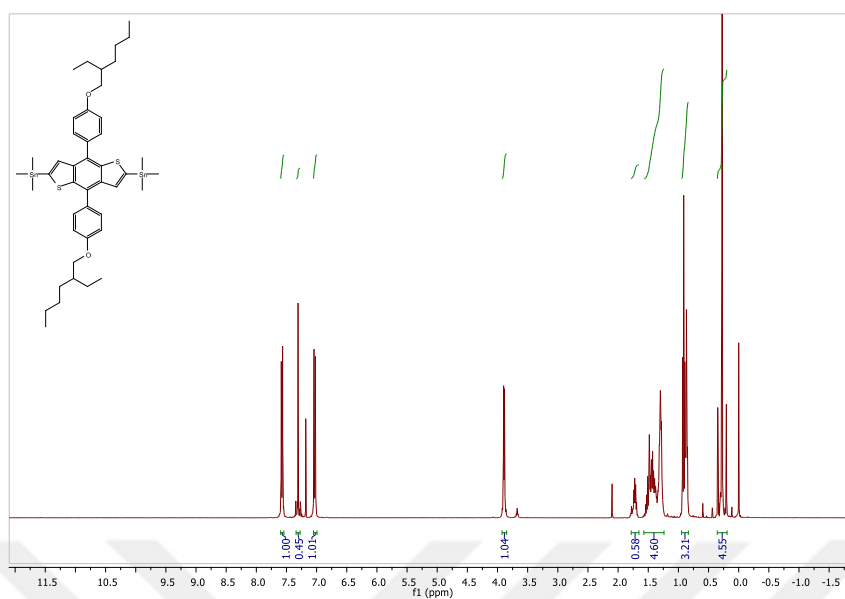


Figure 7.41. ¹H NMR of Compound BDT-Ph

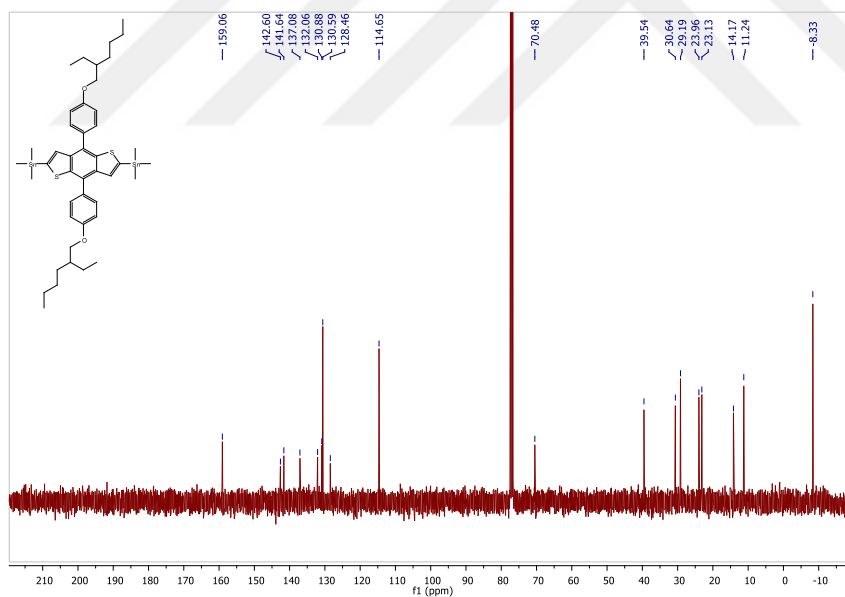


Figure 7.42. ¹³C NMR of Compound BDT-Ph

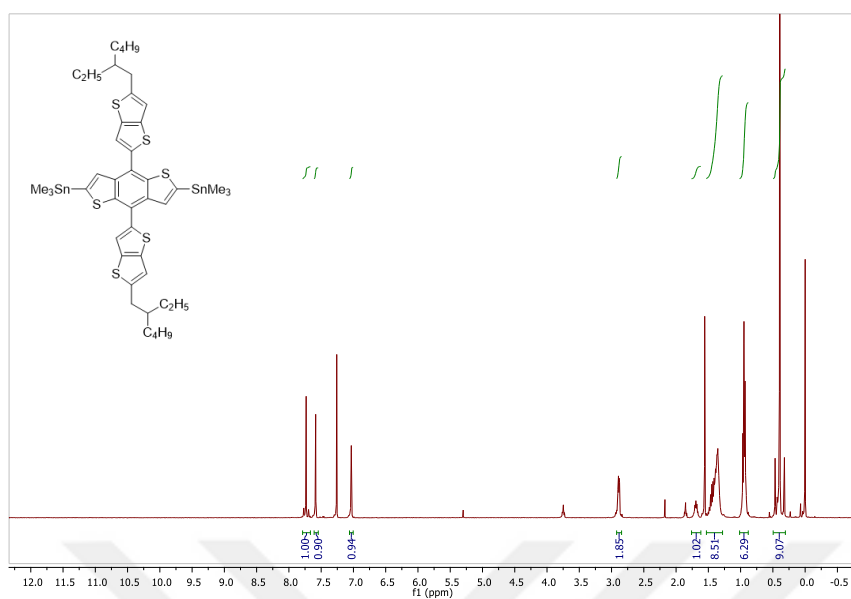


Figure 7.43. ¹H NMR of Compound BDT-TT

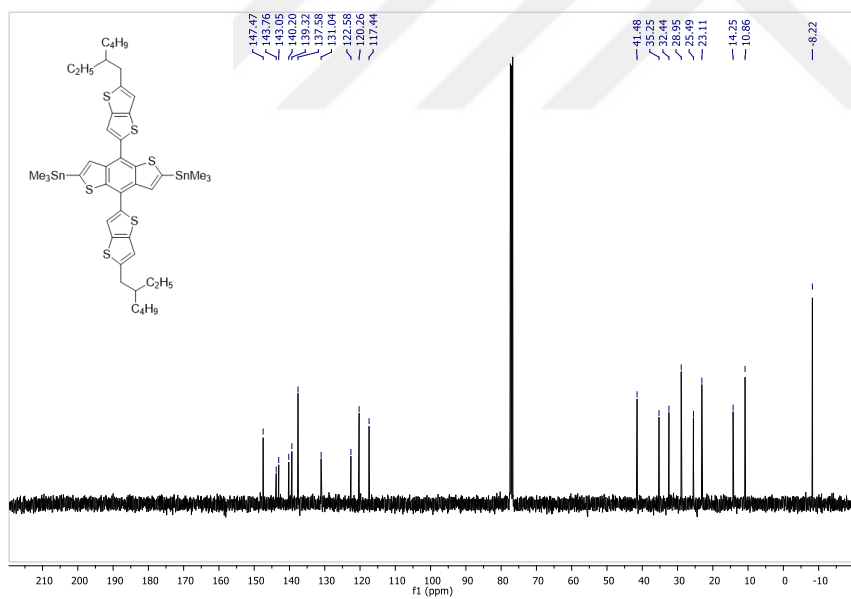


Figure 7.44. ¹³C NMR of Compound BDT-TT

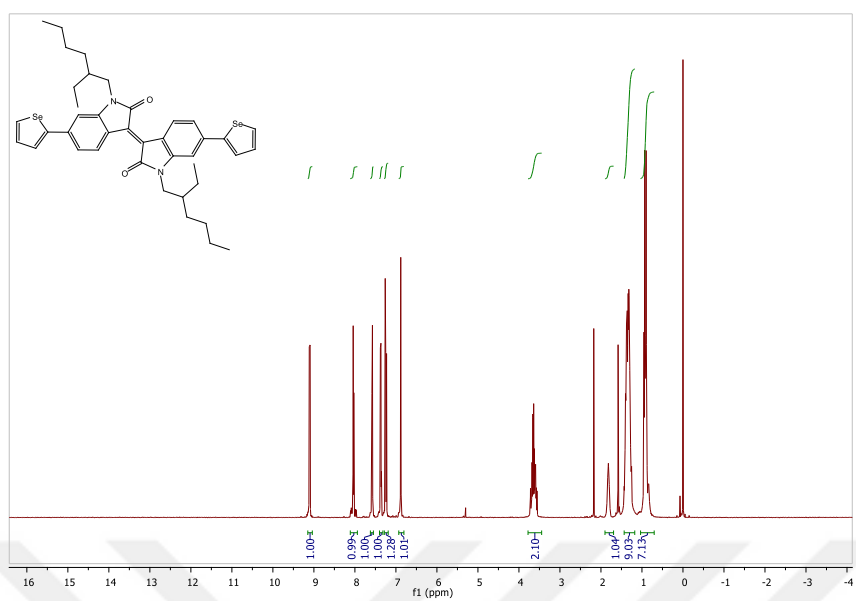


Figure 7.45. ¹H NMR of Compound 6-1

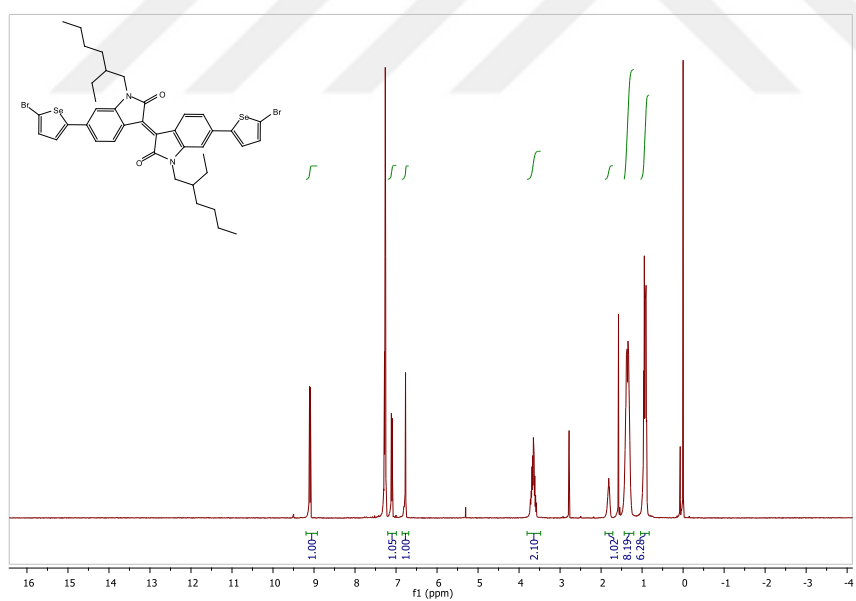


Figure 7.46. ¹H NMR of Compound 6-2

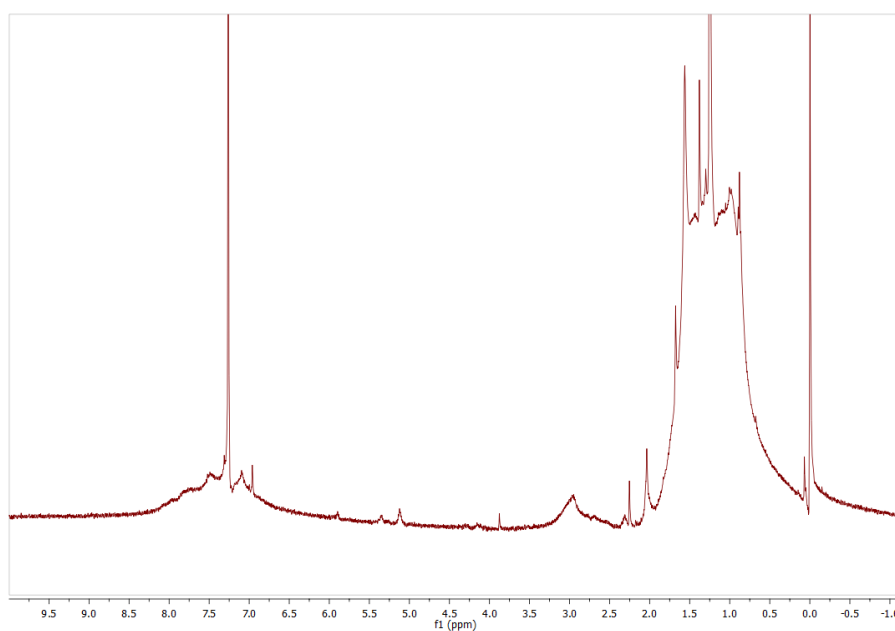


Figure 7.47. ^1H NMR of PBDTSe-BT

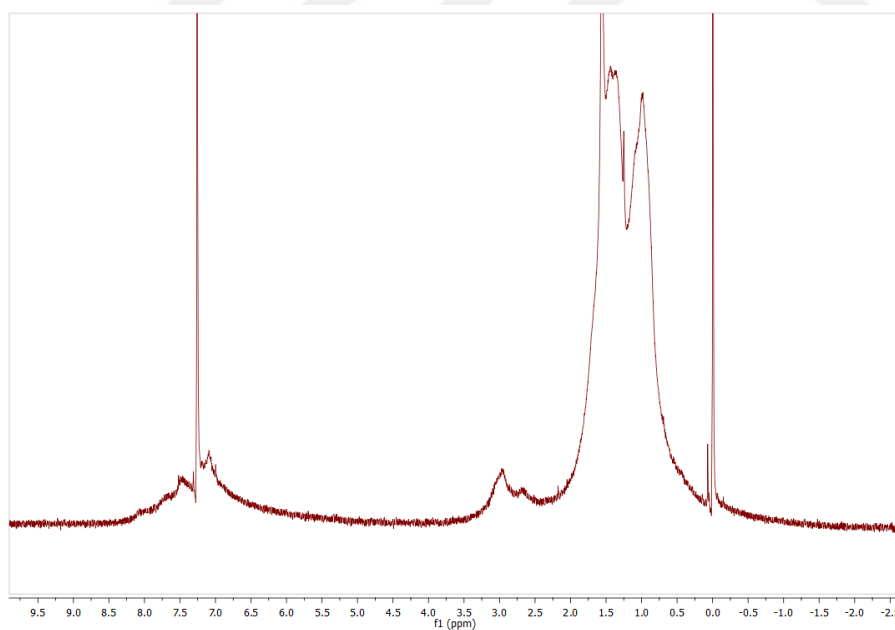


Figure 7.48. ^1H NMR of PBDTSe-FBT

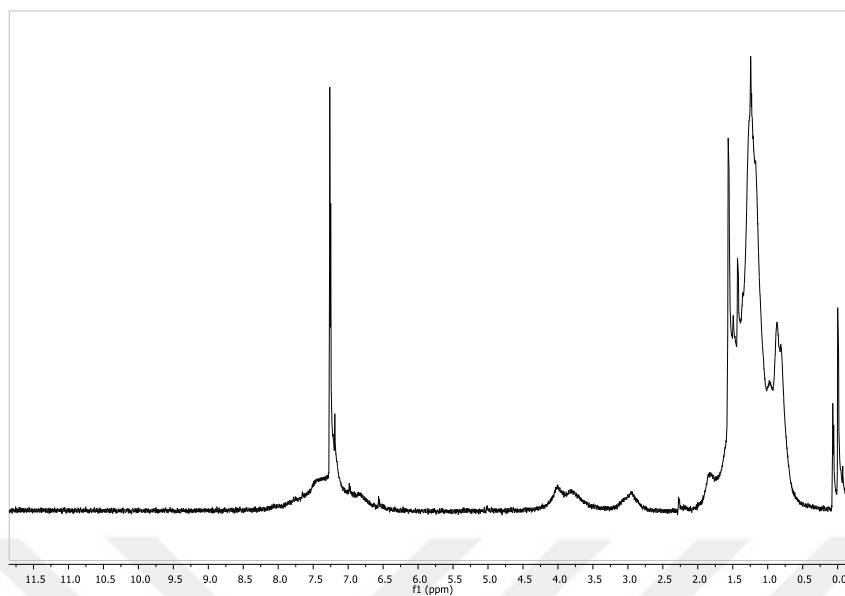


Figure 7.49. ^1H NMR of PBDTSe-TQx

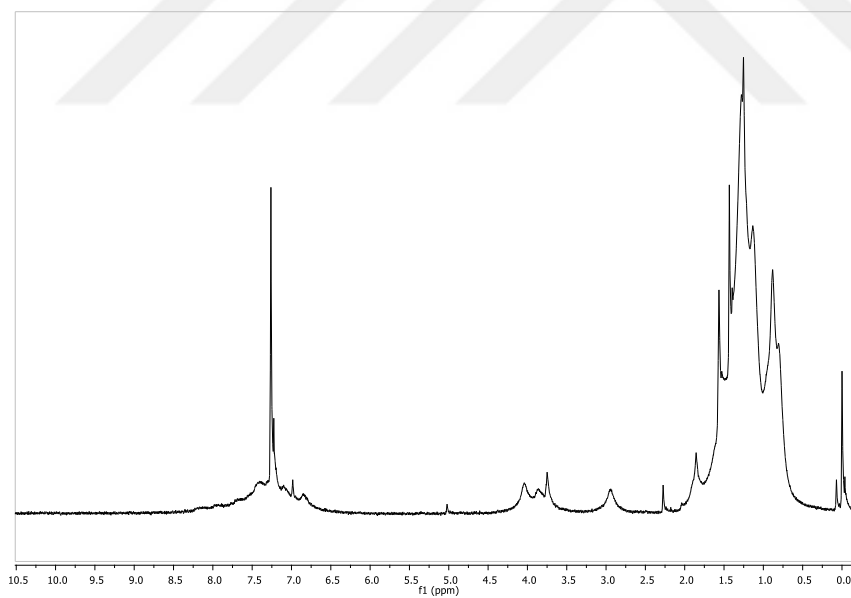


Figure 7.50. ^1H NMR of PBDTSe-SeQx

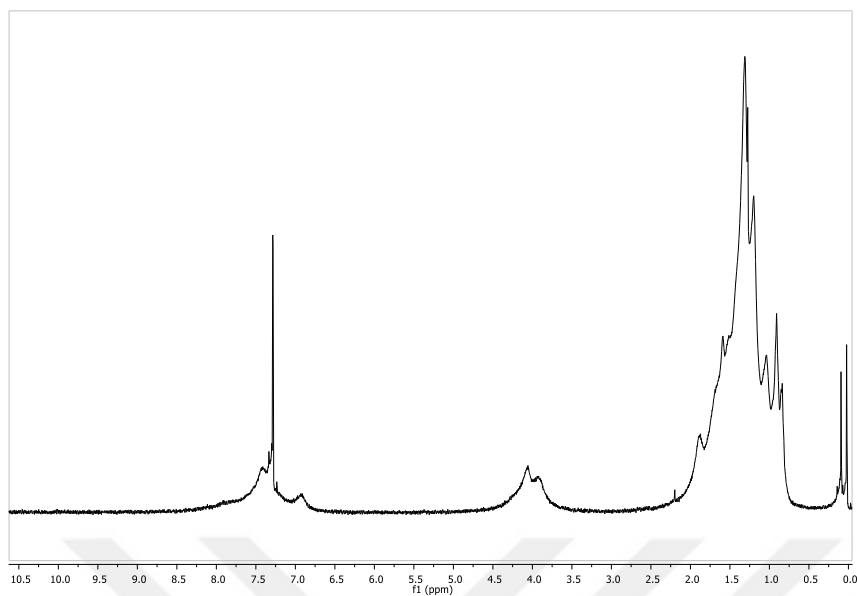


Figure 7.51. ^1H NMR of PBDT-TQx

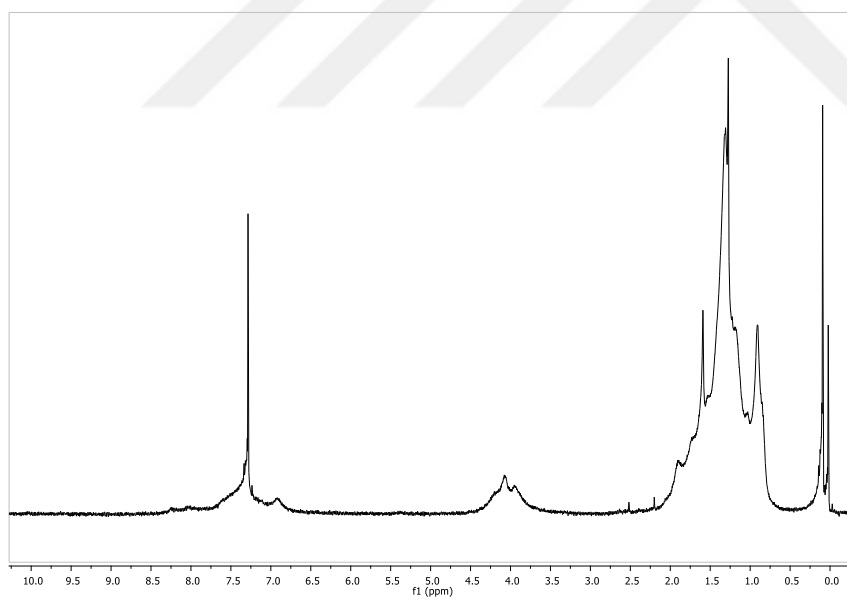


Figure 7.52. ^1H NMR of PBDT-SeQx

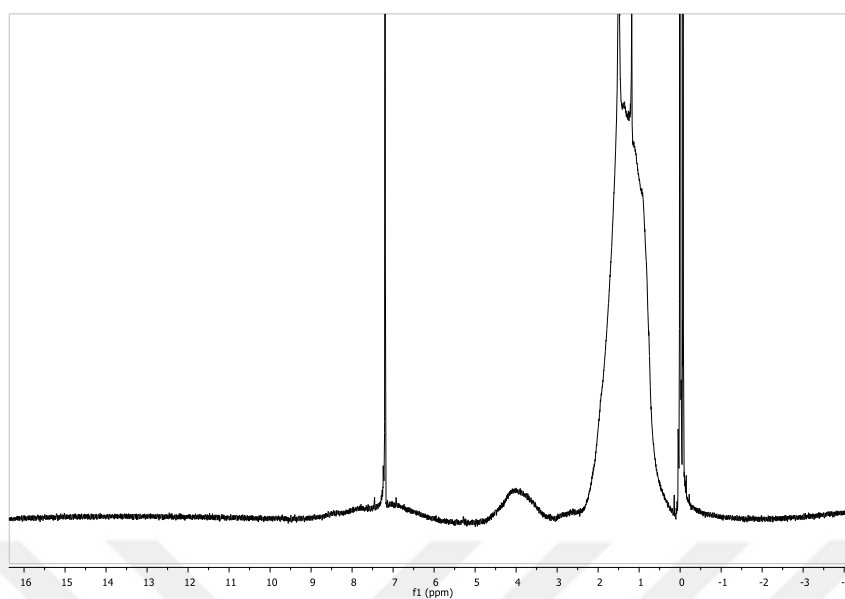


Figure 7.53. ^1H NMR of RP1

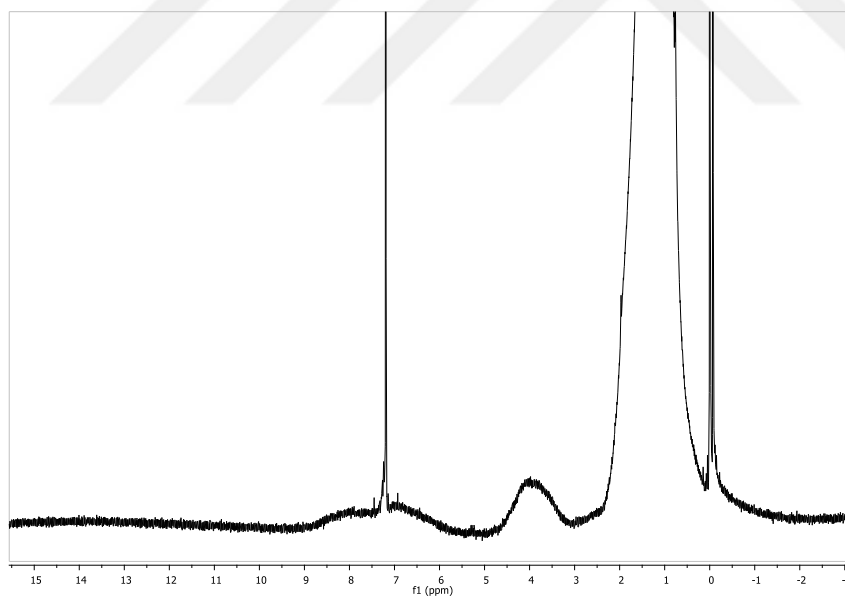


Figure 7.54. ^1H NMR of RP2

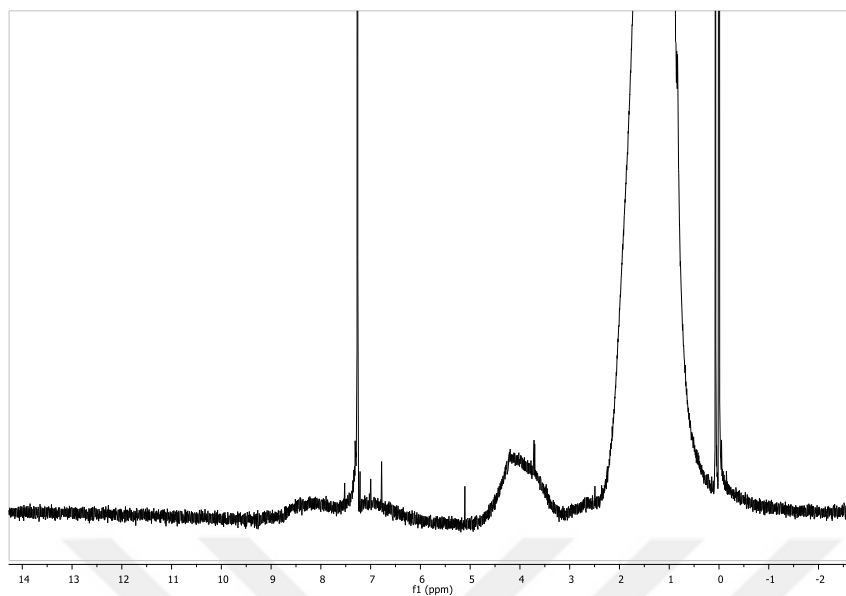


Figure 7.55. ^1H NMR of RP3

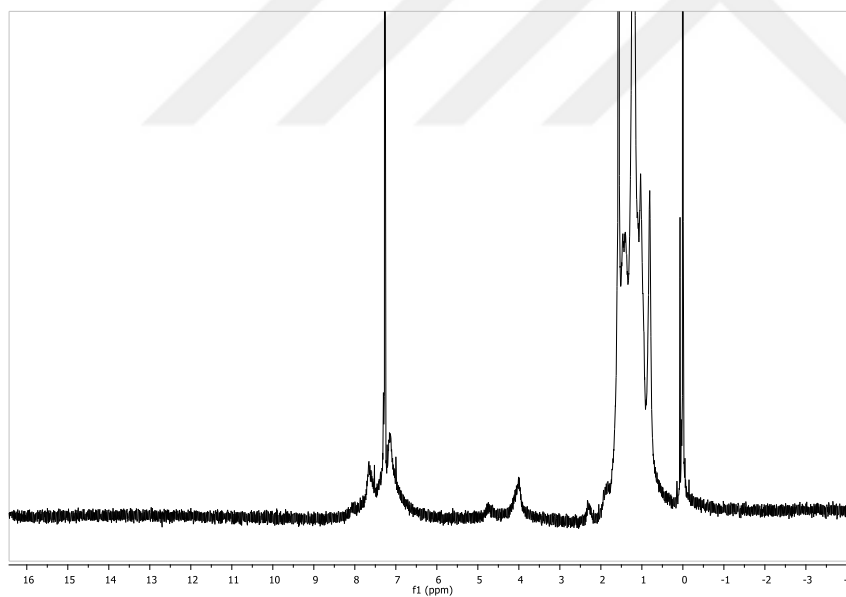


Figure 7.56. ^1H NMR of PBDTPh-BTz

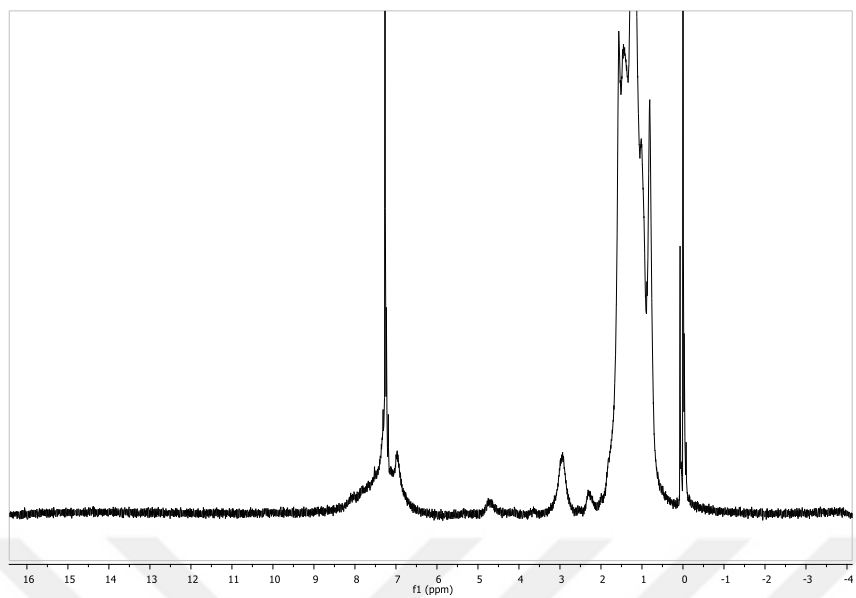


Figure 7.57. ^1H NMR of PBDTT-BTz

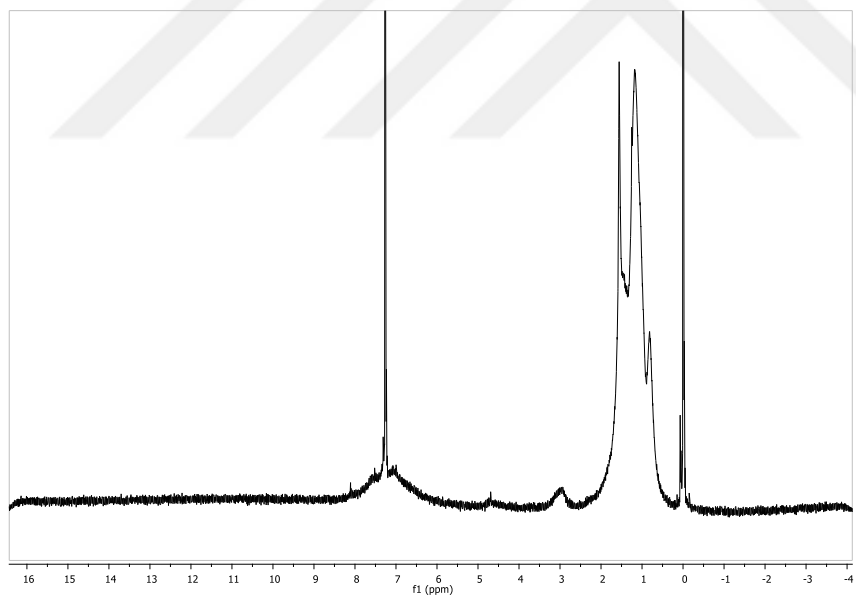
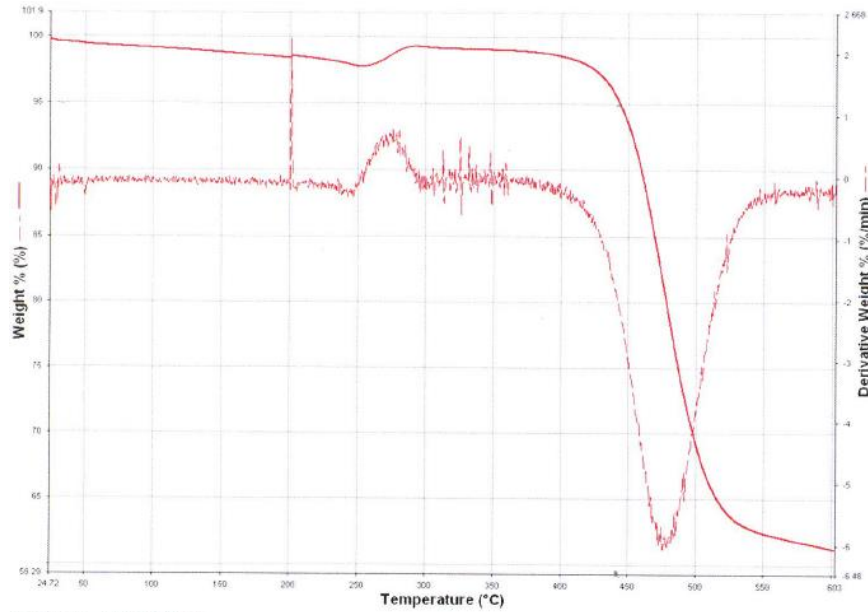


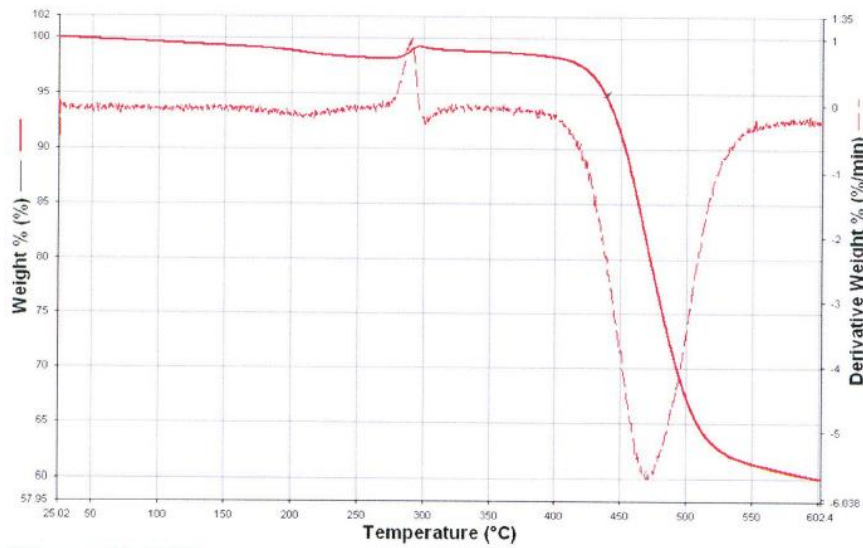
Figure 7.58. ^1H NMR of PBDTTT-BTz

B. TGA Graphs of Polymers



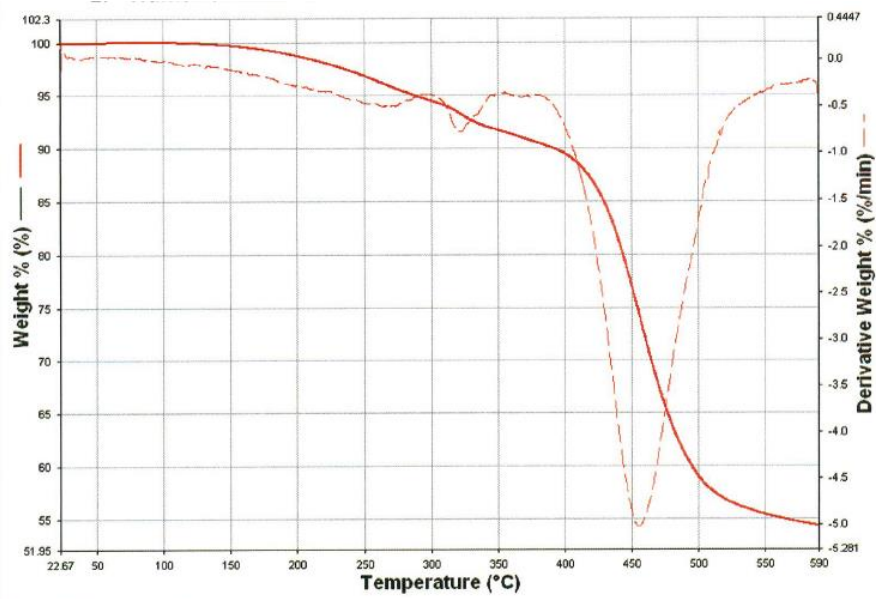
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Figure 7.59. TGA graph of PBDTSe-BT



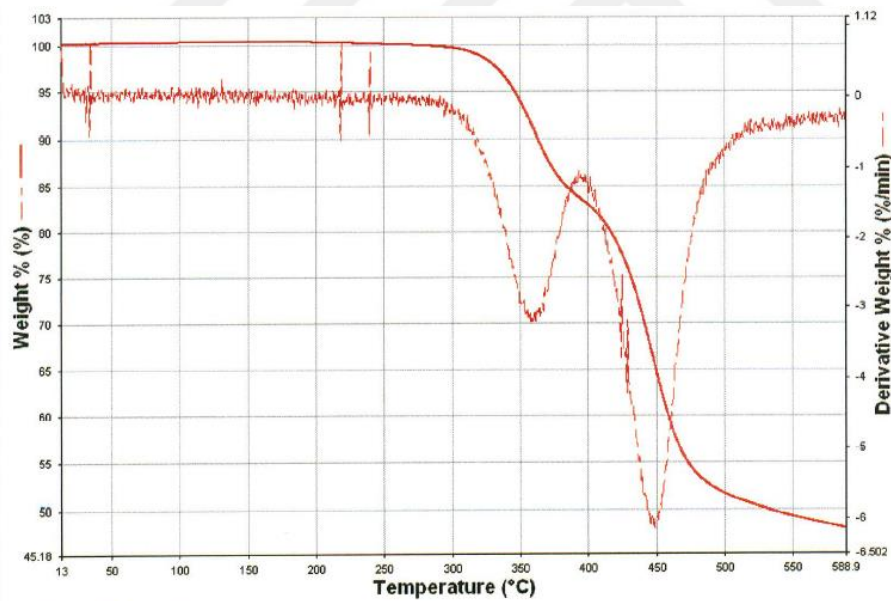
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Figure 7.60. TGA graph of PBDTSe-FBT



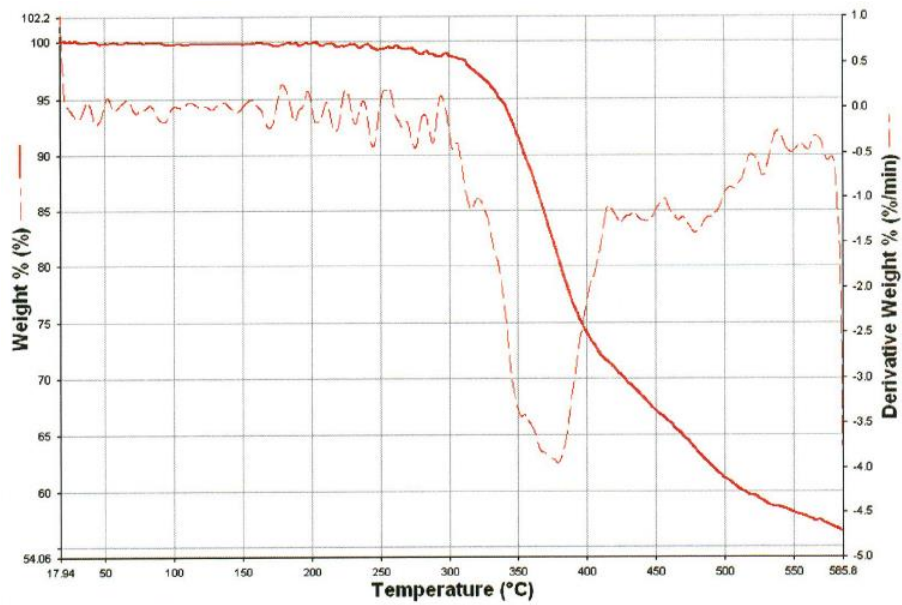
%Kayıp= 45.450%

Figure 7.61. TGA graph of PBDTSe-FFBT



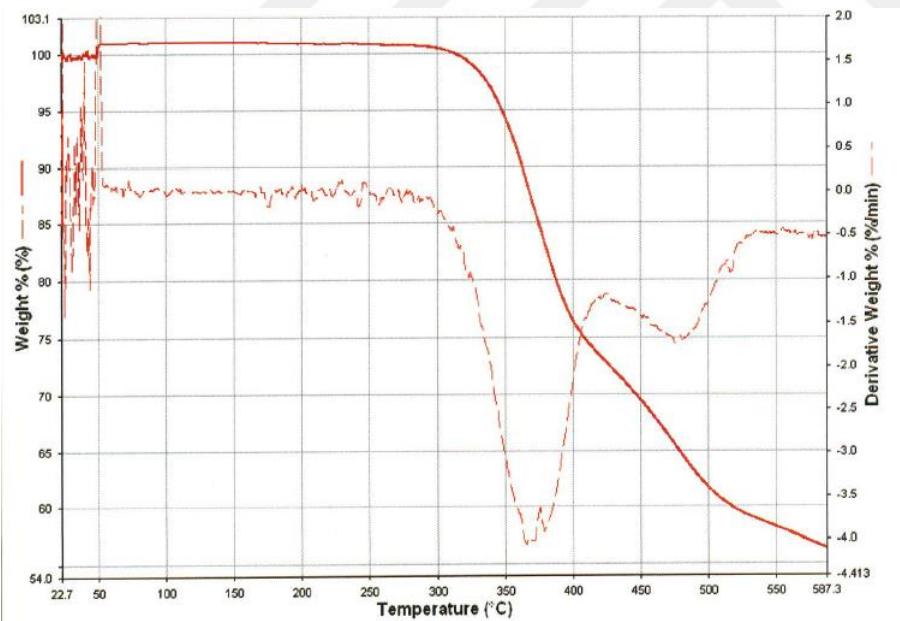
%Kayıp= 52.218%

Figure 7.62. TGA graph of PBDT-TQx



%Kayıp= 42.485%

Figure 7.63. TGA graph of RP1



%Kayıp= 43.437%

Figure 7.64. TGA graph of RP2

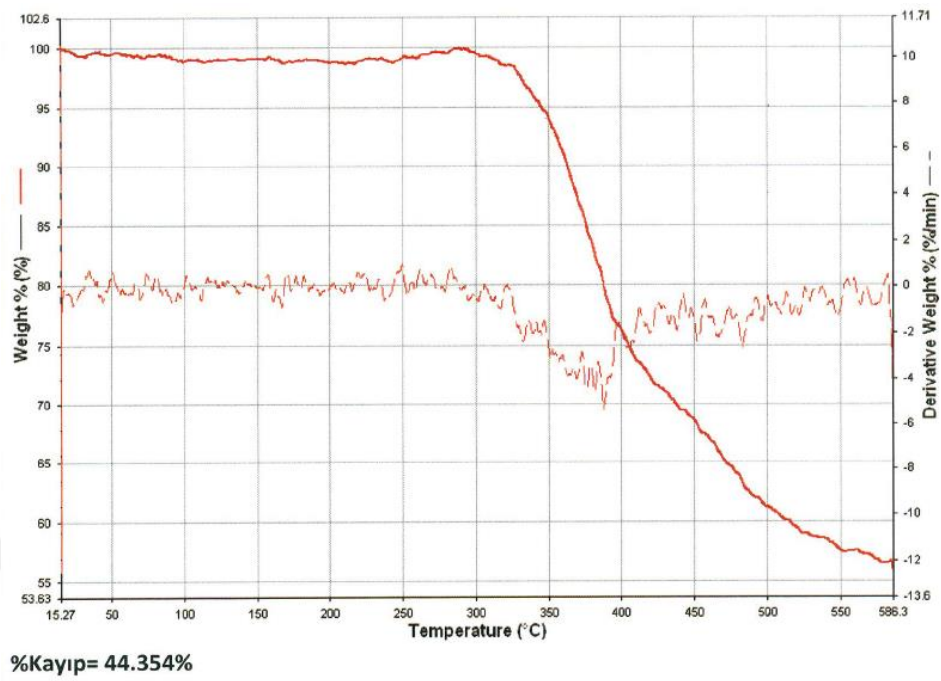


Figure 7.65. TGA graph of RP3

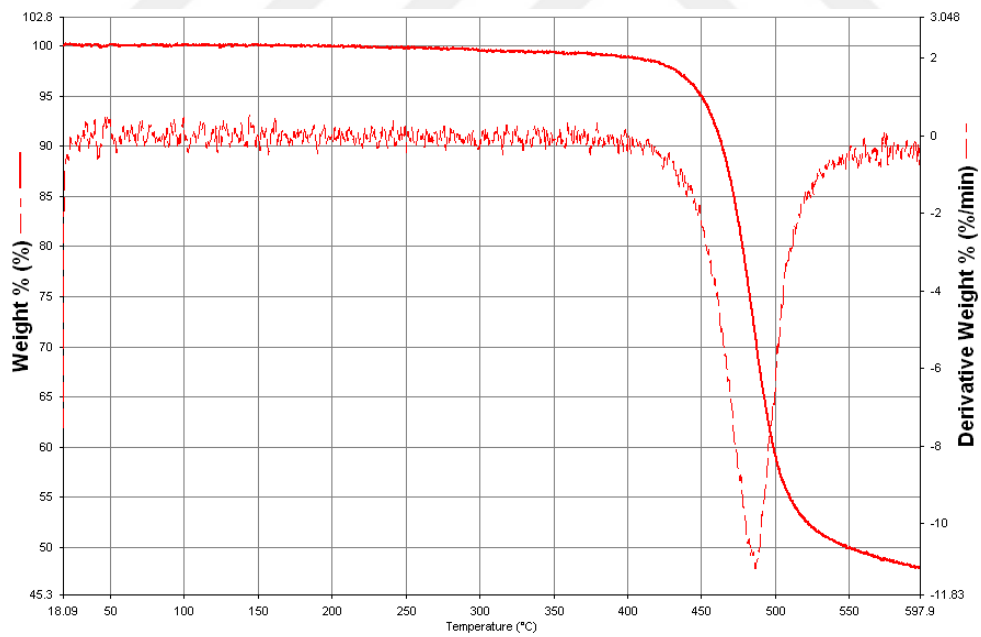
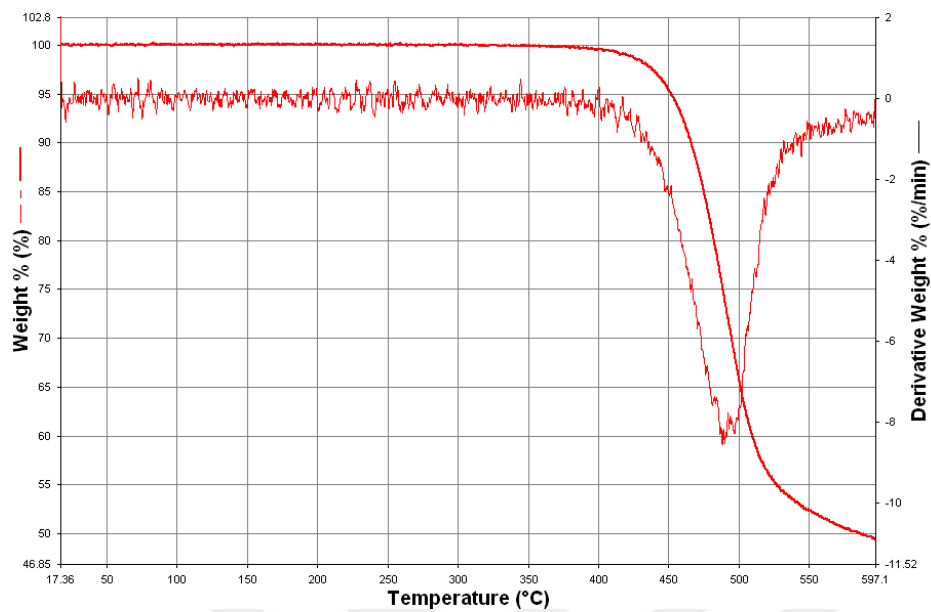
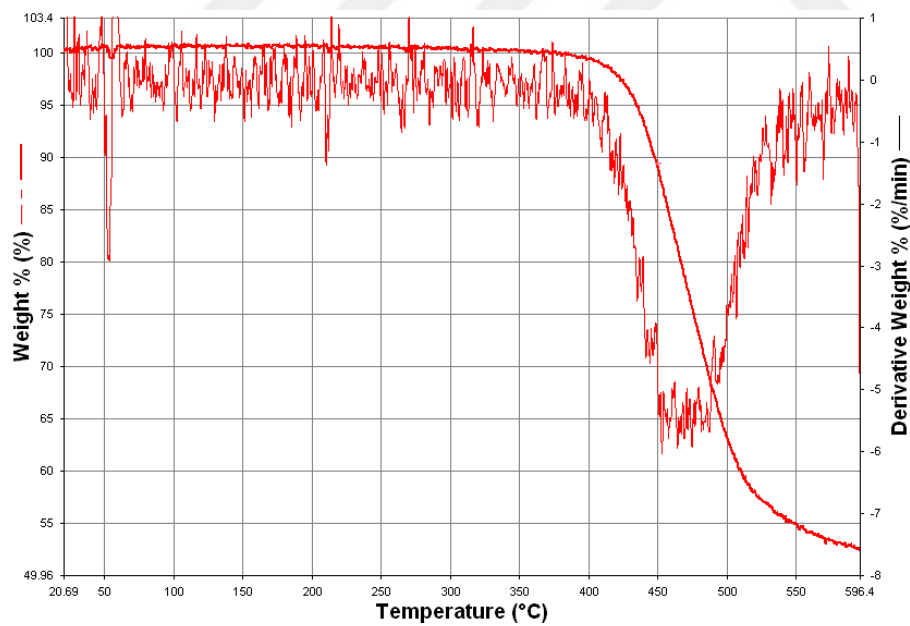


Figure 7.66. TGA graph of PBDTPH-BTz



%Kayıp= 50.674%

Figure 7.67. TGA graph of PBDTT-BTz



%Kayıp= 47.794%

Figure 7.68. TGA graph of PBDTTT-BTz

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EDUCATION

Degree	Institution	Year of Graduation
MS	METU Chemistry	2015
BS (Minor)	METU Chemical Engineering	2014
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PUBLICATIONS

1. Taskaya Aslan S., Alemdar Yılmaz E., Hacıefendioğlu T., Arslan Udum Y.; Toppare L.; Yıldırım E.; Çirpan A. Investigation the Effect of π Bridge and Side Chain on Photovoltaic Properties of Benzodithiophene and Quinoxaline Based Conjugated Polymers. Eur. Polym. J., 169, 111141 (2022)
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 5. Atli G. O., Yilmaz E., Taşkaya Aslan S., Udum Y. A., Toppare L. K., Çırpan A., Synthesis and characterization of optical, electrochemical and photovoltaic properties of selenophene bearing benzodithiophene based alternating polymers, *J. Electroanal. Chem.*, 862, 114014 (2020)
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