SYNTHESIS , SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF PERYLENE CONTAINING CONJUGATED COPOLYMERS

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SYNTHESIS , SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF PERYLENE CONTAINING CONJUGATED COPOLYMERS

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ABSTRACT

SYNTHESIS , SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF PERYLENE CONTAINING CONJUGATED COPOLYMERS

Bayseç, Şebnem

M. Sc. , Polymer Science and Technology

Supervisor: Prof. Dr. Levent Toppare

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The synthesis , spectroscopic and electrochemical properties of a series of donor-acceptor (DA) type polymers by changing the donor unit (thiophene, dithienopyrrole) polymer backbone were investigated.The synthesized CoP1 and CoP2 were designed to investigate the effect of copolymerization and insertion of perylene tetracarboxylic dimide (PDI) on the structure of benzotriazole (BTz) based polymers. For CoP1 1,7-dibromo-perylene diimide,4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole and 2,5 bis(tributylstannyl)thiophene coupled with Stille Coupling. For CoP2 1,7-dibromo-perylene diimide, 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole 4-dodecyl-2,6-bis(tributylstannyl)-4H dithieno[3,2-b:2',3'-d]pyrrole coupled with Stille Coupling. The resultant donnor acceptor type random copolymer indicated that incorporation of PDI into the structure of BTz based polymers leaded to increase in the n-type properties. CoP1; BTz-Th donor-acceptor based conjugated polymers converted to only n-dopable material. CoP2 ; BTz-DTP donor-acceptor based conjugated polymers converted to ambipolar material.

Keywords : Perylene tetracarboxylic diimide , Donor-Acceptor Random Copolymers, Ambipolar property of PDI , Stille Coupling

ÖZ

PERİLEN İÇEREN KONJUGE KOPOLİMERLERİN SENTEZİ,SPEKTROSKOPİK VE ELEKTROKİMYASAL ÇALIŞMALARI

Bayseç, Şebnem

Yüksek Lisans , Polimer Bilimi ve Teknolojisi

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Polimer zinciri üzerinde donör ünitelerini değiştirerek sentezlenen bir seri donör akseptör (DA) tipi polimerlerin sentezi, spektroskopik ve elektrokimyasal özellikleri incelenmiştir. Sentezlenen CoP1 ve CoP2 polimerleri, kopolimer etkileri ve benzotriazol (BTz) içerikli polimerlerin yapısına perilen tetrakarboksilik diimit (PDI) eklendiğinde gerçekleşen etkileri araştırmak için tasarlanmıştır. CoP1 için 1,7-dibromo-perilen diimit,4,7-dibromo-2-dodesil-2H-benzo[d][1,2,3]triazol ve 2,5 bis(tributilstannil) tiyofen Stille reaksiyonu yoluyla birleştirilmiştir. CoP2 için 1,7-dibromo-perilen diimit, 4,7-dibromo-2-dodesil-2H-benzo[d][1,2,3]triazol 4-dodesil-2,6-bis(tributilstannil)-4H dithieno[3,2-b:2',3'-d]pyrol Stille reaksiyonu yoluyla birleştirilmiştir. Sonuçta elde edilen donör akseptör tipi polimerlerden benzotriazol içerikli polimerlerin n-tipi özelliklerinin arttığı gözlenmiştir. Benzotriazol-tiyofen (BTz-Th) içerikli donör-akseptör tipi konjüge polimeri tamamen n-tipi özellikli madde haline gelmiş , benzotriazol- dithienopyrol (BTz-DTP) içerikli donör-akseptör tipi konjüge polimeri ise iki kutuplu madde haline gelmiştir.

Anahtar Kelimeler : Perilen tetracarboksilik diimit, Donör-Akseptör Rastgele Kopolimer,iki kutup özellikli PDI , Stille Reaksiyonu

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ABBREVIATIONS

ACN	Acetonitrile
BTz	Benzotriazole
CB	Conduction Band
CP	Conducting Polymer
CV	Cyclic Voltammetry
DA	Donor-Acceptor
DCM	Dichloromethane
DTP	Dithienopyrolle
EDOT	3,4-Ethylene dioxythiophene
E_g	Band Gap Energy
GPC	Gel Permeation Chromatography
HOMO	Highest Occupied Molecular Orbital
ITO	Indium Tin Oxide
LUMO	Lowest Unoccupied Molecular Orbital
Mo	Molybdenum
Nb	Niobium
NHE	Normal Hydrogen Electrode
NMR	Nuclear Magnetic Resonance
OFET	Organic Field Effect Transistor
PA	Polyacetylene
PANI	Polyaniline
PEDOT	Poly(3,4-Ethylene dioxythiophene)
PDI	Perylene Diimide
PF	Polyfuran

PPy	Polypyrrole
PTh	Polythiophene
Th	Thiophene
THF	Tetrahydrofuran
Ti	Titanium
V	Vanadium
VB	Valance Band
WO_3	Tungsten trioxide

CHAPTER 1

INTRODUCTION

1.1 Conducting Polymers

Some polymers posses the well-known magnetic and conductive characteristics of metals, yet they are light and flexible high-tech materials and are referred as conducting polymers. It is worth mentioning the exciting story of how the first conductive polymer came into reality when a graduate student in Japan accidentially added excess catalyst to link up the acetylene molecules.The material ended up was a highly conductive polyacetylene.

Metals conduct electricity in form of free electrons travelling under the effect of an electrical potential. Free electrons are not tightly connected to any parent metal molecule in the crystalline structure of the atoms and hence , can travel with little afford .

In 1950s researchers attempted doping conductive ions into nonconductive and organic materials by diffusion at high temperatures. A material like silicon could be doped with positive or negative ions. A positively doped material and a negatively doped material were fused together to make a p-n junction which can be used as a check-valve. A diode , so called , could conduct electricity in one direction and not in the reverse. In Japan first transistor was made by succesively fusing an n-doped material to a p which is reversible process.

Conductive polymers have a different mechanism. They have conjugated double bonds in the molecule and an electron can travel through this delocalization.

The discoverers of this conducting polyacetylene; McDiarmid, Shirakawa and Heeger received the nobel prize in chemistry in year 2000 “for the discovery and development of electrically conductive polymers.”

Further research in the field has led to other conjugated polymers, like polythiophenes, polypyrroles and many others.

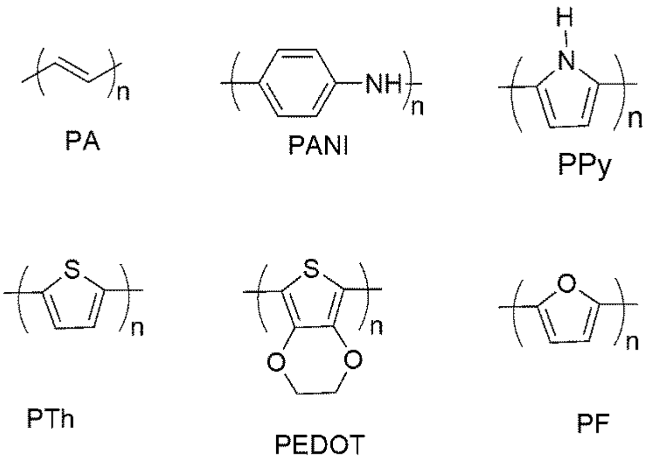


Figure 1.1 Structures of some common conducting polymers

1.2 Electrical conduction of conducting polymers

Four factors are effective to explain the conductivity of conductive polymers.

1.2.1 Band Theory

Solids are classified conductors, semiconducturs and insulators due to their conductivity. Band theory gives an explanation on the differences in electrical properties.

All individual atoms have permitted energy levels for their electrons but for large group of atoms like solids, energy levels are reorganized to form energy bands. In this theory conduction band (CB) and valence band (VB) are considered[1].

The electrons with the lower energy levels occupy the valence band. Valence band is completely filled and separated from conduction band by a large energy gap named as band gap (Eg) for an insulator. In conductors these two bands overlap and electrons easily move to conduction band. In semiconductors there is a smaller band gap between the valence and conduction bands compare to the insulators.

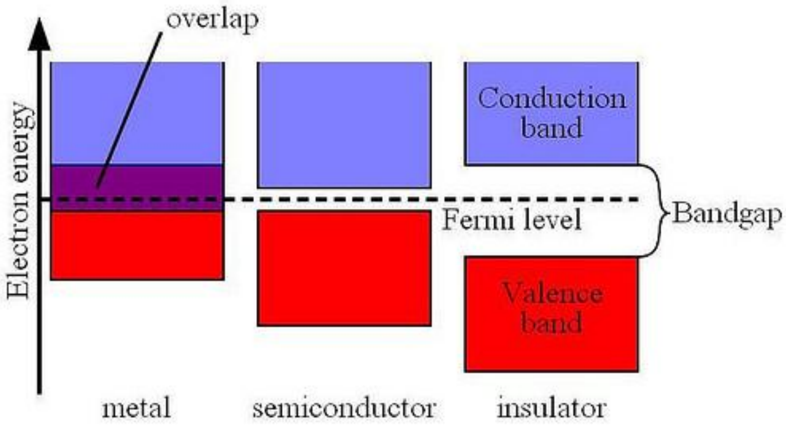


Figure 1.2 Energy band in solids

In order to increase the conductivity of semiconductors, small amounts of doping material can be used. This results in significant increases in conductivity as a result of the narrowing of the gap between the conduction and valence bands.

1.2.2. Charge Carriers

Type of polymer affect the nature of charge carriers in conjugated polymers. The concept of solitons, polarons and bipolarons has been proposed to get a better understanding on the conduction mechanism of CPs[2].

Oxidation or reduction of the polymer breaks the double bond in the polymer backbone, delocalize the polymer and leave a radical cation or anion referred as polaron. Another charge defect is soliton which can be neutral, positively or negatively charged. Charged solitons have no spin , whereas neutral solitons have spin but no charge.The three types of solitons are shown in Fig. 1.3. The positive soliton occurs on polymer chain by the insertion of acceptor band (p-type doping) or electrochemical oxidation, where an electron is removed .The positive soliton is equivalent to stabilized carbonium ion on polymer chain. Negatively charged soliton is produced when an electron is inserted by reduction. The negative soliton is therefore equivalent to stabilized carbanion ion on polymer chain.

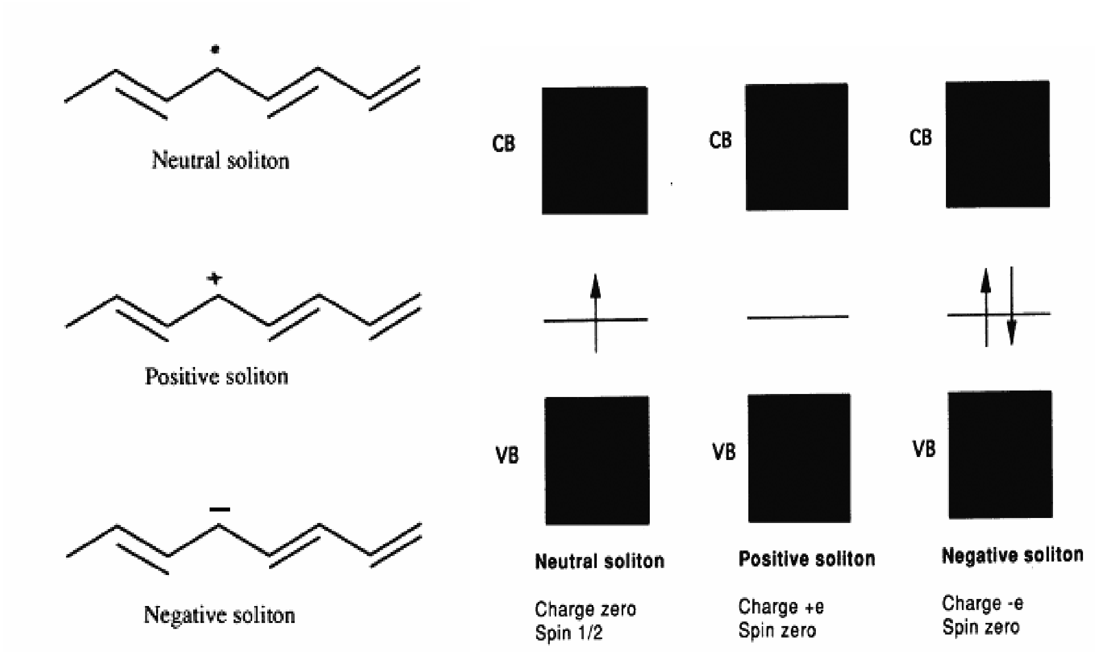


Figure 1.3 Soliton structures of Polyacetylene

Bipolaron occurs if two charged defects are coupled at high doping levels. The neutral polymer has full valence and empty conduction band which are separated by a band gap. When one electron is removed by doping, a polaron band between VB and CB occurs. A second electron removal and generation of bipolarons occur by further oxidation. This process is illustrated in Fig. 1.4.

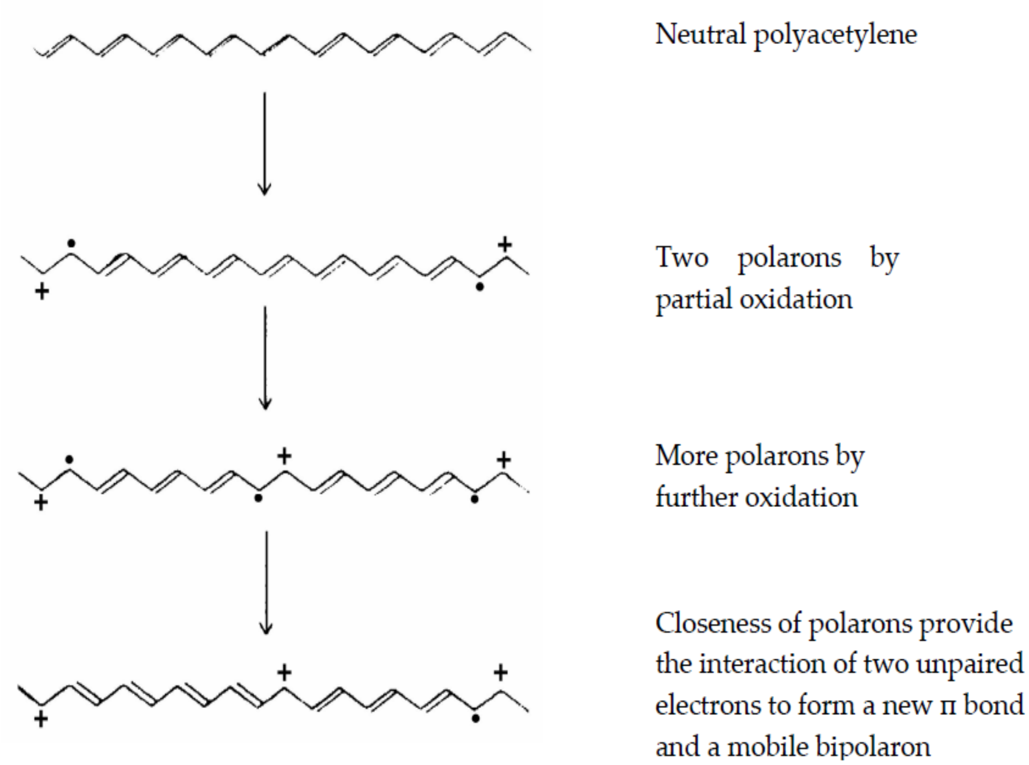


Figure 1.3 a) Formation of polaron and bipolaron in Polyacetylene

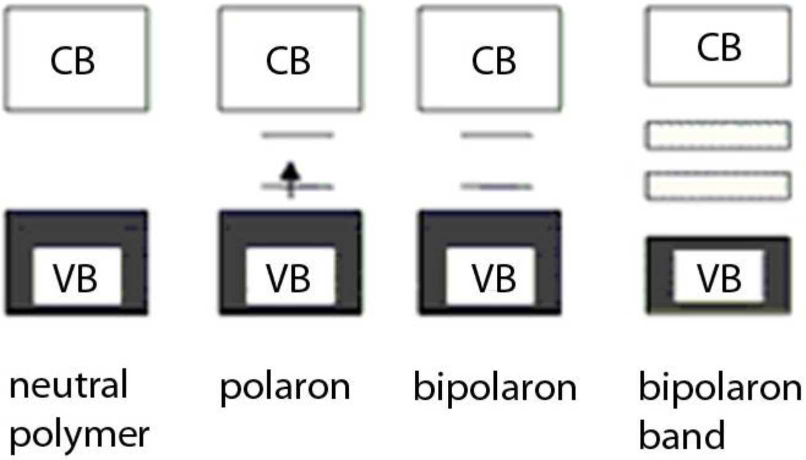


Figure 1.3 b) Band structure of CP as a function of doping level

1.2.3 Doping Process

Doping is defined as the process of changing the conductive properties of polymer by adding trace amounts of impurities. Doping of conducting polymer is done by addition or removal of electrons from CP‘s backbone. The oxidation and reduction is performed by anions or cations named as “dopants” in this process. At this process insulating neutral polymer is converted into an ionic complex and polymer is partially oxidized or reduced. The partial oxidation of the polymer chain is named as p-doping (Fig.1.4) and partially reduction of polymer chain is named as n-doping[3].

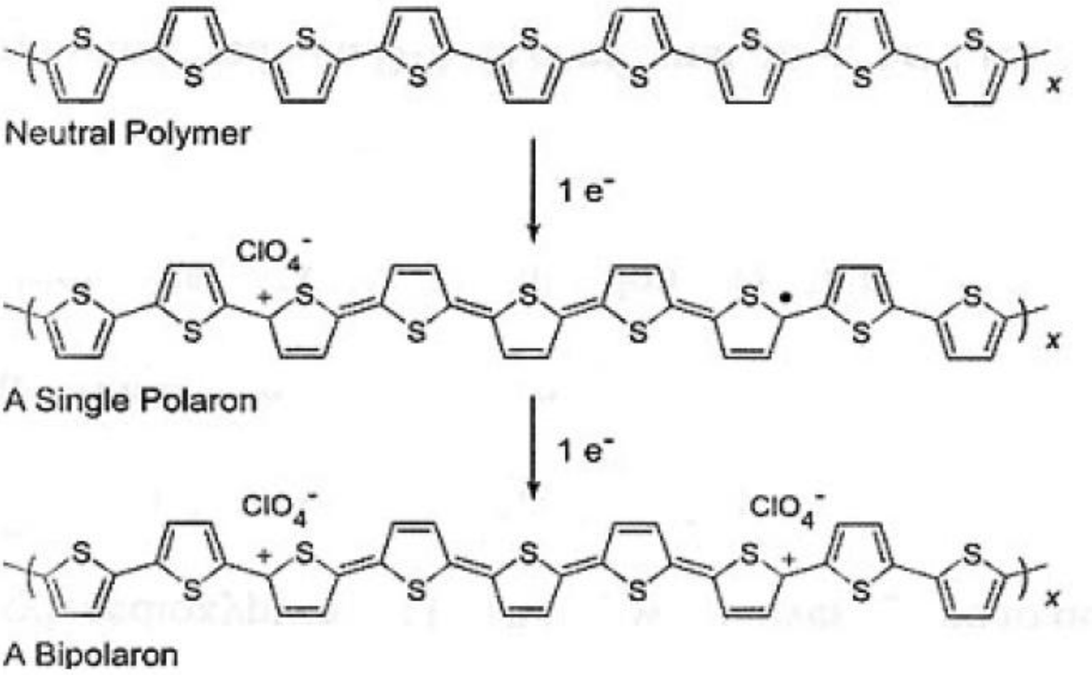


Figure1.4 p-type doping of polythiophene

Doping and de-doping processes can be carried out both by chemically or electrochemically [4].

“Chemical doping involves charge-transfer redox chemistry:

(a) Oxidation (p-type doping)
$(\pi\text{-polymer})_n + 3/2\ ny\ (I_2) \longrightarrow [(\pi\text{-polymer})^{+y}\ (I3^-)_y]_n$
(b) Reduction (n-type doping)
$(\pi\text{-polymer})_n + [Na^+\ (\text{Napthtalide})^-]_y \longrightarrow [(Na^+)_y\ (\pi\text{-polymer})^{-y}]_n + (\text{Naphth})^0$ [4]”

Due to the difficulty in controlling the process and inhomogeneous doping; electrochemical doping is preferred. It is easy to reduce or oxidize the polymer by applying potential.

Electrochemical doping is illustrated by the following examples:

(a) p- type

$$\text{(poly)n+ ny [Li+(BF4-)(sol'n)]} \xrightleftharpoons[\text{Reduction}]{\text{Oxidation}} \text{[(poly)+y (BF4-)y]n+ nyLi(elec'd)}$$

(b) n-type

$$\text{(poly)n+ ny Li(elec'd)} \xrightleftharpoons[\text{Reduction}]{\text{Oxidation}} \text{[(Li+)y(poly)-y]n + n y [Li+(BF4-)] (sol'n)}$$

Doping at any level can be fulfilled by setting the electrochemical cell at a fixed applied voltage and simply waiting for the system to come to electrochemical equilibrium [5].

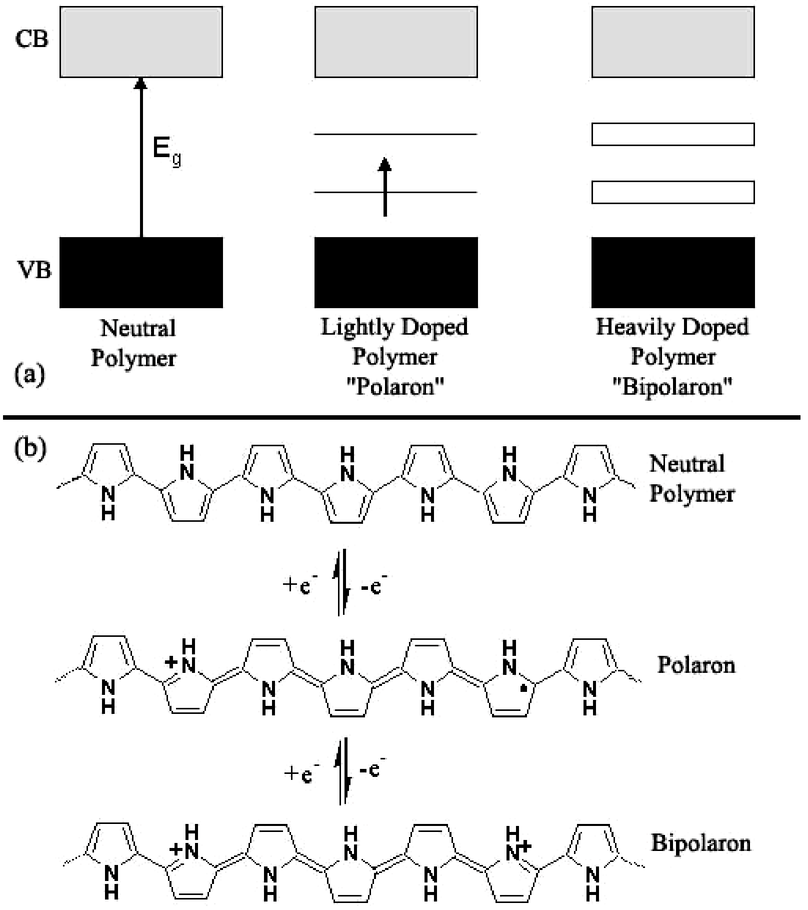


Figure 1.5 Charge carries in PPy and its corresponding energy bands in the mid gap

1.2.4 Hopping Process

In the theory of hopping, charge movements between polymer chains are taken into account. In this mechanism ionic charges occur on the polymer chain which can travel through one molecule to another[6].

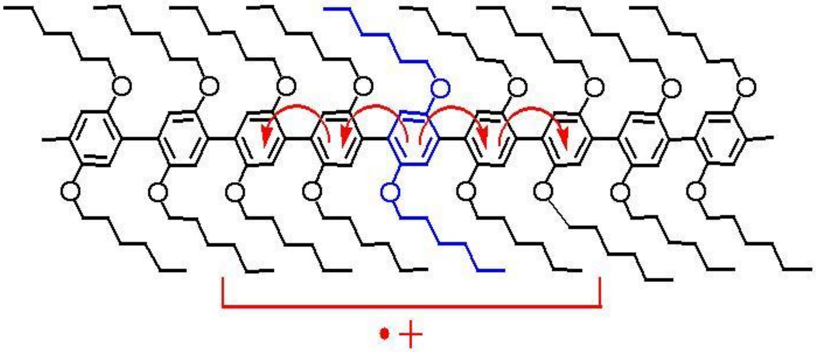


Figure 1.6 The hopping mechanism in poly(p-hydroquinone ethers) [7]

1.3 Synthesis of Conducting Polymers

Chemical and electrochemical polymerizations are main polymerization methods for synthesis of conducting polymers. There are other techniques used for synthesize conducting polymers which are photochemical polymerization, metathesis polymerization, plasma, pyrolysis, solid state polymerizations[7].

1.3.1 Chemical Polymerization

In chemical polymerization addition and condensation polymerizations are the main polymerization methods. For addition polymerization monomers with conjugated double bonds react to form long chain polymer with the use of appropriate catalysts[8]. For condensation polymerization bifunctional monomers react to form polymers[9].

Chemical synthesis provides mass production at low cost. However, products are generally in powder form decreasing the intrinsic properties of the materials such as low conductivity. Also there are side reactions that may affect the polymer backbone.

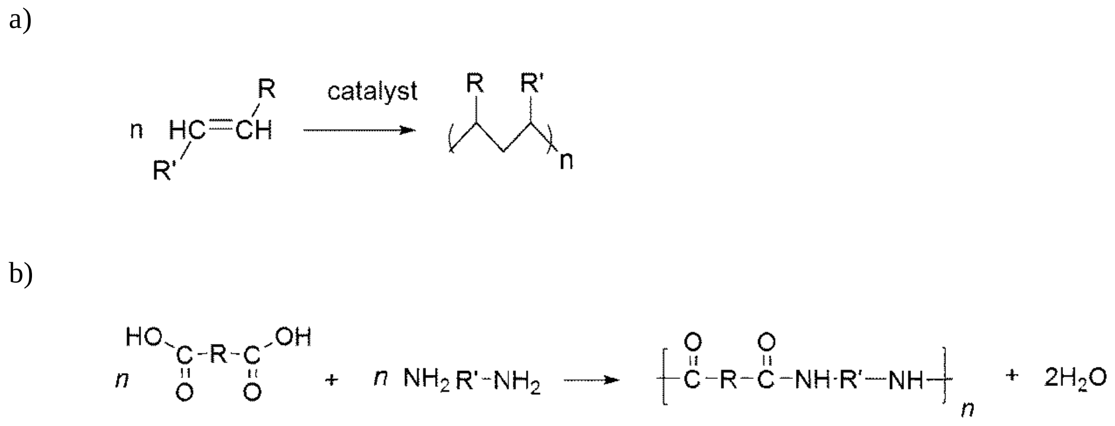


Figure1.7 a) Synthetic routes of addition polymerization **b)** Condensation polymerization of a diacid and a diamine

1.3.2 Electrochemical Polymerization

Electrochemical polymerization is a convenient technique that allows synthesis of desired polymer on an electrode surface which provides to study optical and electrochemical properties of polymers. Also this technique allows controlling the film thickness. The major disadvantage of this technique is that low quantities of polymers are produced. Also these polymers are insoluble, hence cannot be characterized via NMR and GPC[10].

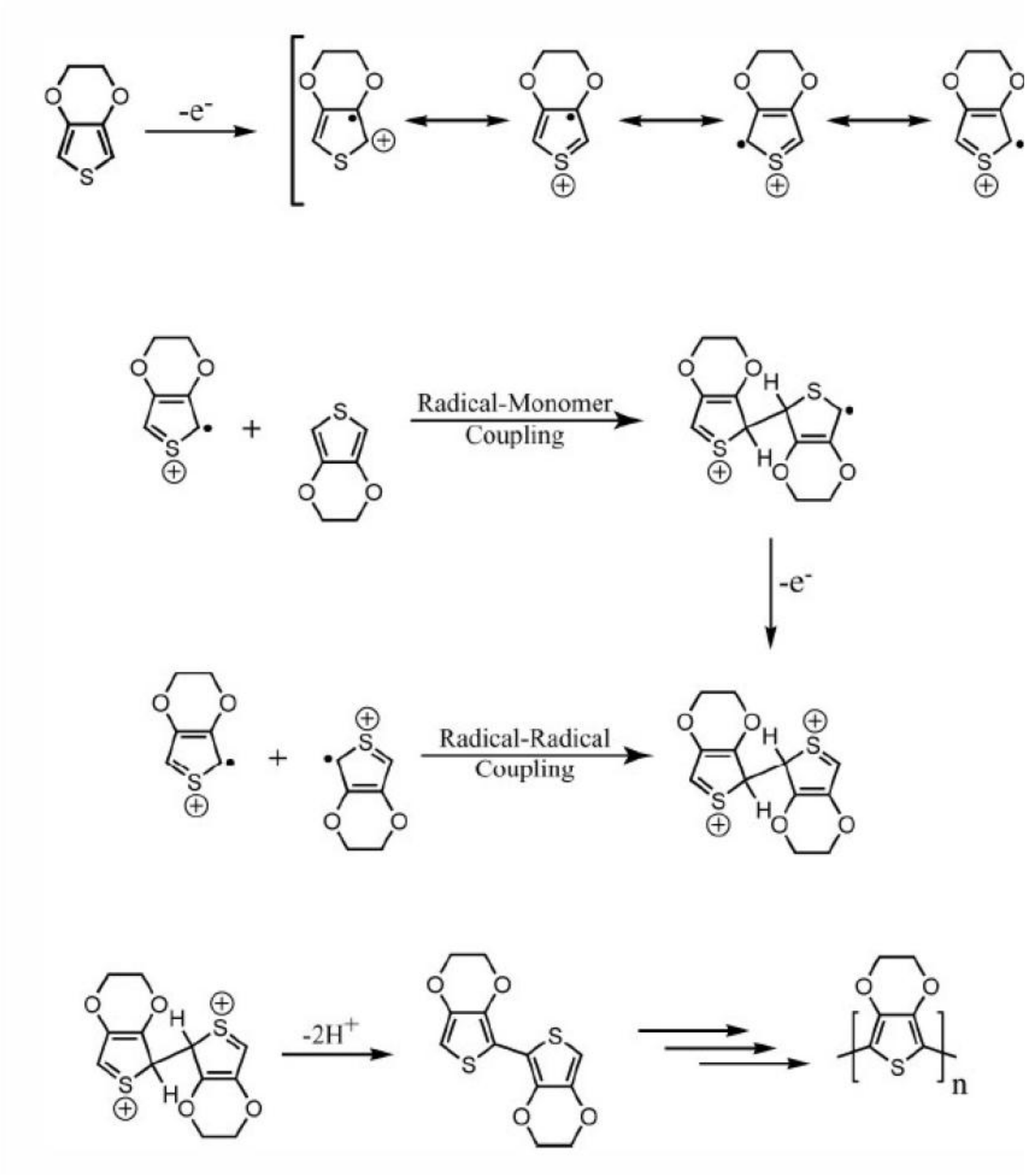


Figure 1.8 Electrochemical polymerization mechanism of EDOT

1.4 Characterization of Conducting Polymers

There are many techniques to characterize conducting polymers. For instance; cyclic voltammetry is used for understanding reduction-oxidation behavior. Also from this technique electronic HOMO-LUMO values are calculated, optoelectronic characterization of π to π^* transitions can be done. Nuclear magnetic resonance is used (NMR) to confirm the structure. Thermogravimetry analysis (TGA) , differential scanning calorimetry (DSC) and gel permeation chromatography are utilized for further characterization.

1.5 Electrochromism

An electroactive material shows new optical absorption band due to oxidation or reduction. Such coloration was first termed as ‘‘electrochromism’’ in 1961 by Platt.

Many chemical species like Viologens transition metal oxides[11], most famously tungsten trioxide (WO_3) systems[12-14] , prussian blue systems[15] , oxides of V, Mo, Nb,and Ti (cathodically coloring), phthalocyanines[16,17] and conducting polymers posses electrochromic properties.

Electrochromism in conjugated polymers occurs through changes in the conjugated polymer’s π-electronic character due to electrochemical oxidation and reduction. In their neutral state conjugated polymers show semiconductor behavior. When electrochemical doping is applied (p-doping or n-doping), the band gap is modified producing several energy levels between HOMO and LUMO. Polarons and bipolarons are generated which are responsible for high conductivity and optical changes[18].

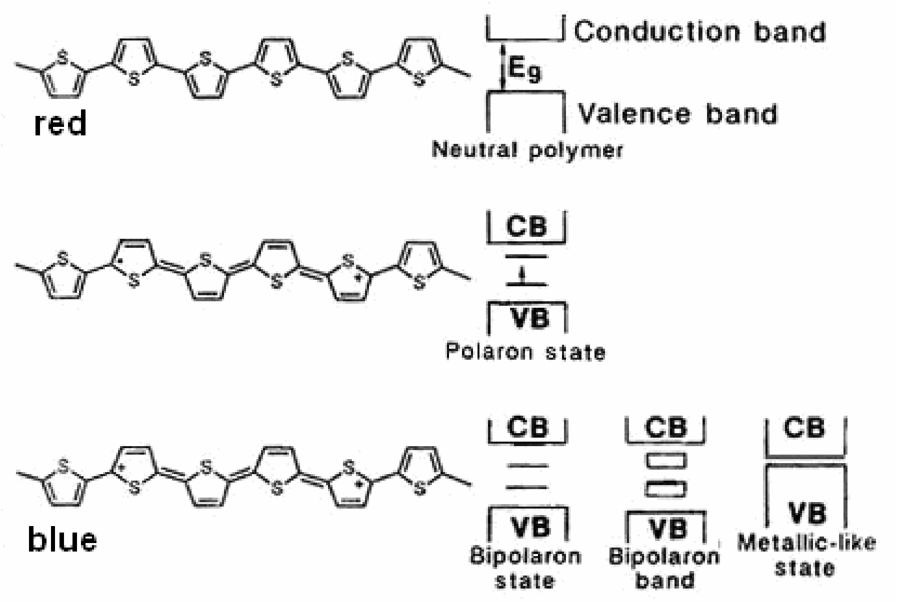
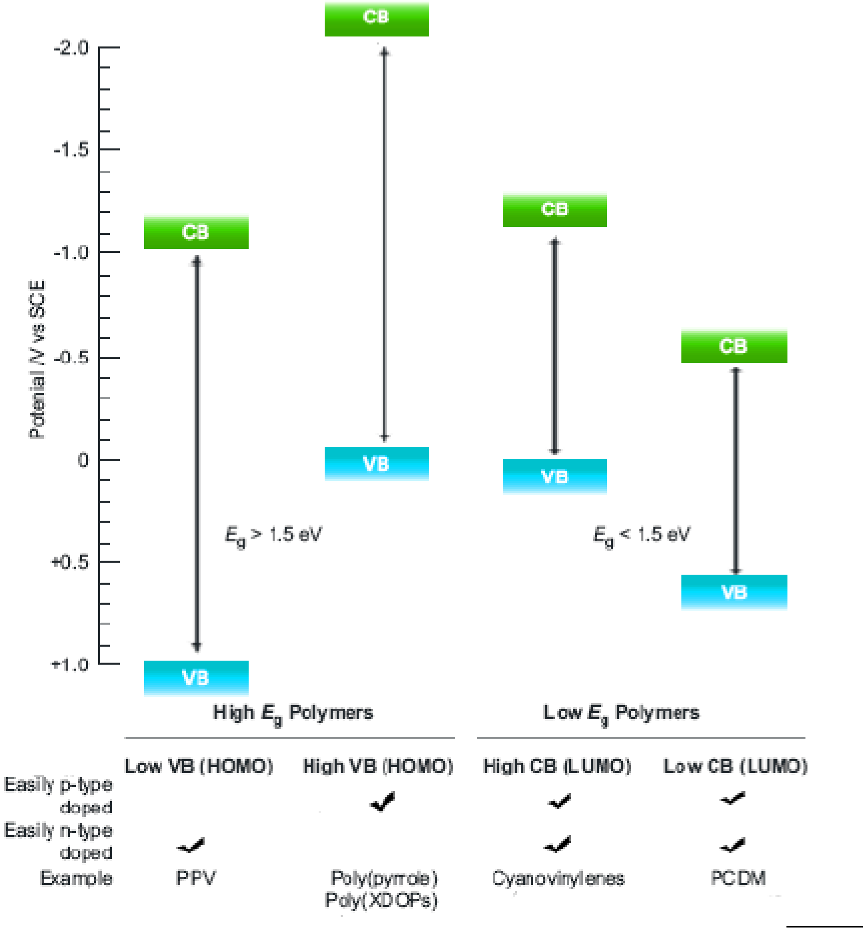


Figure 1.9 Evolution of electrochromic band structure

As seen from Figure 1.9 accessible color states can be obtained by band gap control. Primarily band gap tuning is achieved by chain and pedant group modification. Introducing of electron donating moieties into chain causes an increase in the HOMO energy together with a decrease in the oxidation potential of polymer.

1.6 Low Band Gap Systems

π -conjugated polymers composed of donor-acceptor moieties are designed to obtain small band gap which can facilitate charge transfer between HOMO and LUMO. Facilitating charge transfer between energy levels increased the conductivity of CPs. Besides this low band gap provides easy doping of polymer and stability at doped states compared to neutral forms[19]. Polymers having band gap values higher than 2 eV are called mid to high band gap polymers. Polymers are considered relatively low band gap materials that have band gap value lower than 1.5 eV.



	High E_g Polymers		Low E_g Polymers	
	Low VB (HOMO)	High VB (HOMO)	High CB (LUMO)	Low CB (LUMO)
Easily p-type doped		✓	✓	✓
Easily n-type doped	✓		✓	✓
Example	PPV	Poly(pyrrole) Poly(XDOPs)	Cyanovinylenes	PCDM

Figure 1.10 Possibilities for positioning of band edges in both high and low band gap polymers**.**

1.7 Donor-Acceptor Theory

Modification of band gaps can be done by several methods like planarity control, interchain effects, bond lenth alternation, resonance effects and donor-acceptor approach. The main effect that our interest is donor-acceptor approach. This theory is based on the coupling of donor and acceptor units. Hence, in this theory monomer structure can be modified. Here polymers have an ionization potential close to that of donor and an electron affinity close to that of the acceptor due to the hybridization between the highest state of the HOMO level of the donor with the lowest state of the LUMO level of the acceptor[20,21].

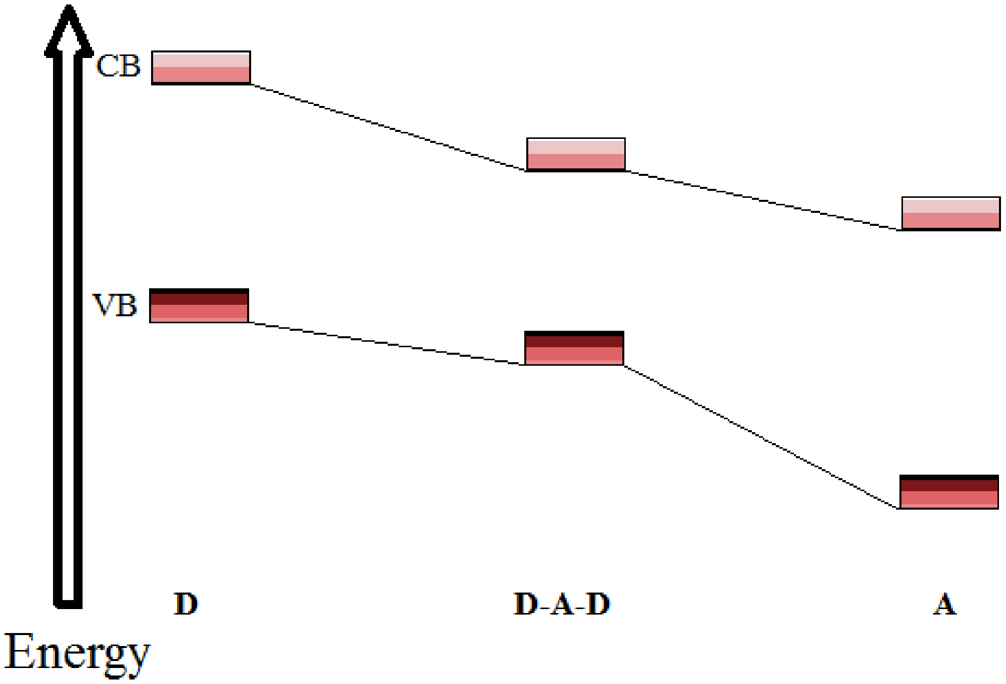


Figure 1.11 Donor-Acceptor Theory

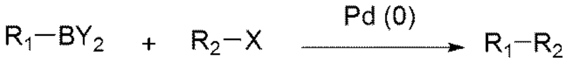
1.8 Synthetic methods for D-A type materials

For the synthesis of D-A-D (donor-acceptor-donor) type materials there are mainly three types of coupling reactions; Negishi Coupling, Suzuki Coupling and Stille Coupling. They are palladium catalyzed cross coupling reactions. In case of Negishi coupling an organozinc compound reacts with an organic halide in the presence of nickel or palladium as the catalyst and produces covalently bonded carbon-carbon bond[22,23]. The coupling reaction is illustrated in Figure 1.12

$$RX + R'ZnX \xrightarrow{Pd\ (0)} R-R'$$

Figure1.12 Representation of Negishi Coupling

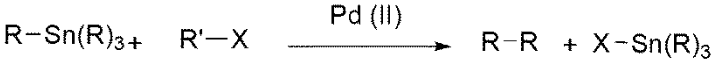
In case of Suzuki coupling an aryl or vinyl- boronic acids reacts with an aryl- or vinyl- halide catalyzed by a palladium (0) complexes. This coupling reactions is used to synthesize poly- olefins, poly-styrenes and substituted biphenyls[24-26]. The coupling reaction is illustrated in Figure 1.13



$$R_1{-}BY_2 \quad + \quad R_2{-}X \xrightarrow{\text{Pd (0)}} R_1{-}R_2$$

Figure 1.13 Representation of Suzuki Coupling

Stille Coupling reaction takes place between an organotin compound with sp^2 hybridized organic halide catalyzed by palladium.



$$R{-}Sn(R)_3 + \quad R'{-}X \xrightarrow{\text{Pd (II)}} R{-}R \; + \; X{-}Sn(R)_3$$

Figure 1.14 Representation of Stille Coupling

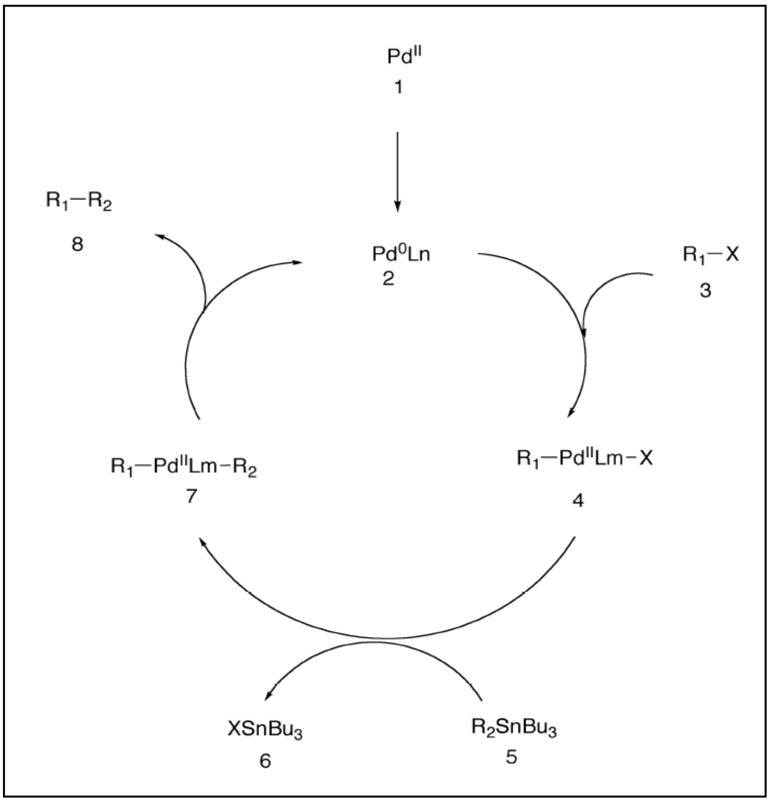


Figure 1.15 Catalytical cycle in Stille Coupling reaction

As given in figure 1.15 the reaction mechanism of Stille coupling reaction starts with the reduction of the catalyst from Pd(II) to active Pd (0) (1→ 2). The oxidative addition of the organohalide (3) gives a cis intermediate which rapidly isomerizes to the trans intermediate 4. Transfer of ligand reaction with organostannane (5) takes place and forms intermediate 7. After reductive elimination the desired product 8 is obtained.

1.9 As n-type material: Perylene diimide derivatives

Perylene molecule (Figure 1.16a) have been known for nearly 100 years when Kardos found a way to synthesize perylene dimides in the beginning of 1910s. Perylene derivatives have been used as commercial products and they are still recognized as an important class of high-performance pigments[27].

In this study a perylene diimide (Figure 1.16b) derivative was used. Perylene diimides (PDI) have a strong absorption in the visible region and have high termal and photochemical stabilities[28,29]. PDI are described as n-type semiconductor and also features relatively low reduction potential which enables their use as electron acceptors for organic electronics and in other related research[30,31].

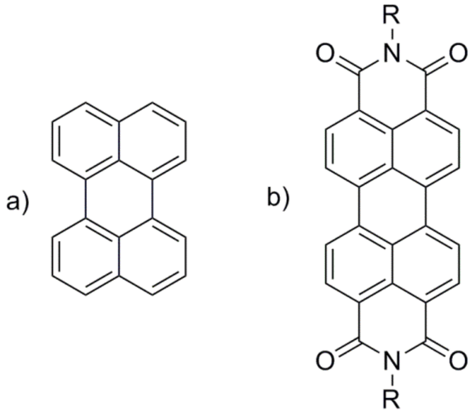


Figure 1.16 a)structure of perylene b) structure of Perylene-3,4,9,10-tetracarboxylic diimide

1.10 Aim of work

Perylene tetracarboxylic diimide (PDI) is one of the n-type organic semiconductor. This semiconductor has strong π-π molecular interaction and strong electron accepting ability. Although there are lots of studies conducted on optoelectronic application, electrochromic studies of the PDI based polymer was rarely studied. Most PDI based polymers exhibited n-type properties as expected. P-dopable PDI containing conjugated polymers were rarely observed due to the high oxidation potential of the resulting polymers . Therefore synthesis of ambipolar PDI based conjugated polymers is the aim of this project. With this motivation PDI coupled with different donor moities to investigate optical and electronic property changes.

CHAPTER 2

EXPERIMENTAL

2.1 Materials and Methods

All chemicals and solvents to synthesize random copolymers CoP1 and CoP2 were purchased from commercially available sources. Tetrahydrofuran (THF) was dried with benzophenone and sodium. Benzotriazole (Sigma-Aldrich), Bromine (Br_2) (Sigma-Aldrich), Hydrobromic acid (HBr, 47 %) (Merck), Sodium borohydride ($NaBH_4$) (Sigma-Aldrich), Thiophene (Th) (Sigma-Aldrich), 1-Bromododecane (Sigma-Aldrich), Potassium *tert*-butoxide ($K^+(OtBu)^-$) (Sigma-Aldrich), Perylene-3,4,9,10-tetracarboxylic dianhydride (Sigma-Aldrich), Imidazole (Fluka A.G. Buchs), Dihexyl ketone (Sigma-Aldrich), Ammonium acetate (NH_4OAc) (Merck), Sodium cyanoborohydride ($NaBH_3OAc$), 3,3′-bibromo-2,2′-bithiophene (Sigma-Aldrich), 2,2′ bis(diphenylphosphino)- 1,1′-binaphtyl (BINAP) (Sigma-Aldrich), Sodium *tert*-butoxide (NaOtBu) (Sigma-Aldrich), Tris(dibenzylideneacetone) dipalladium (0) (Pd_2dba_3) (Sigma-Aldrich), Bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl$) (Sigma-Aldrich), n-Butyllithium (n-BuLi) (Acros) , Tributyl tinchloride ($SnBu_3Cl$) (Sigma-Aldrich),Ethanol (EtOH) (Sigma-Aldrich), Methanol (MeOH) (Sigma-Aldrich), Dichloromethane (DCM) (Sigma-Aldrich), Hexane (Sigma-Aldrich), Petroleum ether (Merck), Ethyl acetate (Sigma-Aldrich), Toluene (Sigma-Aldrich) were used as received. “4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole [32]”, “2,5 bis(tributylstannyl)thiophene [33]”, “4-dodecyl-2,6-bis(tributylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole [34-36]” and “1,7-dibromo-perylene dianhydride [37]” were synthesized with previously described procedures.

2.2 Equipment

Structures of monomers and polymers were analyzed with NMR. ^1H and ^{13}C NMR were recorded on Bruker Spectrospin Avance DPX-400 Spectrometer with TMS as internal standard. Thermal properties of polymers were analyzed by thermal gravimetric analysis technique (TGA) which is Perkin Elmer Pyris 6 TGA. Polymers are heated from 30 ^oC to 750 ^oC at 10 ^oC/min under nitrogen atmosphere. Molecular weights of polymers were determined by gel permeation chromatography (GPC) which is GPC220. Polystyrene was used as standard and THF was used as the solvent. For electrochemical studies , Voltalab 50 potentiostat in a three electrode system were used. Indium tin oxide (ITO) coated glass was used as the working electrode, Ag wire was used as the pseudo reference electrode (Fc/Fc$^+$ (0.3V)) and Pt wire used as counter electrode. The electrolytes were 0.1 M $NaClO_4$-$LiClO_4$ in acetonitrile (ACN) . Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated by taking normal hydrogen electrode (NHE) values as -4.75 eV. Spectroelectrochemical studies were performed by Varian Cary 5000 UV-Vis spectrophotometer. Colorimetry studies performed with Minolta CS-100 spectrophotometer [38].

2.3 Procedure

2.3.1 Synthesis of random copolymers

All reagents were commercially available and used without further purification. CoP1 and CoP2 consist of "4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole [32]", "1,7-dibromo-perylene dianhydride [37]" for both polymer and "2,5 bis(tributylstannyl)thiophene [33]" for CoP1, "4-dodecyl-2,6-bis(tributylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole [34-36]" for CoP2.

2.3.1.1 Synthesis of "2-dodecyl-2H-benzo [d][1,2,3] triazole"

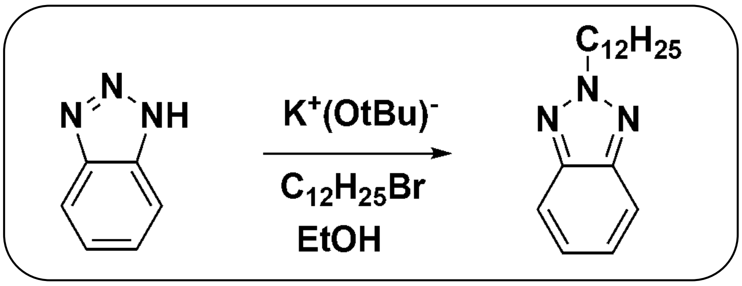


Figure 2.1 Synthesis of 2-dodecyl-2H-benzo [d][1,2,3] triazole

Benzotriazole (5.0 g , 42mmol) , methanol (50 ml) and potassium *tert*-butoxide (5.0 g , 44 mmol) , 1-bromododecane (12.2 g , 49 mmol) were refluxed for 12 hour in a three- neck round bottom flask. After the reaction was finished, methanol was evaporated under reduced pressure. Then extracted with chloroform and water. The organic residue was dried with Mg_2SO_4 , filtered and solvent (chloroform) was evaporated. The product was purified by column chromatography over silica gel 3:2 (chloroform : hexane). The final product obtained as in figure2.1 with colorless oil with yield 30%. The product solidified in fridge after waiting for 12 hours. ^1H (400 MHz, $CDCl_3$, δ): 7.86 (d, 2H) , 7.35 (d, 2H) , 4.71 (m, 1H) , 2.10 (m, 2H), 1.3-1.2 (m , 18H) , 0.87 (m, 3H).

2.3.1.2 Synthesis of "4,7-dibromo-2-dodecyl- 2H- benzo [d] [1,2,3] triazole"

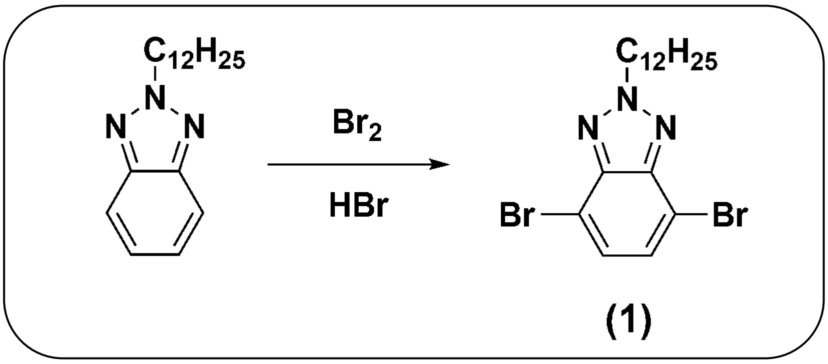


Figure 2.2 Synthesis of 4,7-dibromo-2-dodecyl- 2H- benzo [d] [1,2,3] triazole

" 2-Dodecyl-2H-benzo [d][1,2,3] triazole" (3.7g ,13.1 mmol) was dissolved in 47% HBr (5.8 M , 15ml) and mixture stirred 1 hour at 100 °C. After 1 hour bromine (Br_2) (5.9 g , 36 mmol) was added in mixture and heated for 12 hour at 135 °C .After 12 hour , the reaction mixture was cooled to room temperature. Aqueous solution of $NaHCO_3$ was added and the product was extracted with chloroform ($CHCl_3$) . The organic layer dried with Mg_2SO_4 , filtered and solvent (chloroform) was evaporated under reduced pressure. The crude product was purified by column chromatography with silica gel 1:1(chloroform : hexane). The final product obtained as in figure 2.2 with light yellow oil in yield 70% . ^1H (400 MHz, $CDCl_3$, δ): 7.37 (s, 2H) , 4.70 (m, 2H) , 2.06 (m, 2H) , 1.18 (m, 18H), 0.81(m , 3H) .

2.3.1.3 Synthesis of “1-hexylheptyl amine”

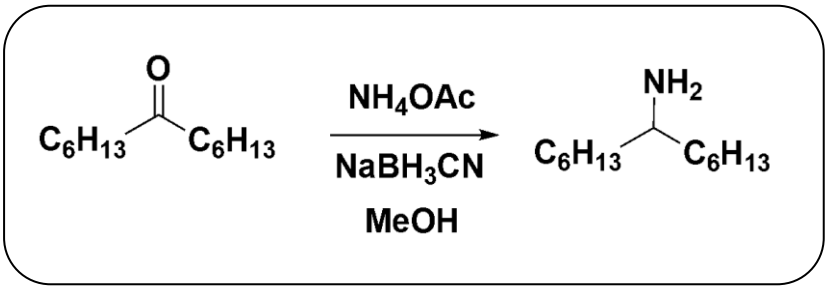


Figure 2.3 Synthesis of 1-hexylheptyl amine

Dihexyl ketone (2 g, 10.08 mmol) , ammonium acetate (8 g , 103.7 mmol) , sodium cyanoborohydride (0.45 g , 7.16mmol) and 30 ml methanol was mixed in a round-bottom flask. The reaction continued 56 hour. After that ; fuming HCl was added. While HCl was adding white particles occured and precipitated. Then solvent (methanol) was removed under reduced pressure. At the same time 200 ml distilled water and KOH was mixed. The crude product was dissolved in distilled water and KOH solution was added in to obtain pH =10 . The pH was controlled by indicator strip. After pH of product was stabilized , extraction was done with chloroform ($CHCl_3$)and water. The pure product was obtained after solvent (chloroform) evaporation as in figure 2.3 white solid. . ^1H (400 MHz, $CDCl_3$, δ): 2.55-2.65 (m, 1H), 1.15-2.28 (m,20H), 0.81 (t, 6H) 13C NMR (100 MHz , CDCl3) δ 51.2 , 38.1 , 31.8 ,29.4,26.1 , 22.6.

2.3.1.4 Synthesis of " N,N'- Bis(1-hexylheptyl)-perylene-3,4,9,10-bis(dicarboximide) "

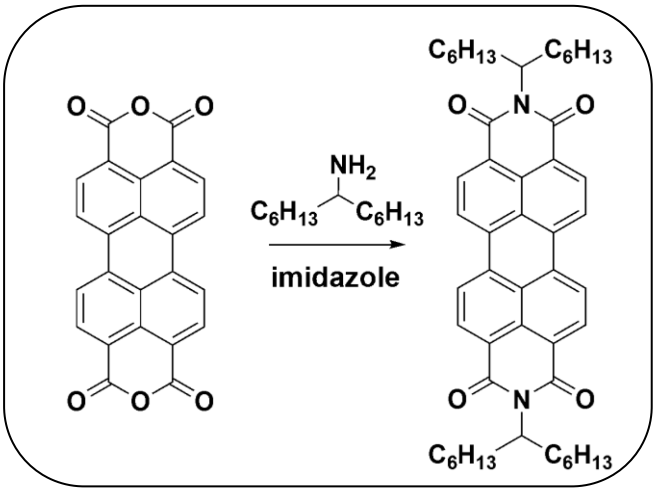


Figure 2.4 Synthesis of N,N'- Bis(1-hexylheptyl)-perylene-3,4,9,10-bis(dicarboximide)

Perylene-3,4,9,10-tetracarboxylic dianhydride (0.78 g , 2mmol) , 1-hexylhetylamine (1g , 5mmol) and imidazole (4 g , 58.7 mmol) was refluxed overnight at 120 ^{o}C under argon gas. The crude product was purified by column chromatography over silica gel with ethyl acetate. The product obtained as in figure 2.4 red solid.

2.3.1.5 Synthesis of “1,7-dibromo-N,N’-Bis(1-hexylheptyl)-perylene-3,4,9,10-bis(dicarboximide)”

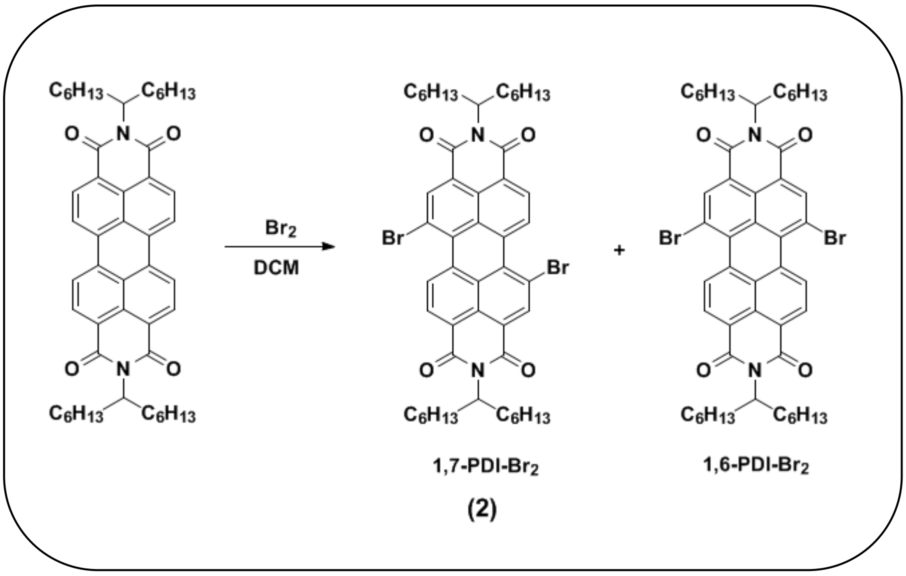
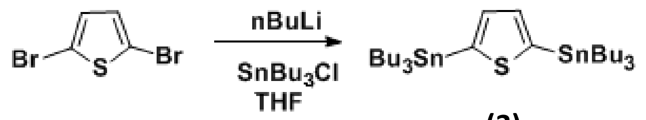


Figure 2.5 Synthesis of 1,7-dibromo-N,N’-Bis(1-hexylheptyl)-perylene-3,4,9,10-bis(dicarboximide)

In a reaction vessel imidized perylene 10 g and 30 ml DCM solution was prepared. After that 27 ml bromine was added. The reaction was refluxed for 96 hour to increase the double-sided bromination. After 96 hour excess bromine was removed by air bubbling and solvents removed under reduced vacuum. Column chromatography was done to purify the residue with silica gel , eluted with dichloromethane (DCM) / petroleum ether(PE) (1:3 to 1:1 v/v). 1,6 and 1,7-PDI-Br_2 which was regio-isomeric mixture was obtained after column chromatography. To seperate them recrystallization was done with THF and MeOH mixture solution(THF:MeOH = 1:3 ,v:v). After recrystallization 1,7- PDI- Br_2 was obtained as insoluble residue in solution. 1H NMR (CDCl3, 400 MHz, ppm) δ: 9.42 (d, J=8.1 Hz,2H), 8.84 (br s,2H), 8.56-8.67 (br m, 2H) 5.09 (m, 2H), 2.11-2.22 (m, 4H), 1.75-1.82 (m, 4H), 1.11-1.21(m, 32H), 0.75 (t,J=7.09 Hz, 12H). 13C NMR (CDCl3, 100 MHz, ppm) δ: 129.3, 128.4, 127.2, 120.7, 55,32.3, 31.8, 29.2, 26.9, 22.6.

2.3.1.6 Synthesis of “2,5-tributylstannilated thiophene”



(3)

Figure2.6 Synthesis of 2,5-tributylstannilated thiophene

2,5-dibromo thiophene and THF which was dried with Na and benzophenone placed in 200 ml flask.The reaction vessel was placed in isoterm and temperature lower to -78^{o}C with dry ice. n-BuLi is added dropwise and the solution stirred at -78^{o}C for 1 hour.$SnBu_3Cl$ was added in one portion then the mixture was allowed to room temperature slowly and stirred for 24 hour. After 24 hour, the mixture was poured into 100 ml of cool water and extracted by hexane.The crude product dried by Mg_2SO_4 and filtered. The final product was obtained as figure 2.6 yellow-brown liquid after evaporation of solvent (chloroform) under reduced presure. 1H NMR (400 MHz, CDCl3, ppm) δ : 7.27 (s, 2H), 1.57 (m, 12H), 1.27 (m, 12H), 1.22 (m, 12H), 0.85 (m, 18H). 13C NMR (100 MHz , CDCl3) δ 140.6 ,134.7 ,28.0 ,26.8, 26.3, 25.8 , 16.5 , 12.6 , 12.5 , 9.86.

2.3.1.7 Synthesis of “4-dodecyl-4H-dithieno[3,2-b:2′,3′-d] pyrrole”

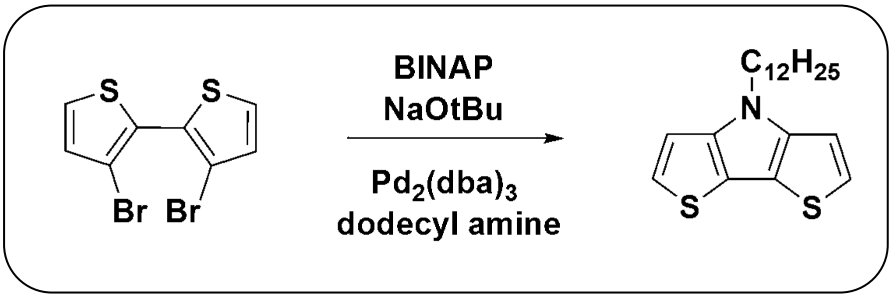


Figure 2.7 Synthesis of 4-dodecyl-4H-dithieno[3,2-b:2′,3′-d] pyrrole

3,3′-Dibromo-2,2′-bithiophene (1.95 g , 6 mmol) , sodium *tert*-butoxide (NaOtBu , 1.1g,11.4mmol) , Tris(dibenzylideneacetone)dipalladium (0) (Pd_2dba_3 , 0.16 g , 0.18 mmol) and 2,2′ bis(diphenylphosphino)- 1,1′-binaphtyl (BINAP , 0.45 g , 0.72 mmol) were dissolved in dry toluene (20ml) under argon gas . Dodecyl amine (0.91 g , 4.87 mmol) was added to mixture and reaction takes place under argon gas at 110 ^oC for 12 hour. The product is extracted with ethyl acetate and distilled water. The organic layer dried with Mg_2SO_4 and filtered then solvent is evaporated under reduced pressure. The crude product was purified by column chromatography with silica gel , 2:1 (dichloromethane and hexane). The product obtained as figure 2.7 white solid with 80% yield. ^{1}H NMR(400 MHz, $CDCl_3$, δ) 6.95 (d, J=5.33 Hz, 2H), 6.83 (d, J= 5.29 Hz , 2H), 3.99 (t, J= 7.03 Hz, 2H), 1.64- 1.74 (m,2H), 1.07-1.21 (m, 18H), 0.78 (t, J=7.07 Hz, 2H) ^{13}CNMR (100 MHz , CDCl3) δ 143.8, 121.6, 109.8, 46.3, 30.8, 29.3, 28.6, 28.5, 28.4, 28.3, 28.2, 25.9, 21.6

2.3.1.8 Synthesis of “4- dodecyl-2,6-bis(tributylstannyl)-4H-dithieno [3,2-b:2′,3′-d]pyrrole”

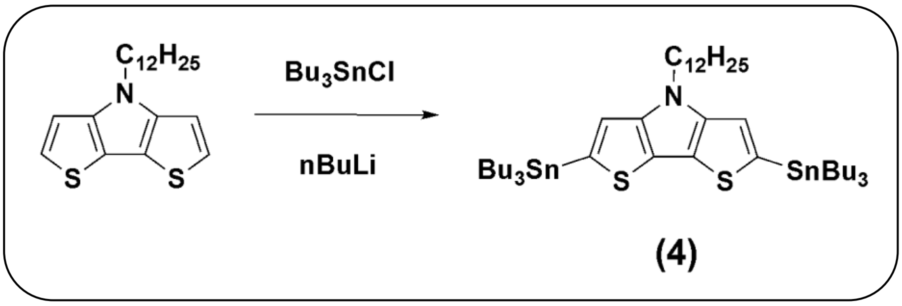


Figure 2.8 Synthesis of 4-dodecyl-2,6-bis(tributylstannyl)-4H-dithieno [3,2-b:2′,3′-d]pyrrole

4-Dodecyl-4H-dithieno[3,2-b:2′,3′-d] pyrrole (3mmol, 0.8g) was dissoled in dry THF and cooled to -78 ^oC under argon gas. n-BuLi (7.5mmol , 4.4ml) was added dropwise and the mixture was stirred for 1 hour then slowly warmed to room temperature. Then reaction was cooled -78^{o}C again and Bu_3SnCl (7.5 mmol, 7.5 ml) was added in one portion. The reaction mixture stirred overnight at room temperature. The product was extracted with chloroform and distilled water , dried by Mg_2SO_4 and filtered. The final product was obtained as figure 2.8 brown liquid with 88% yield. after evaporation of solvent (chloroform) under reduced presure. 1H NMR (CDCl3, 400 MHz, ppm) δ: 6.88 (s, 2H), 4.13 (t, J= 6.97 Hz, 2H), 1.57 (m, 12H), 1.27 (m, 12H), 1.20 (m, 12H), 0.85 (m, 18H).^{13}CNMR (100 MHz , CDCl3) δ 146.9 , 121.2,117.06 , 109.99,46.39 , 28.01 , 26.87 , 25.89 , 16.46, 12.60 , 9.9.

2.3.1.9 Synthesis of copolymer 1 (CoP1)

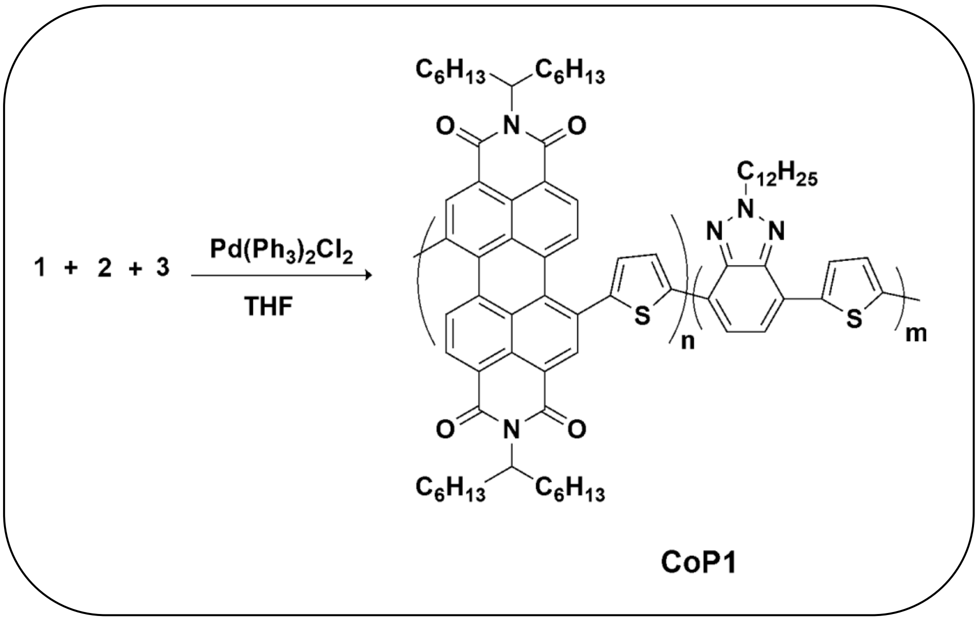


Figure 2.9 Synthesis of copolymer 1 (CoP1)

Equivalent number of moles of 1,7-dibromo-perylene diimide (0.88 g , 0.966 mmol) , 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole (0.43 g , 0.966 mmol) and twice equivalent number of mole of 2,5-bis(tributylstannyl)thiophene (1.28 g , 1.932 mmol) were mixed in dry THF (50ml) in the presence of $Pd(PPh_3)_2Cl_2$ (0.15 g) under argon atmosphere. The reaction mixture refluxed for 4 days. Tributyl(thiophen-2-yl)stannane and bromobenzene were added as an end capper and refluxed for 2 days. The reaction ended and the solvent is removed under vacuum.Polymer is washed methanol and soxhlet extraction was done by methanol , hexane and acetone respectively to remove the short chain oligomers and remnant catalyst.Lastly polymer was taken from filter by chloroform and dried under reduced pressure. CoP1 was obtained as dark purple solid with a yield of 15%. Gel permeation chromatography (GPC) ; number average molecular weight (Mn):12000 g mol^{-1}, weight average molecular weight (Mw): 27000 g mol^{-1} , polydispersity index (PDI): 2.2 . 1H NMR (CDCl3, 500 MHz, ppm) δ: 8.66, 8.31, 8.41, 7.65, 7.63, 7.32, 7.31(BTZ, PDI, thiophene), 5.08 (N-CH2 attached to BTZ and PDI), 2.16 (-CH2) , 1.48(-CH2) , 1.07-1.25 (-CH2), 0.74 (-CH3)

2.3.1.10 Synthesis of copolymer 2 (CoP2)

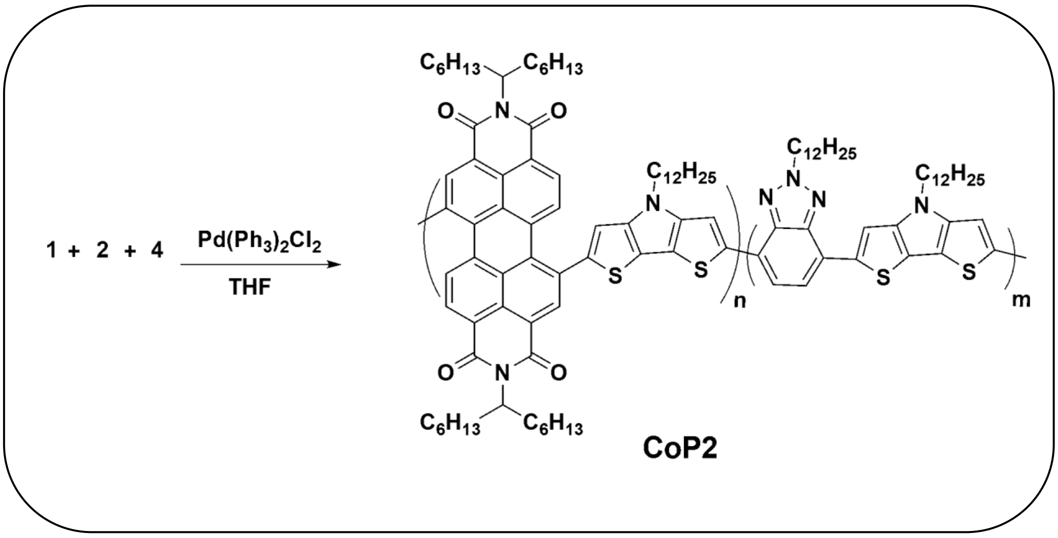


Figure 2.10 Synthesis of copolymer 2 (CoP2)

For the synthesis of CoP2 same procedure was applied with equivalent number of moles of 1,7-dibromo-perylene diimide (0.45 g , 0.5 mmol) , 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole (0.22 g , 0.5 mmol) and twice equivalent number of mole of 4-dodecyl-2,6-bis(tributylstannyl)-4H dithieno[3,2-b:2',3'-d]pyrrole (1.25 g , 1mmol) . CoP2 was obtained as dark brown solid with a yield of 18% . Gel permeation chromatography (GPC) ; number average molecular weight (Mn):12000 g mol^{-1}, weight average molecular weight (Mw): 17000 g mol^{-1} , polydispersity index (PDI): 1.4 . ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 8.71, 8.67, 8.32, 8.11, 7.41, 7.39, 7.29, 6.98 (DTP, BTz and PDI), 5.09 (N-CH_2 attached to BTZ and PDI), 4.15 (N-CH_2 peak of DTP), 2.15(-CH_2), 1.83 (CH_2), 1.82 (CH_2), 1.12 (CH_2), 0.75 (CH_3).

CHAPTER 3

RESULTS & DISCUSSION

3.1 Electrochemical Characterization of Random Copolymers

In this study, synthesis and preliminary optoelectronic properties of DA type polymers were reported.CoP1 and CoP2 were synthesized via Stille cross coupling reaction as in figure 3.1.

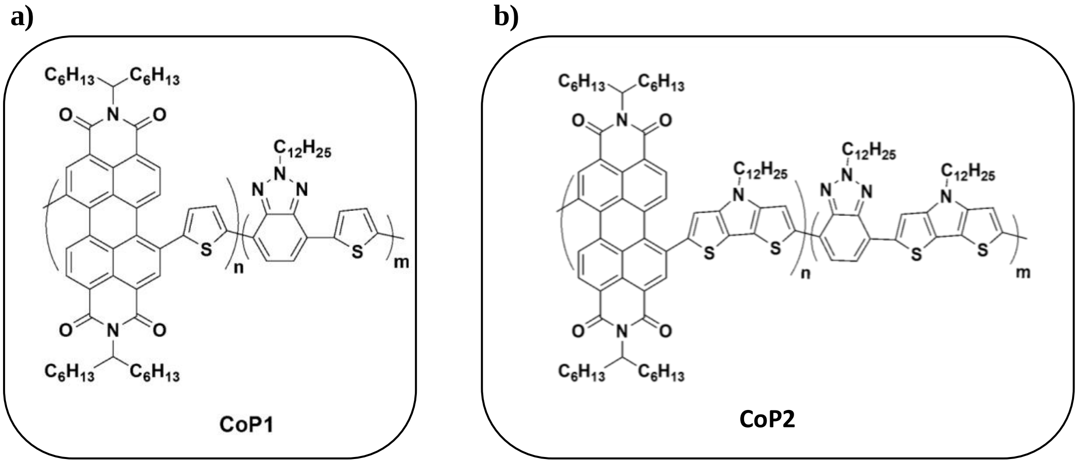


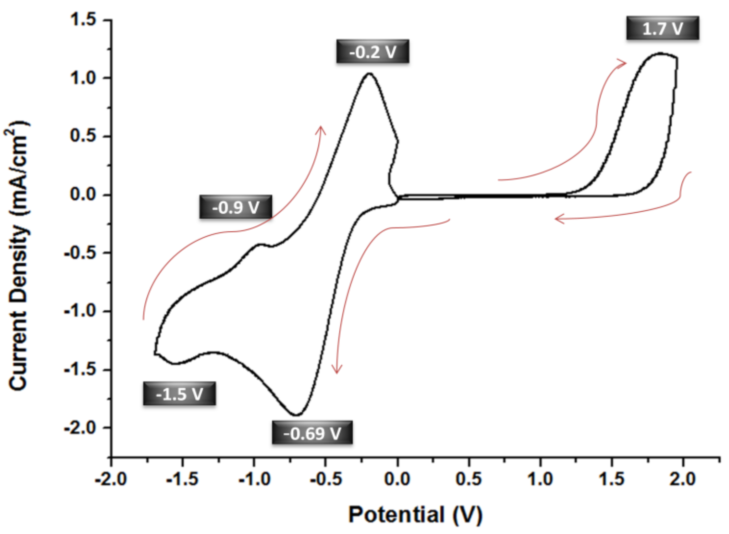
Figure3.1 Structures of CoP1 and CoP2

Cyclic voltammetry (CV) studies were performed in an electrolyte solution consisting of 0.1 M $NaClO_4$-$LiClO_4$ in acetonitrile (ACN) to probe the redox behaviors of the corresponding polymers and determine HOMO and LUMO energy levels of the polymers. First, CoP1 and CoP2 were dissolved in chloroform ($CHCl_3$, 5mg/ml) and spray coated on ITO. CV studies were recorded in a three electrode cell where ITO was the working electrode and Pt wire the counter. A Ag wire calibrated with respect to ferrocenium redox couple (Fc/Fc^+) was used as the reference electrode. Electronic properties of the polymers were summarized in Figure 3.2 c .

As seen from Figure 3.2, both polymers showed reversible reduction couples as most of the PDI based conjugated polymers have. Although, p-dopability in perylene tetracarboxylic dianhydride (PDI) based polymers were rarely observed, CoP2 showed p doping property as well as n-doping property. The absence of the p-doping for PDI based polymers was ascribed to the high oxidation potential of the polymer. Therefore, lowering the oxidation potential and alignment of the HOMO level of the polymer by structural modification can be the reason for p-doping property of CoP2. Incorporation of the dithienopyrrole (DTP) in polymer backbone instead of thiophene caused an increase in the HOMO energy level due to the electron donating nature of the nitrogen in DTP structure. As a result of this, CoP2 had two reversible oxidation couples at 0.98 V and 1.21 V and had a reversible reduction couple at -1.25 V . Ambipolar nature of the CoP2 enables to calculate HOMO and LUMO energy levels from oxidation and reduction onsets using cyclic voltammogram [33]. Corresponding HOMO-LUMO energy levels were determined as -5.75/-4.41 eV with an electronic band gap of 1.34 eV. CoP1 showed n dopable property due to PDI unit which causes a high electron affinity.CoP1 had two reversible reduction couples at -0.69 V and -1.5 V. LUMO energy level of CoP1 was calculated from the reduction onset and calculated as -4.74 eV. Due to the absence of p-dopable property of CoP1, HOMO energy level of polymer calculated in a different way. Relative HOMO energy level was estimated from LUMO energy level and optical band gap derived from the absorption edge in the absorption spectra of the polymer and determined as- 6.37eV.

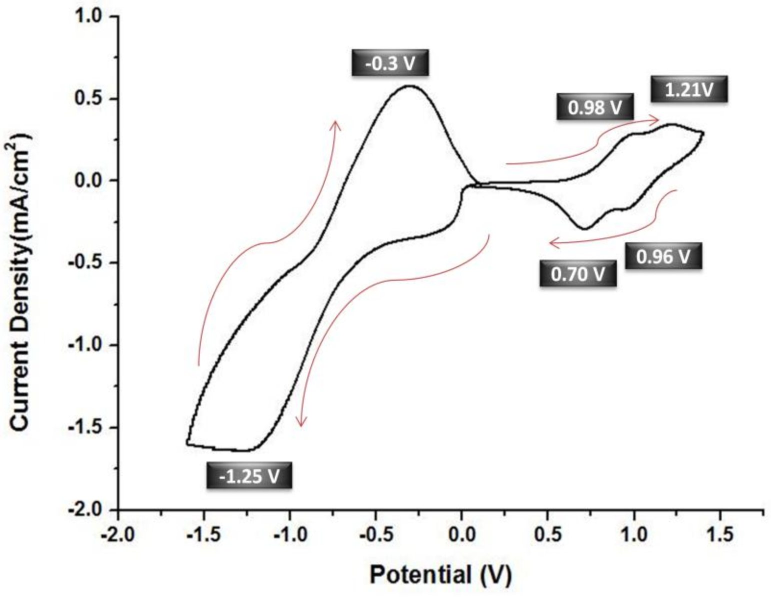
Both polymers showed low-lying LUMO levels which is crucial for n-type conjugated polymers compared to other PDI containing polymers. This can be due to additional electron accepting unit inserted on the polymer backbone.

a)



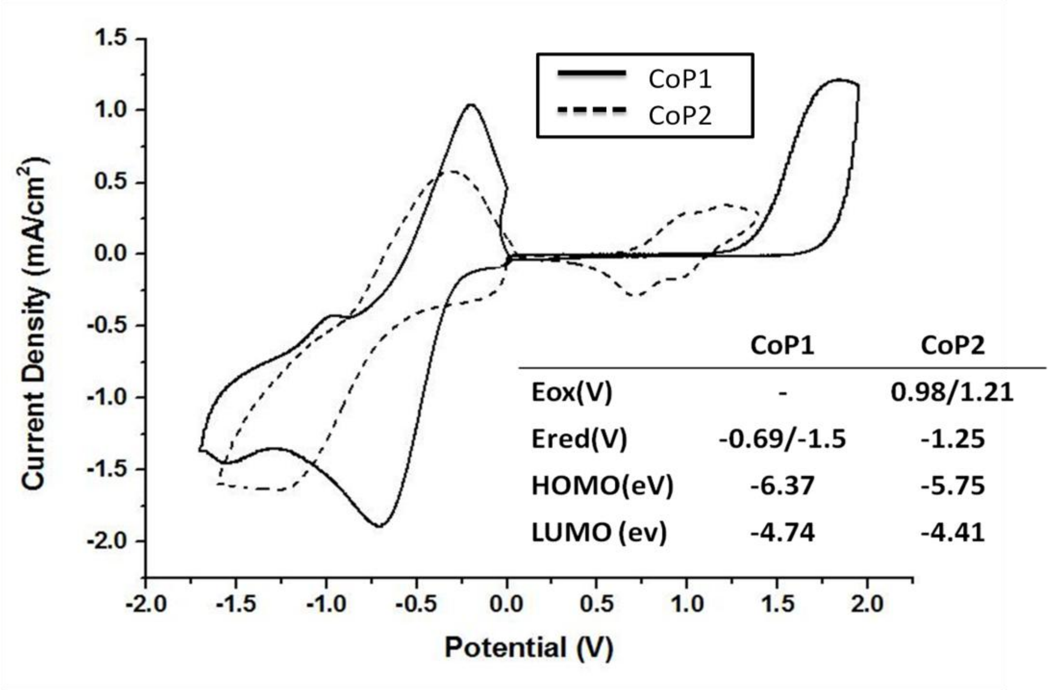
-0.2 V
1.7 V
-0.9 V
-1.5 V
-0.69 V
Current Density (mA/cm^2)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
Potential (V)

b)



-0.3 V
0.98 V
1.21V
0.96 V
0.70 V
-1.25 V
Current Density(mA/cm^2)
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
Potential (V)

c)



	CoP1	CoP2
Eox(V)	-	0.98/1.21
Ered(V)	-0.69/-1.5	-1.25
HOMO(eV)	-6.37	-5.75
LUMO (ev)	-4.74	-4.41

Figure 3.2 CVs of a) CoP1 and b) CoP2 and c)oxidation/reduction potentials and HOMO-LUMO levels of polymer films in 0.1 M $NaClO_4$-$LiClO_4$/ACN.

3.2 Spectroelectrochemistry of Random Copolymers

Spectroelectrochemical studies were performed to determine changes in optical properties during oxidation and redox processes. Spray-coated polymers were stepwise oxidized and reduced by an external voltage and spectral responses were recorded using UV-Vis-NIR spectrophotometry. Besides, colorimetric studies were performed to investigate the polymers color scientifically. For this study; luminance (L), hue (a), and saturation (b) was used according to International Comission on Illumination (CIE) system.

Oxidative and reductive spectroelectrochemistry were performed for CoP1 and CoP2. During oxidative spectroelectrochemistry of CoP1, the absence of the formation of polarons and bipolaron proved that this material was not p-dopable. Also irreversible color change is another information that this material was not p-dopable. During stepwise reduction, peak around 556 nm was expected to decrease due to the formation of the charge carriers (polaron and bipolaron). However, polaron formation of the polymers coincided with peak around neutral state and instead of decrease in absorption slightly shifted peaks were seen in the spectra. (Figure 3.3 b). The polymer was purple (L: 63.672, a: 6.256, b: 0.391) in its neutral state. During reduction process CoP1 showed multichromism with the change in the color from purple to grey (L: 61.740, a: -3.056, b: 0.061) at 0.6V and blue (L: 42.914, a: 5.913, b: 18.627) at -1.3 V.(Figure 3.5 a) respectively.

For CoP2 both oxidation and reduction processes studied. During oxidation process CoP2 showed two absorption maxima due to π-π* transition at 471 nm and 708.4 nm. Polaron bands and bipolaron bands intensified at around 553.9 nm and 1119.2 nm respectively (Figure 3.4a) .The polymer was brown (L: 50.687 , a: 2.418 , b: 37.785) in its neutral state. Due to the formation of polaron band in visible region, in the highly oxidized state a continuous absorption band through the NIR tailing into the visible region of the spectrum cause observation of black color (L:40.081 , a:2.591 , b: -1.037) (Figure 3.5 b). During reduction process again the polymer had two maxima due to π-π* transition at around 473.2 nm and 683.48 nm while new absorption observed at 535.9 nm and 747.1 nm due to polaron and bipolaron bands respectively (Figure 3.4b). In reduced state CoP2 was blue (L: 43.212 , a: -4.887 , b: -12.494) at -1.6V. (Figure 3.5b)

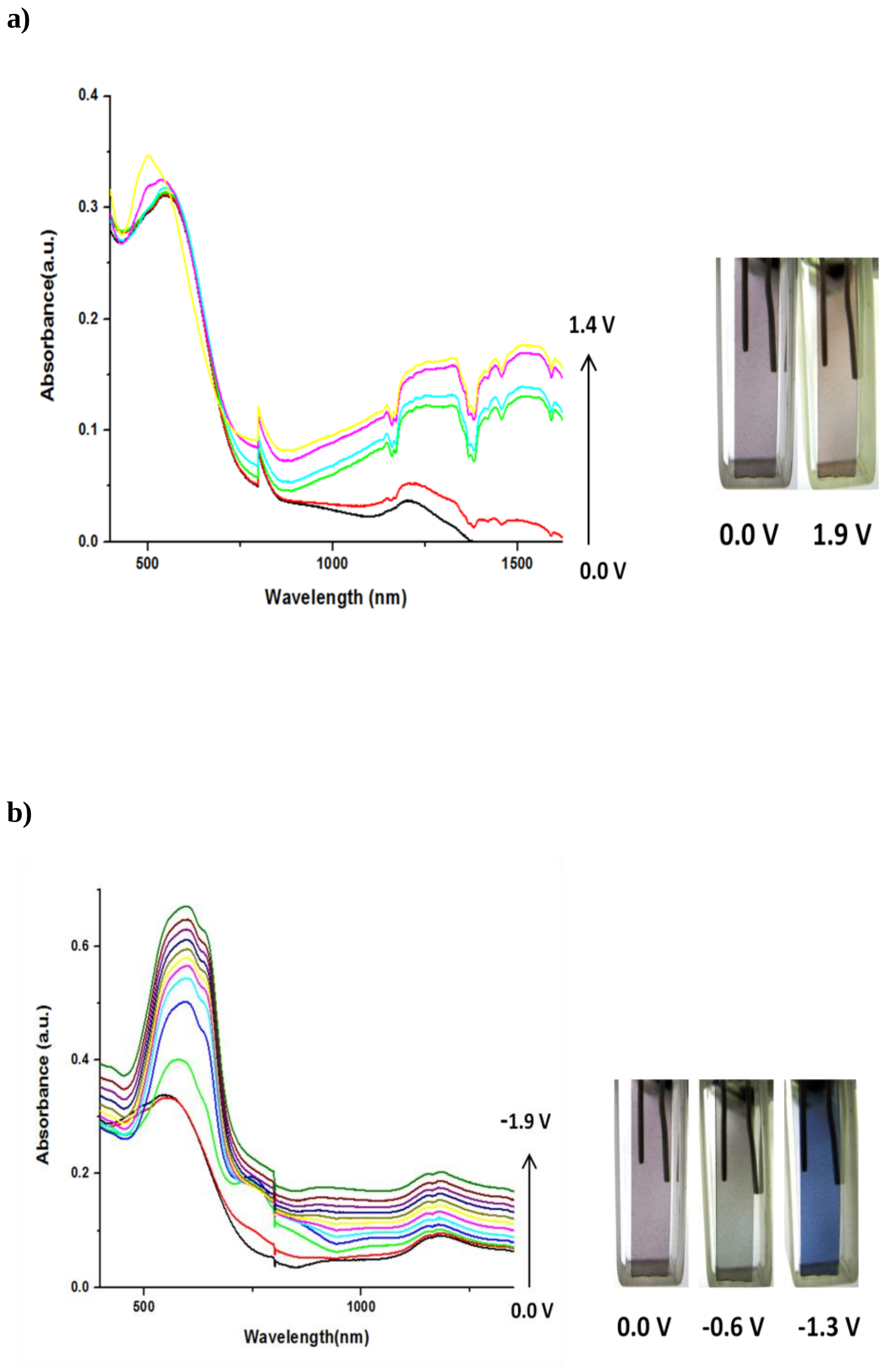


Figure 3.3 Spectroelectrochemistry and colors of CoP1 in 0.1 M $NaClO_4$-$LiClO_4$/ACN solution a) between 0.0 V and 1.4 V b)between 0.0V and -1.9 V

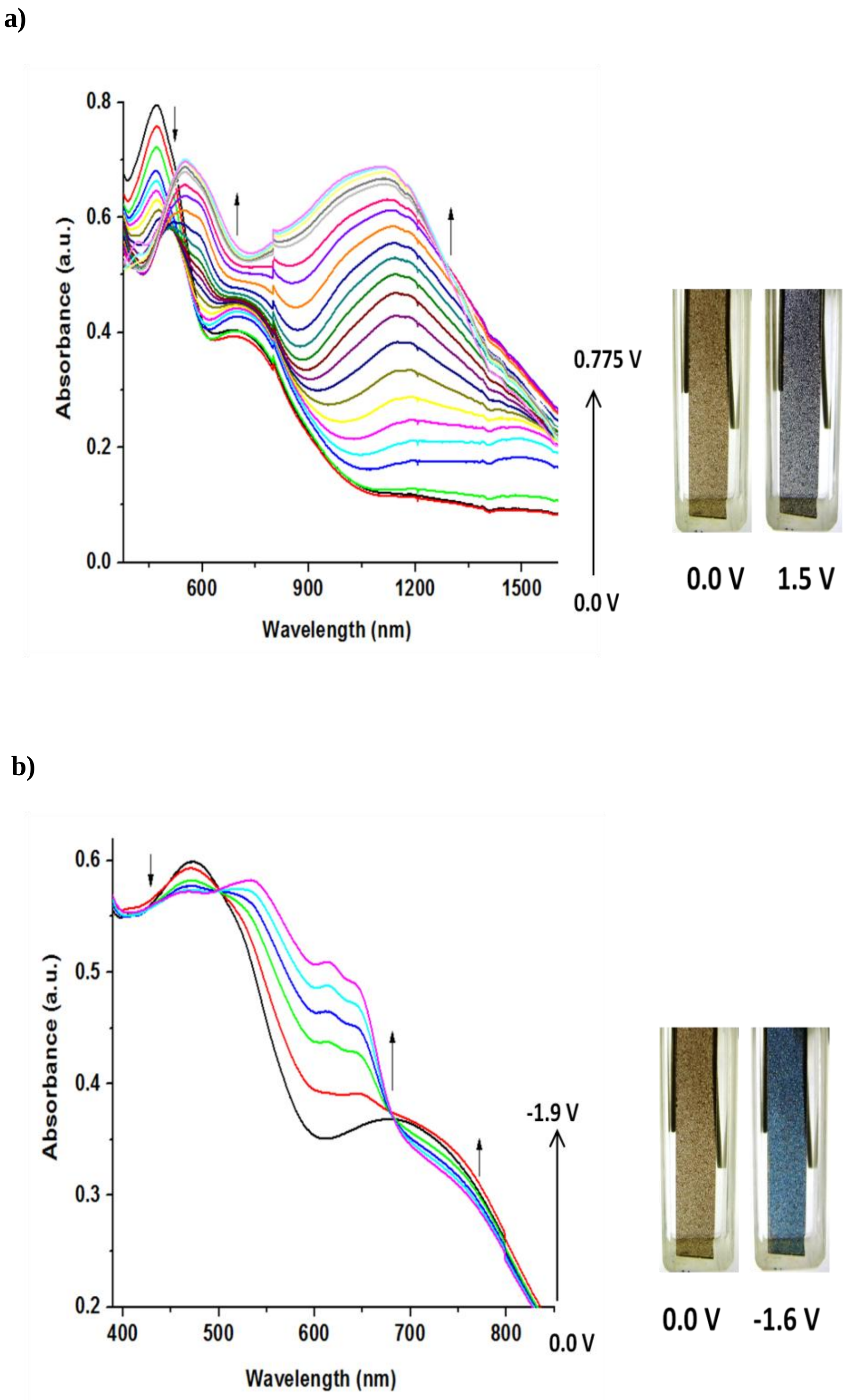
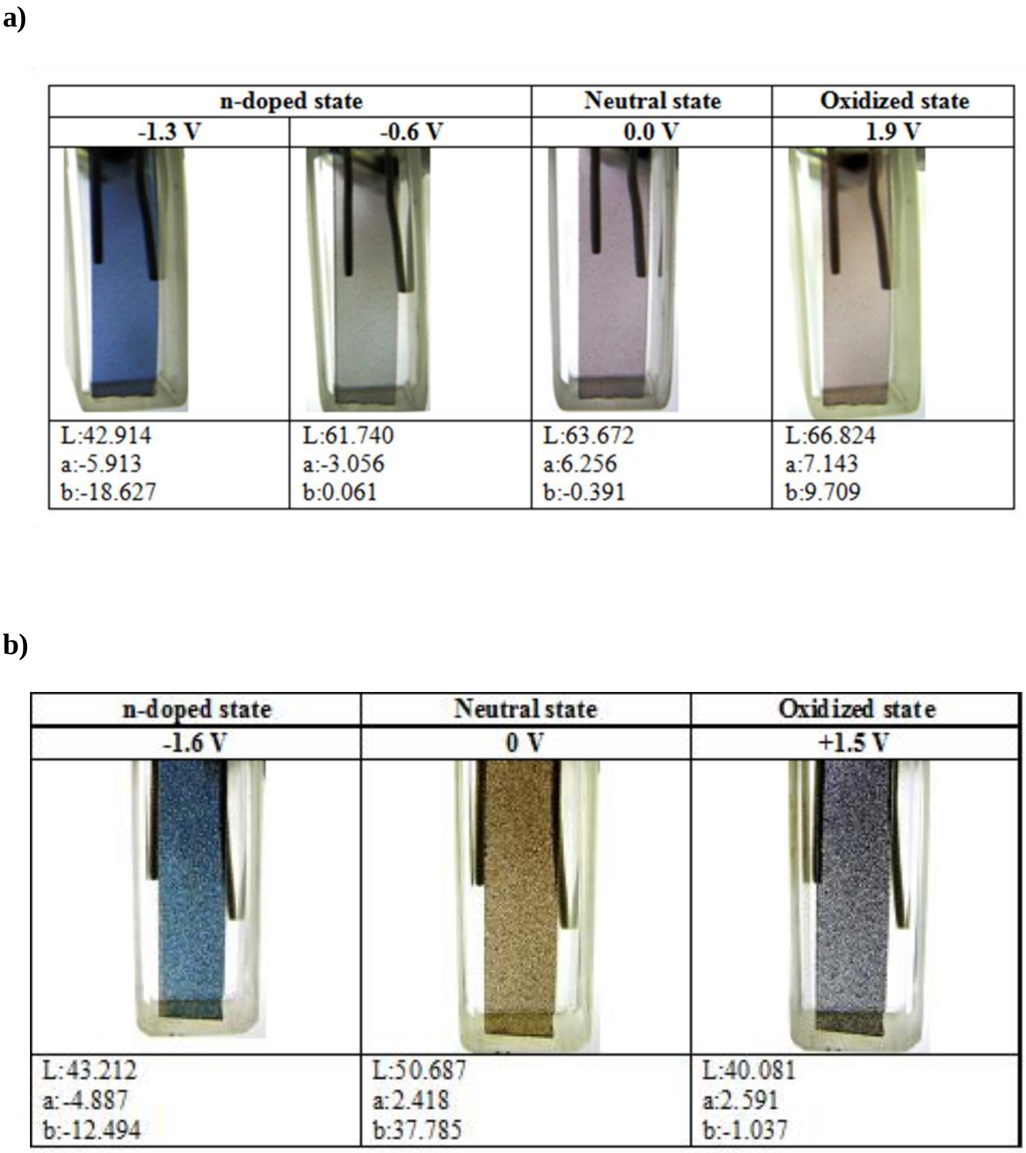


Figure 3.4 Spectroelectrochemistry and colors of CoP2 in 0.1 M $NaClO_4$-$LiClO_4$/ACN solution a) between 0.0 V and 0.775 V b)between 0.0V and -1.9 V



a)

n-doped state		Neutral state	Oxidized state
-1.3 V	-0.6 V	0.0 V	1.9 V
L:42.914 a:-5.913 b:-18.627	L:61.740 a:-3.056 b:0.061	L:63.672 a:6.256 b:-0.391	L:66.824 a:7.143 b:9.709

b)

n-doped state	Neutral state	Oxidized state
-1.6 V	0 V	+1.5 V
L:43.212 a:-4.887 b:-12.494	L:50.687 a:2.418 b:37.785	L:40.081 a:2.591 b:-1.037

Figure 3.5 Colors and L,a,b values of a) CoP1 b) CoP2

3.3 Optical Properties of Random Copolymers

The absorption spectra of copolymers were measured both in solution form (in chloroform) and thin film form (on ITO surface) and were depicted in Figure 3.6. The optical properties of the polymer were also summarized in Table 3.1 . Three absorption maxima were observed for CoP1 and CoP2 in their neutral state. These absorption peaks around higher wavelength was assigned to π–π* transition localized on donor or acceptor whereas peaks localized on low wavelength were attributed to intramolecular charge transfer inherent to the donor-acceptor system. Absorption peaks of CoP1 were around 317, 359 nm and 536 nm in solution. Red shift in the absorption spectra of thin film was not observed for CoP1.

When the absorption spectra of CoP2 compared with CoP1, absorption of DTP containing copolymer shifted to longer wavelength and has a broad absorption almost covering all visible region. The absorption peak at 692 nm was also observed in addition to 472 and 319 nm peaks. For CoP2 there was a 25 nm red shift in thin film form. This shift was observed in low energy region which was attributed to aggregation in solid state.

Optical band gaps of polymers were determined from the π-π* transition onsets which was observed as 1.63 eV for CoP1 and 1.12 eV for CoP2. Band gap of the CoP2 was consistent with the absorption spectra. Optical band gap of the polymers were lower than the electronic band gap. This difference between the energy gap determined by CV and optical measurements has been attributed to the energy difference due to the creation of a free hole and a free electron in CV measurements and the electron and hole bound in an exciton (exciton binding energy). If exciton binding energy is higher, difference between bands gaps is observed as seen in our study.

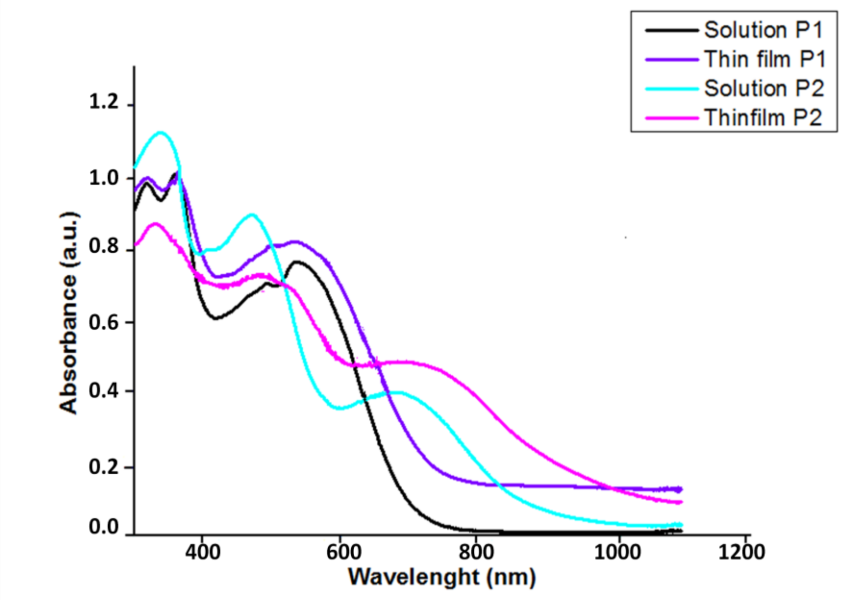


Figure3.6 The absorption spectra of polymers in chloroform solution and thin film on ITO surface

Table 3.1 a) Optical and electronic band gap of CoP1 and CoP2 b) UV-Vis absorption spectra wavelengths

a)

	CoP1	**CoP2**
Eg^{op}(eV)	**1.63**	**1.12**
Eg^{ec}(eV)	**-**	**1.33**

b)

	λ max (nm) thin film	**λ max (nm) solution**	**λ onset (nm)**
CoP1	**536**	**536**	**761,3**
CoP2	**497-717**	**472-692**	**1108,1**

3.4 Thermal Gravimetric Analysis (TGA) of CoP1 and CoP2

Thermal gravimetric analysis of copolymers were determined to weight loss when exposure to gradually increased high temperature. CoP1 had two degredation temperature. The first one was at 320 °C with 20% weight loss. The second one was at 430 °C with 50% weight loss. CoP2 had one degredation temperature which is around 430 °C with 57% weight loss. When the structures of copolymers were considered ; the difference caused from thiophene(Th) or dithieno pyrrole (DTP). DTP unit was fused structure when comparing with Th unit. So Th unit could be easily degredated from structure of CoP1.

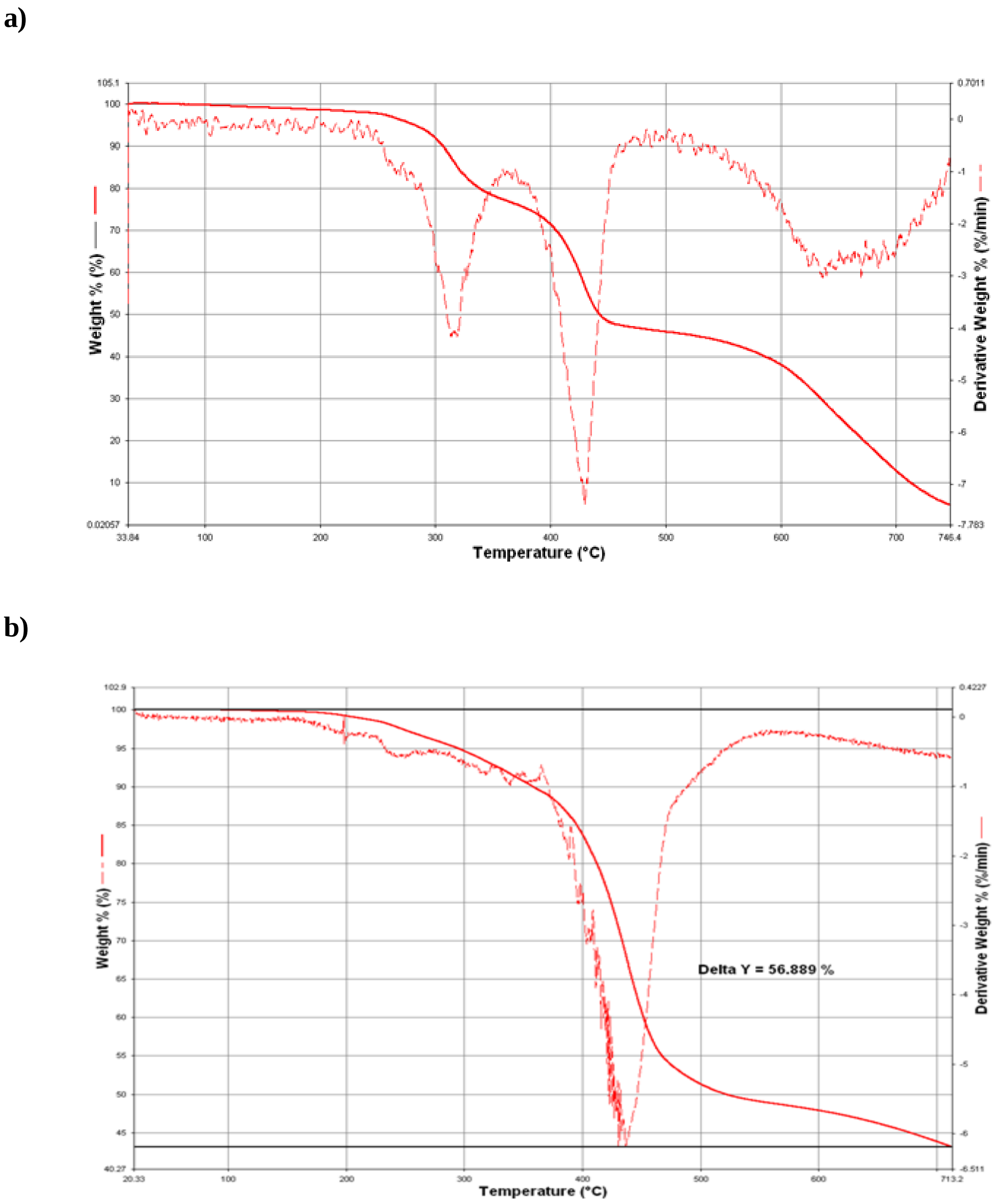


Figure 3.7 TGA results of a)CoP1 b)CoP2

3.5 Stability of CoP2

Stability and electrochemical reversibility of copolymers were tested by CV. Long term stability and reversibility of the CoP2 figured out by current changes. CoP2 was subjected to 0V and +1.2V with 100 mV/s scan rate under atmospheric conditions. The results showed in Figure 3.7 and indicated that after repetitive 100 cycles, CoP2 retained its electroactivity.

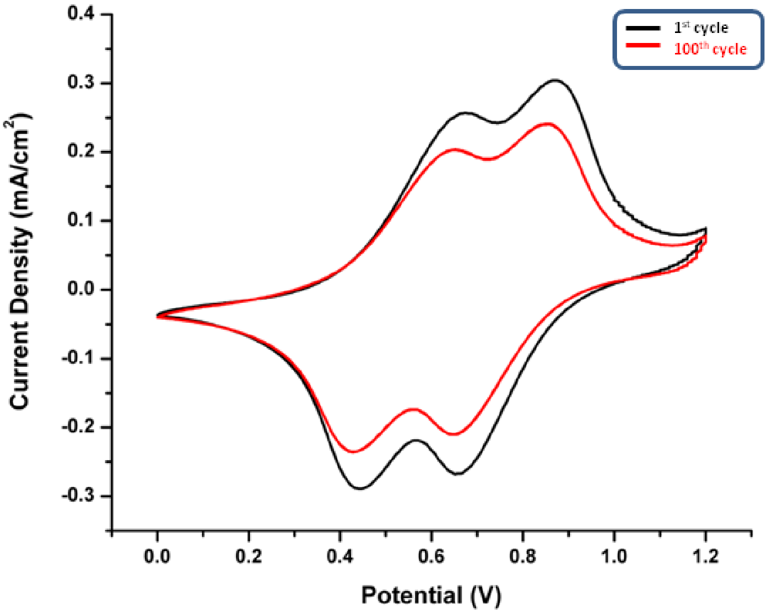


Figure3.8 Cyclic voltammetry of CoP2 to show long term stability and electrochemical reversibility after repeated cycling (up to 100 cycles) between 0 and 1.2 V with a scan rate of 100 mV/s

3.6 Kinetic Studies of CoP2

Chronoamperometry study of CoP2 were studied by subjecting potential between nutral and oxidized states in 0.1 M $NaClO_4$-$LiClO_4$/ACN. Transmittance change between oxidized and neutral states was monitored in 470, 580 and 1115 nm with a time of 5 seconds. Optical contrasts of CoP2 at different waveleneghts were determined as 9 % at 470 nm, 10 % at 580 nm and 22 % at 1115 nm. Switching times of the CoP2 were also investigated and found as 1.6 s (1115 nm), 0.9 s (580 nm) and 0.8 s (470 nm). It is notewothy to state that CoP2 showed fast switching time at 580 nm,1115 nm compared to homopolymers. This can be explianed by the reducing steric hindrance by inserting PDI as a spacer betwwen units. Due to PDI insertion and ejection of dopant ion can be easy.

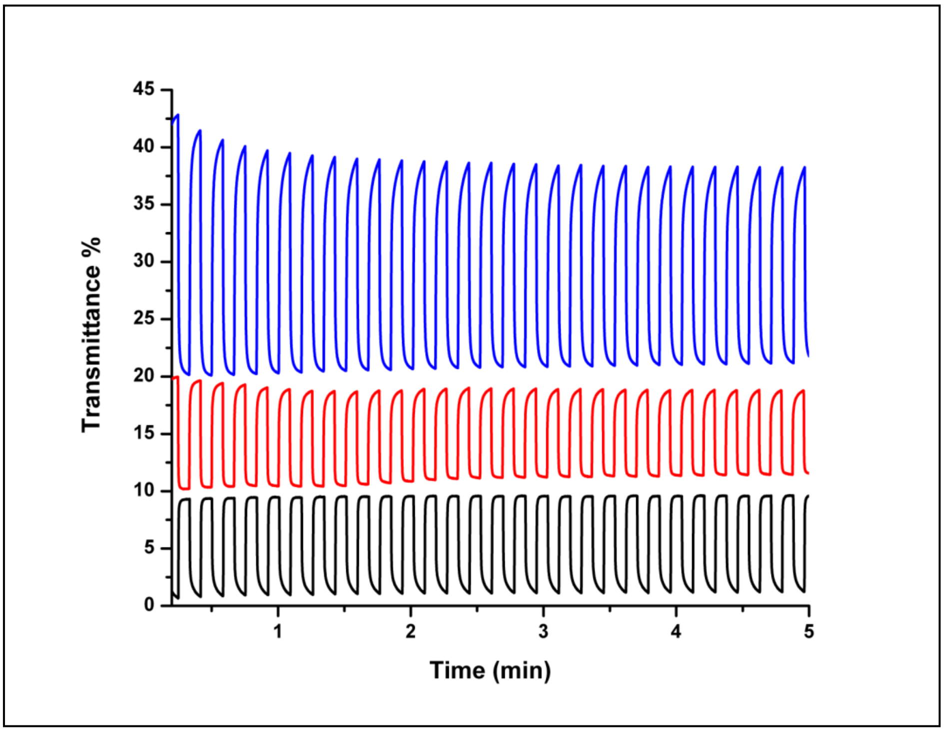


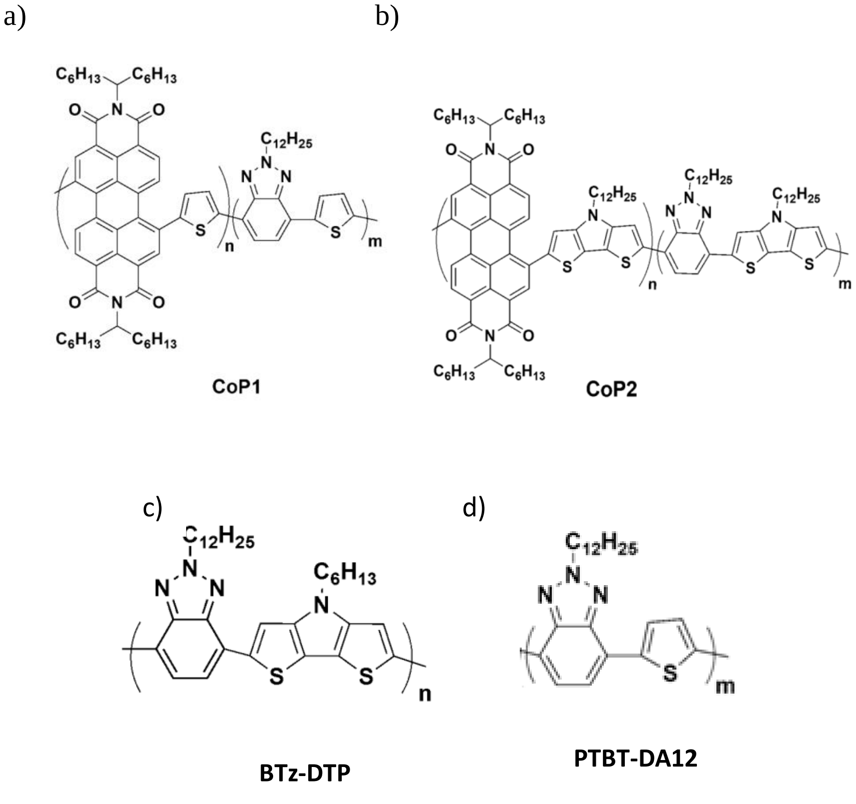
Figure3.9 Percentage transmittance change of CoP2 in 0.1 M $NaClO_4$-$LiClO_4$/ACN solution at visible and NIR region

3.7 Comparison of Random Copolymers with Alternating BTz-Th and BTz-DTP

Benzotriazole based conjugated polymers generally have high lying LUMO energy levels due to low electron accepting ability compared to their sulphur and selenium analogs. This is the result of the electron donating nature of nitrogen in triazole ring. Unlike BTZ, PDI based conjugated polymers have low lying LUMO energy levels due to the strong electron accepting nature. When the alignments of energy level were compared, CoP1 and CoP2 exhibited low lying LUMO energy levels compared to BTZ and PDI based conjugated polymers. This can be the result of additional electron accepting unit that was inserted in polymer backbone. Because, LUMO energy level of the polymer determined by the electron acceptor unit through molecular orbital hybridization in donor-acceptor arrangement and

BTZ or PDI can lower the LUMO level. When Electronic properties of CoP1 and CoP2 were compared with the homopolymers of BTZ-Th[32] and BTZDTP[38], it proved that incorporation of PDI increased n-type property of BTZ based polymers. BTZ-Th homopolymer was turned to pure n-dopable material whereas BTZ-DTP homopolymer studies indicated ambipolar nature.

The optical contrast values were lower compared to PBTZ-DTP Low optical contrast of CoP2 can be explained by spectroelectrohemisty because there is a small tranmittance change in neutral to the fully oxidized states


a) CoP1

b) CoP2

c) BTz-DTP

d) PTBT-DA12

Figure 3.10 Structures of a) CoP1, b) CoP2, c) BTz-DTP[38] , d) PTBT-DA12[32]

Table 3.2 Comparison of the optical and electronic properties between random copolymers and their homopolymer counterparts , PTBT-DA12[32] and BTzDTP[38]

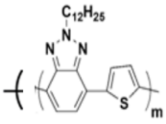
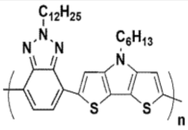
Polymers	 PTBT-DA12	 PBTZDTP	**CoP1**	**CoP2**
Eg^{ec} (eV)	1.93	-	-	1.34
Eg^{op} (eV	1.73	1.72	1.63	1.12
HOMO-LUMO	-5.45/-3.50	−4.75/−3.03	- 6.37 /-4.74	-5.75/-4.41
p-dopable	√	√	×	√
n-dopable	√	×	√	√

Table 3.3 Comparison of the switching time of CoP2 PTBT-DA12[32] and PBTZ-DTP[38]

Polymers	**Optical contrast (ΔT%)**	**Switching times (second)**
CoP2	9 (470 nm) 10 (580 nm) 22 (1115 nm)	1.6 0.9 0.8
PTBT-DA12	27 (530 nm) 12(700 nm)	1.7 2.3
PBTZ-DTP	42 (542 nm) 26.5 (765 nm) 70 (1345 nm)	0.8 2.5 2.4

CHAPTER 4

CONCLUSION

Copolymerization towards obtaining air stable, n-type polymer semiconductors was highlighted.These polymers are very rare and in particular they have low LUMO levels and high electron affinity that make them good candidate for use in photovoltaic device. In organic materials perylene diimides have attracted much attention as organic n-type semiconductors according to their strong π-π molecular interaction and strong electron accepting ability. Besides these properties perylene diimides cover a strong absorption in the visible region and has high photochemical stability which are very important for device applications. Especially ambipolar property is very rare for the polymers containing perylene tetracarboxylic dimide (PDI) moiety . In this study it was observed that polymer which was only p-dopable became n-dopable upon inserting perylene moiety on polymer backbone (CoP1). Also when perylene tetracarboxylic dimide (PDI) coupled with a strong electron donating group such as DTP , the resulting polymer had ambipolar property (CoP2). Thanks to DTP group, CoP2 showed the lowest band gap that was reported up to now. Also polymer neutral state color is important in accordance with the absorption wavelength which is directly relevant with the efficiency of solar cell. Both polymers showed full visible absorption. Color of CoP1 is dark purple and CoP2 is dark brown that made them great candidate for solar cell applications. Another attractive point is organic field effect transistors (OFET) application for PDI based polymers. Ambipolar , solution processible and absorbtion of visible region properties are all provided by PDI based polymers. CoP1 and CoP2 require further investigations for their use in OFETs.

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APPENDIX A

NMR DATA

NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer. Chemical shifts δ were reported in ppm relative to $CHCl_3$ (^{1}H: δ = 7.27) , (^{13}C: δ = 77.0) and CCl_4 (^{13}C : δ = 96.4) as internal standards.

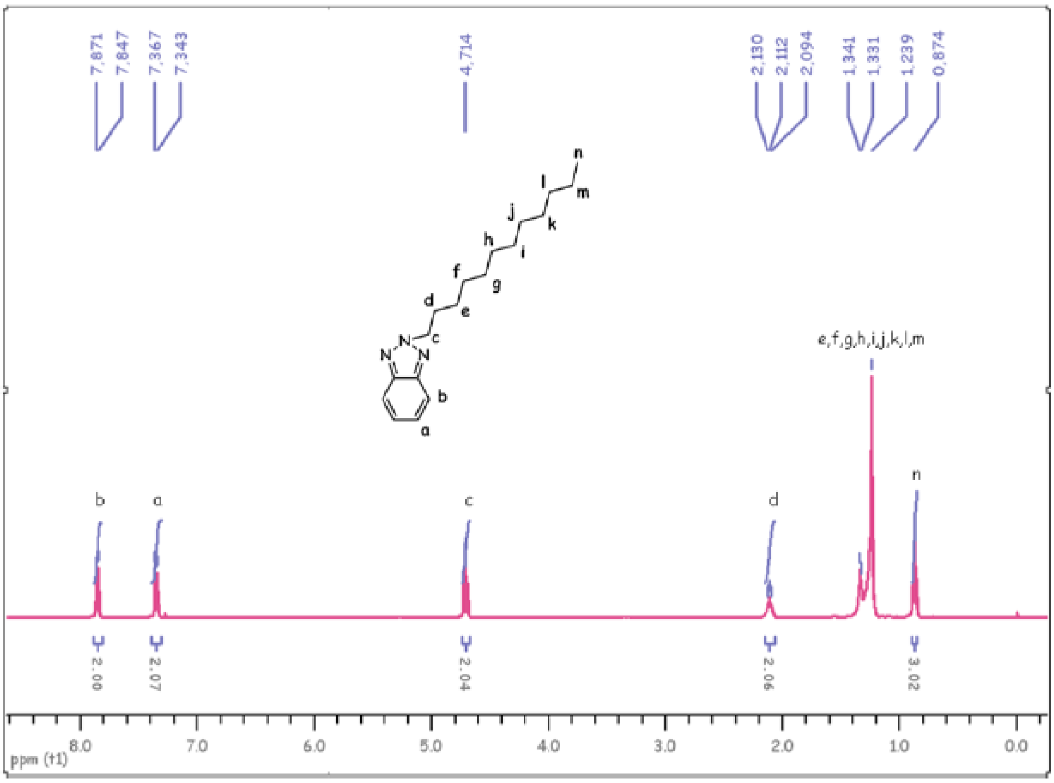

Figure A.1 ^{1}H-NMR spectrum of 2-dodecyl -2H benzo[d][1,2,3]triazole

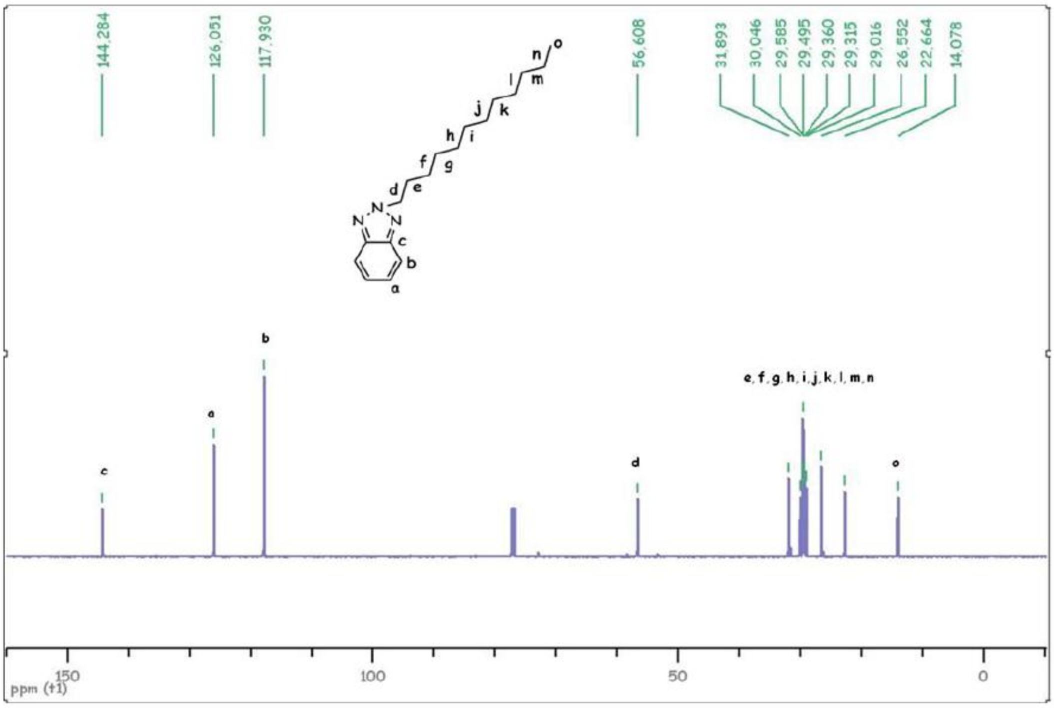

Figure A.2 ^{13}C-NMR spectrum of 2-dodecyl -2H benzo[d][1,2,3]triazole

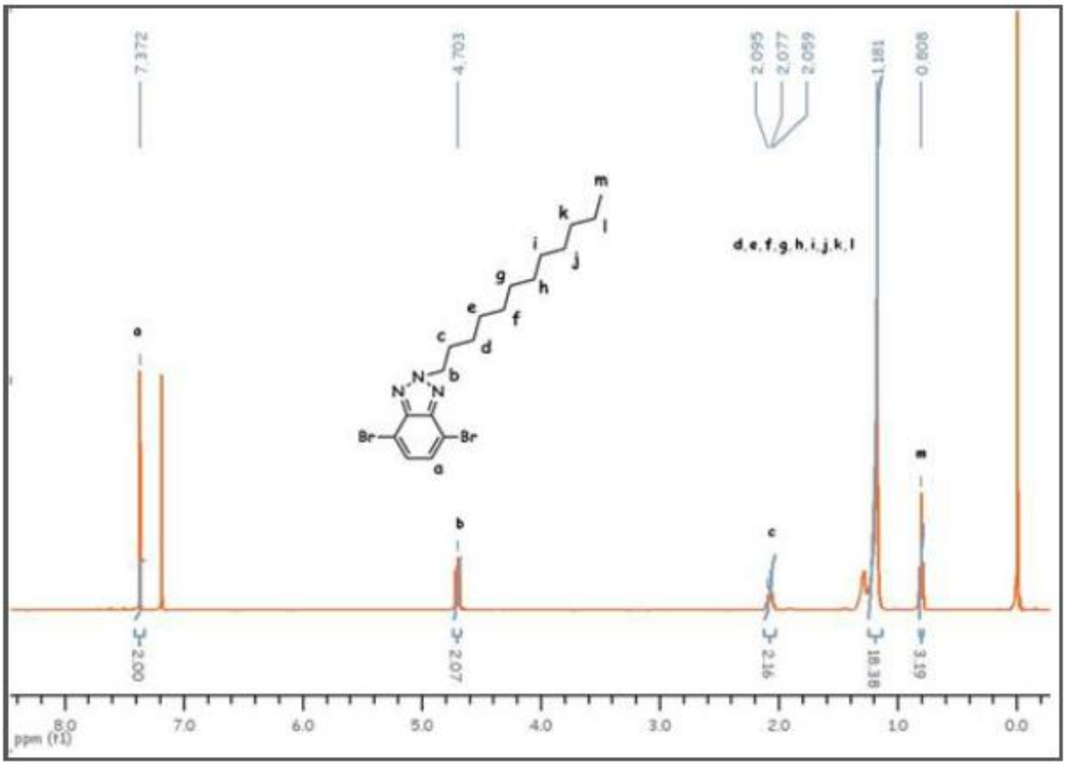

Figure A.3 ^{13}H-NMR spectrum of 4,7 –dibromo-2-dodecyl -2H benzo[d][1,2,3]triazole

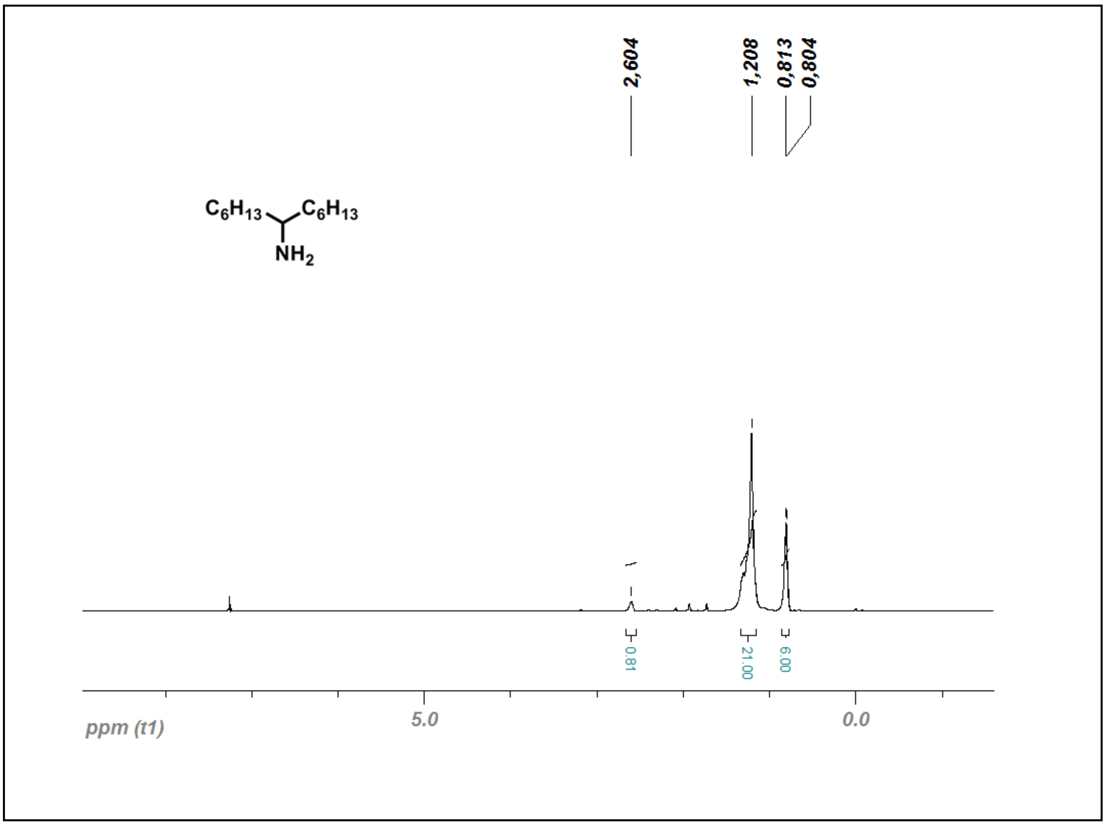

Figure A.4 ^{1}H-NMR spectrum of 1-hexylheptyl amine

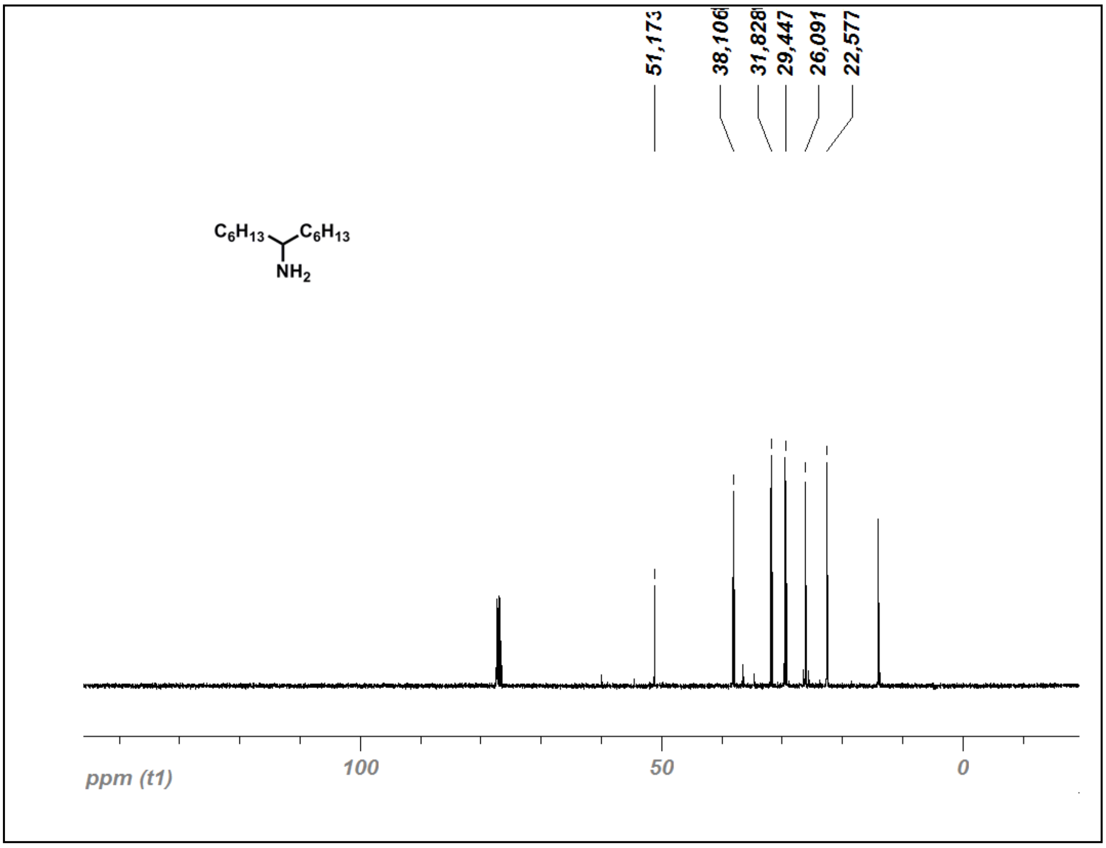

Figure A.5 ^{13}C-NMR spectrum of 1-hexylheptyl amine

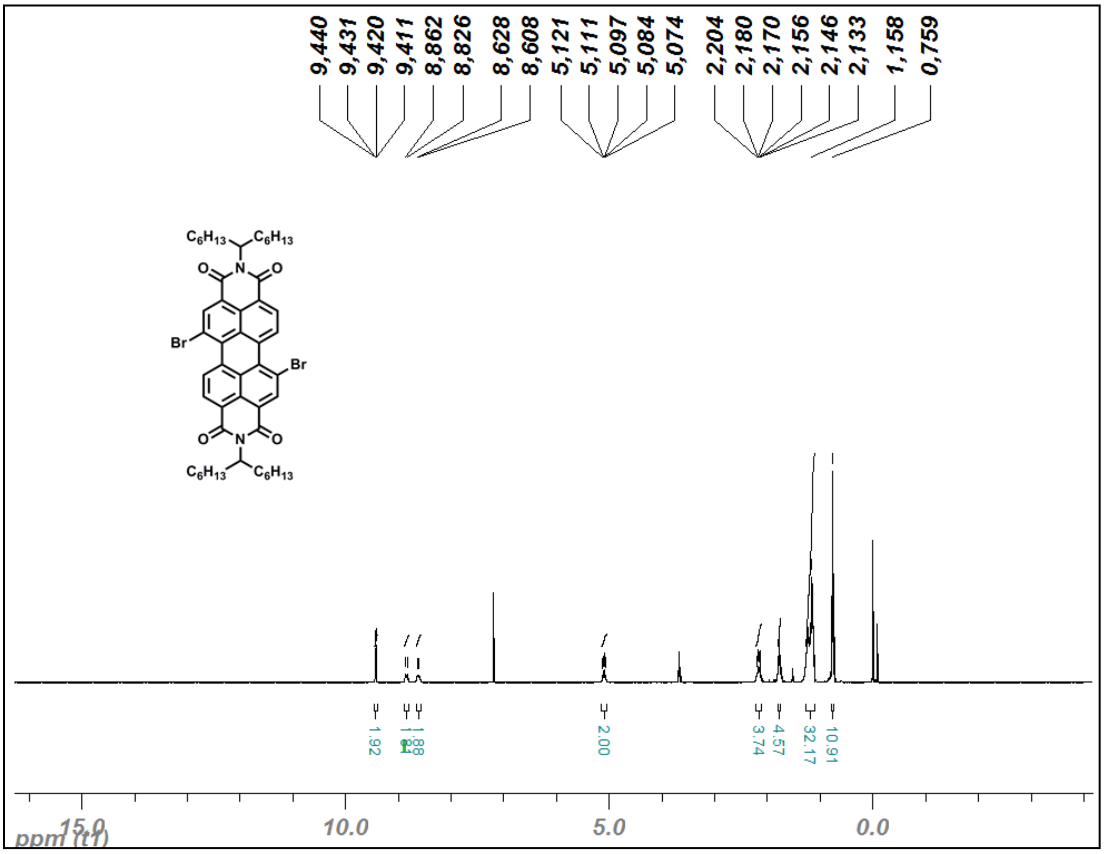

Figure A.6 ^{1}H-NMR spectrum of 1,7-dibromo-N,N'-Bis(1-hexylheptyl)-perylene-3,4,9,10-bis(dicarboximide)

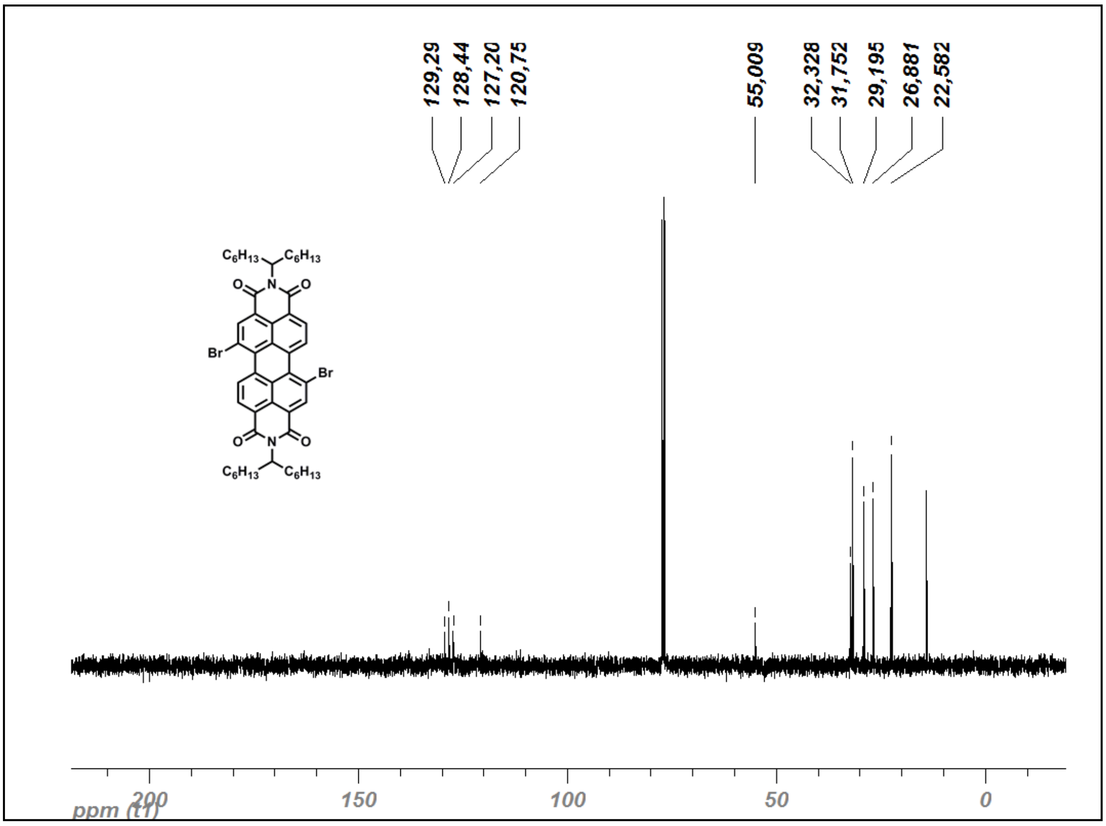

Figure A.7 ^{13}C-NMR spectrum of 1,7-dibromo-N,N’-Bis(1-hexylheptyl)-perylene-3,4,9,10-bis(dicarboximide)

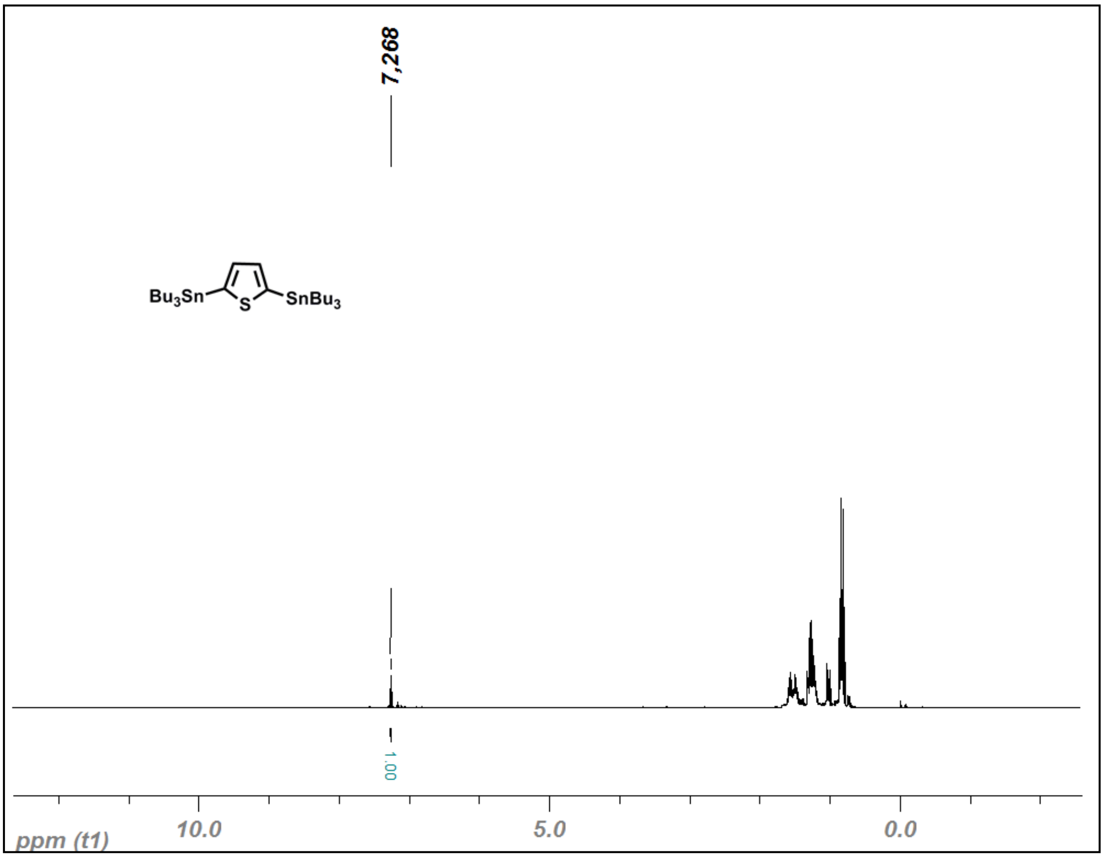

Figure A.8 ^{1}H-NMR spectrum of 2,5-tributylstannilated thiophene

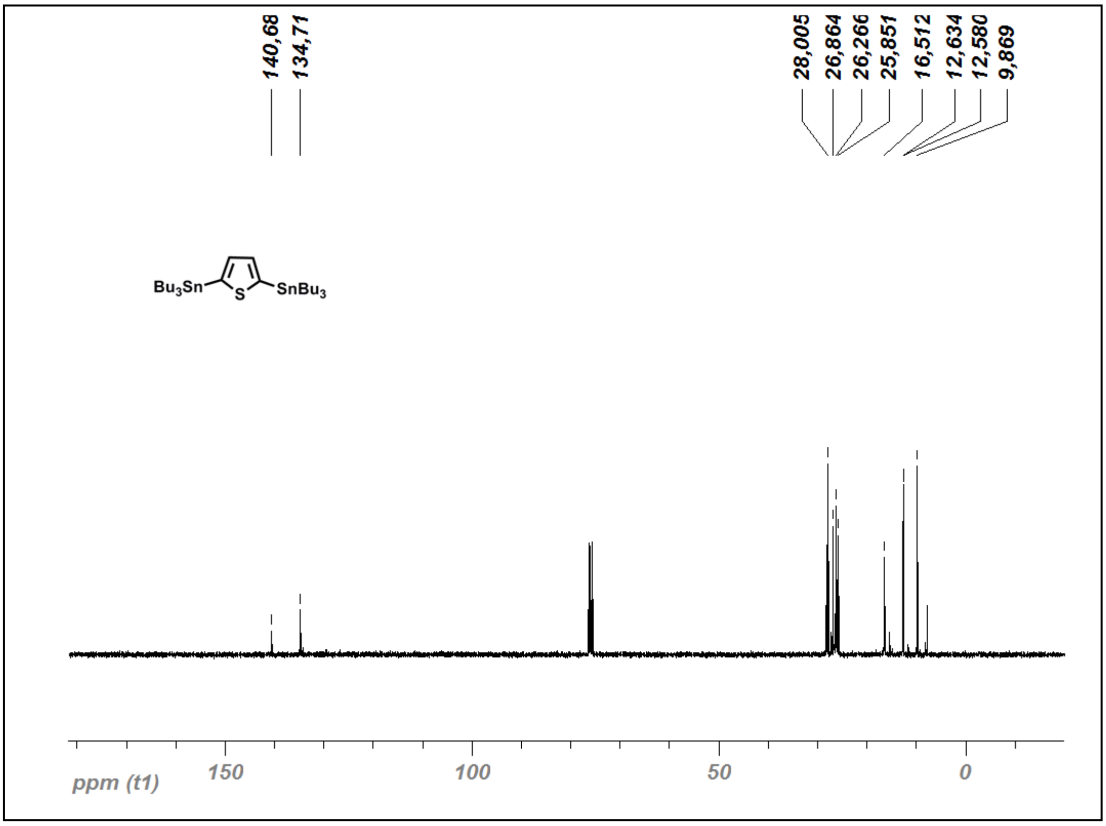

Figure A.9 ^{13}C-NMR spectrum of 2,5-tributylstannilated thiophene

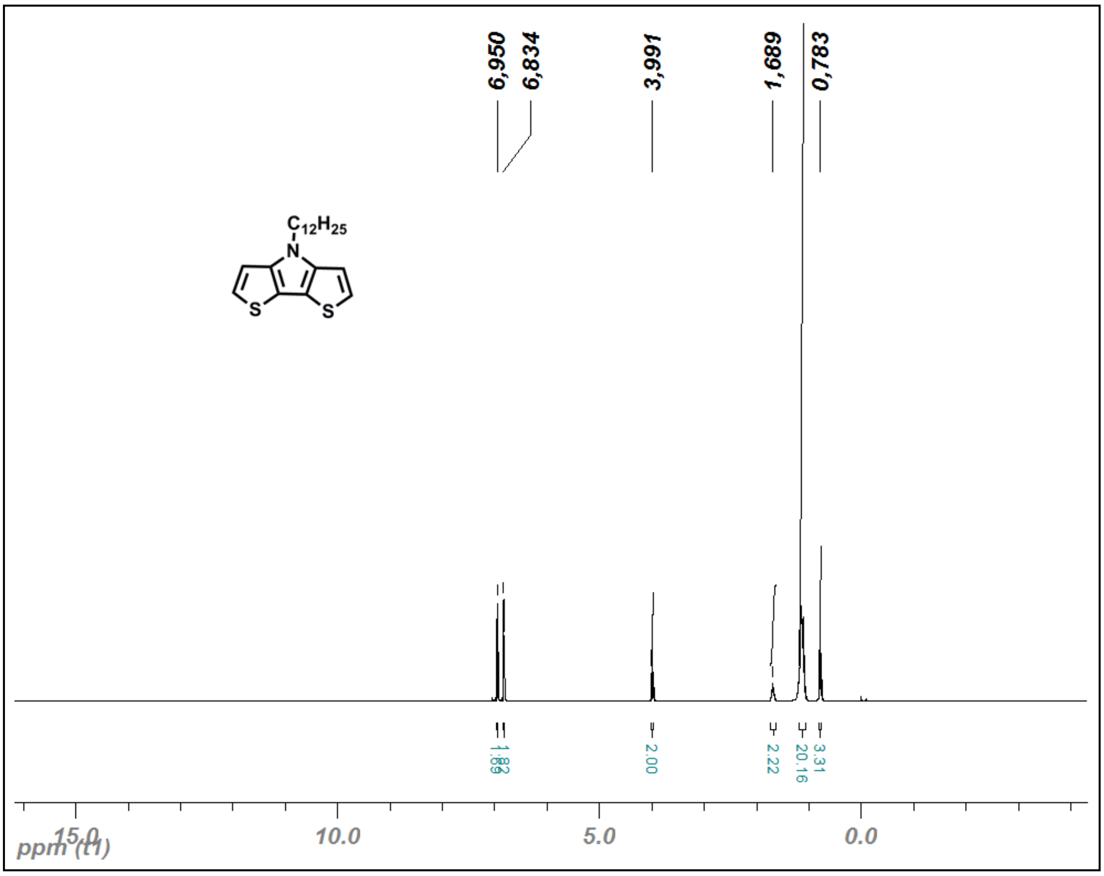

Figure A.10 ^{1}H-NMR spectrum of 4-dodecyl-4H-dithieno[3,2-b:2´,3´-d] pyrrole

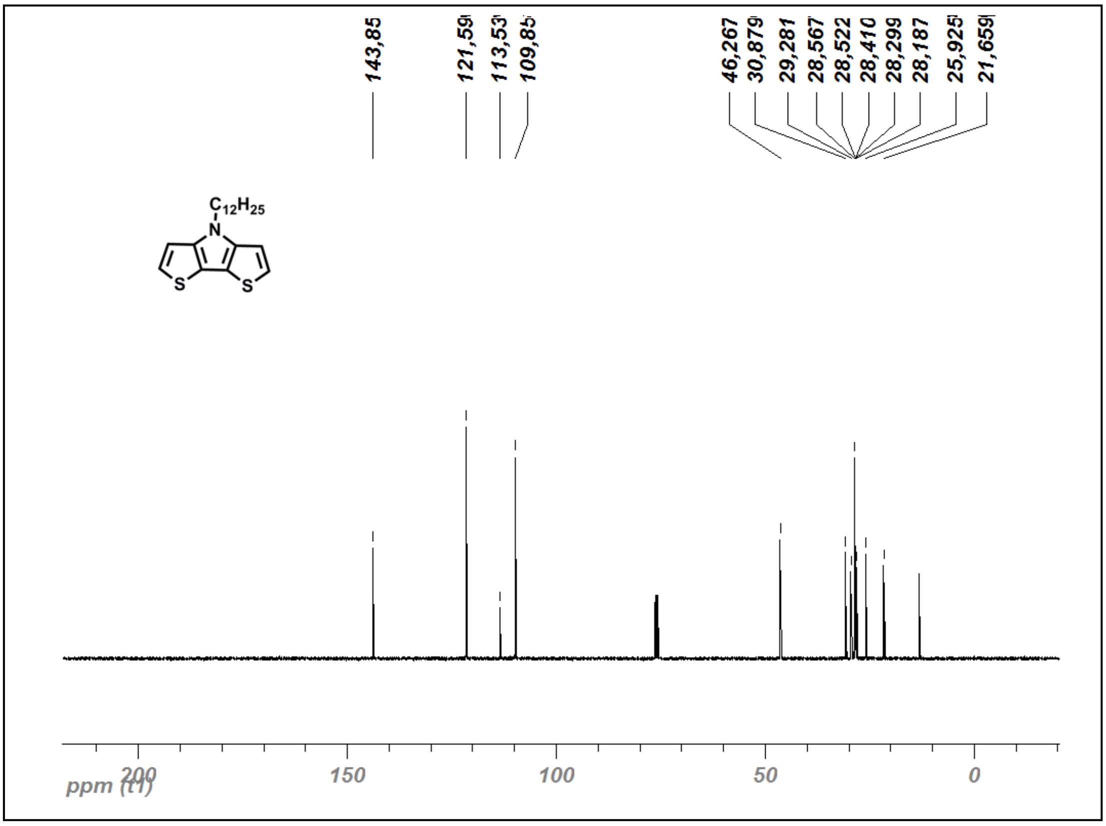

Figure A.11 ^{13}C-NMR spectrum of 4-dodecyl-4H-dithieno[3,2-b:2′,3′-d] pyrrole

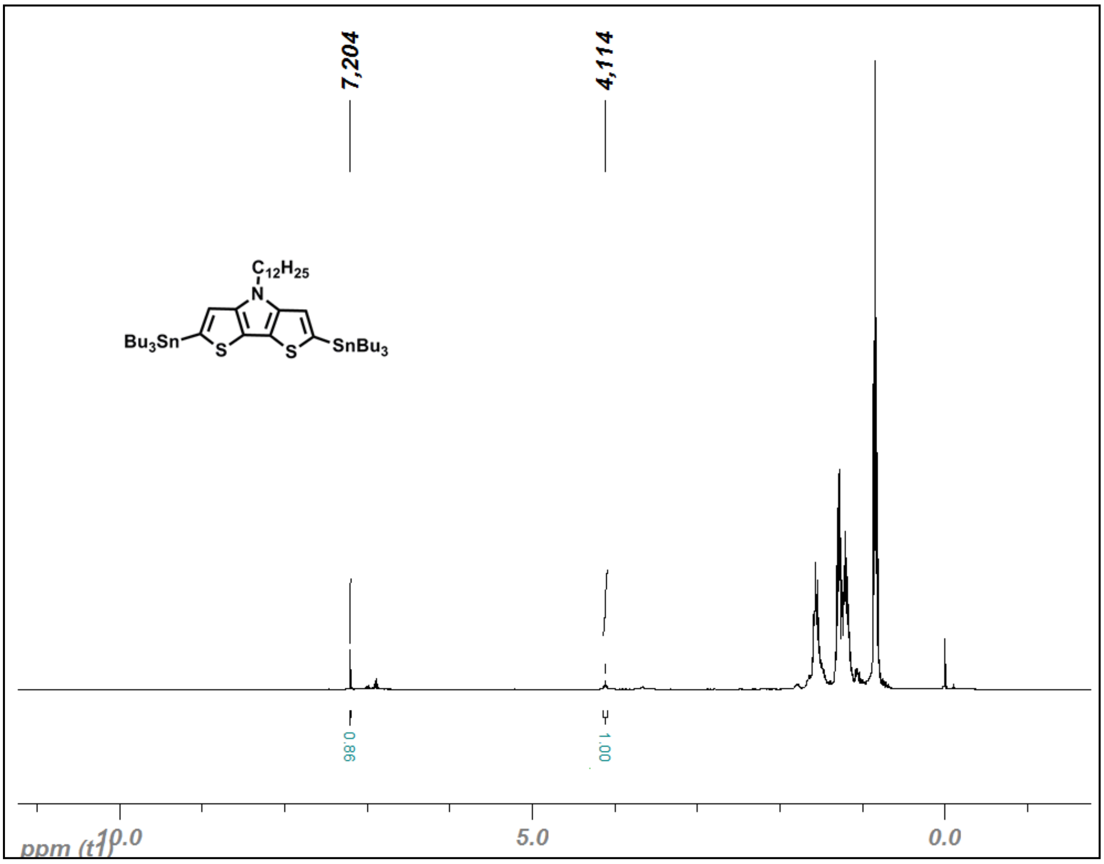

Figure A.12 ^{1}H-NMR spectrum of 4-dodecyl-2,6-bis(tributylstannyl)-4H-dithieno [3,2-b:2´,3´-d]pyrrole

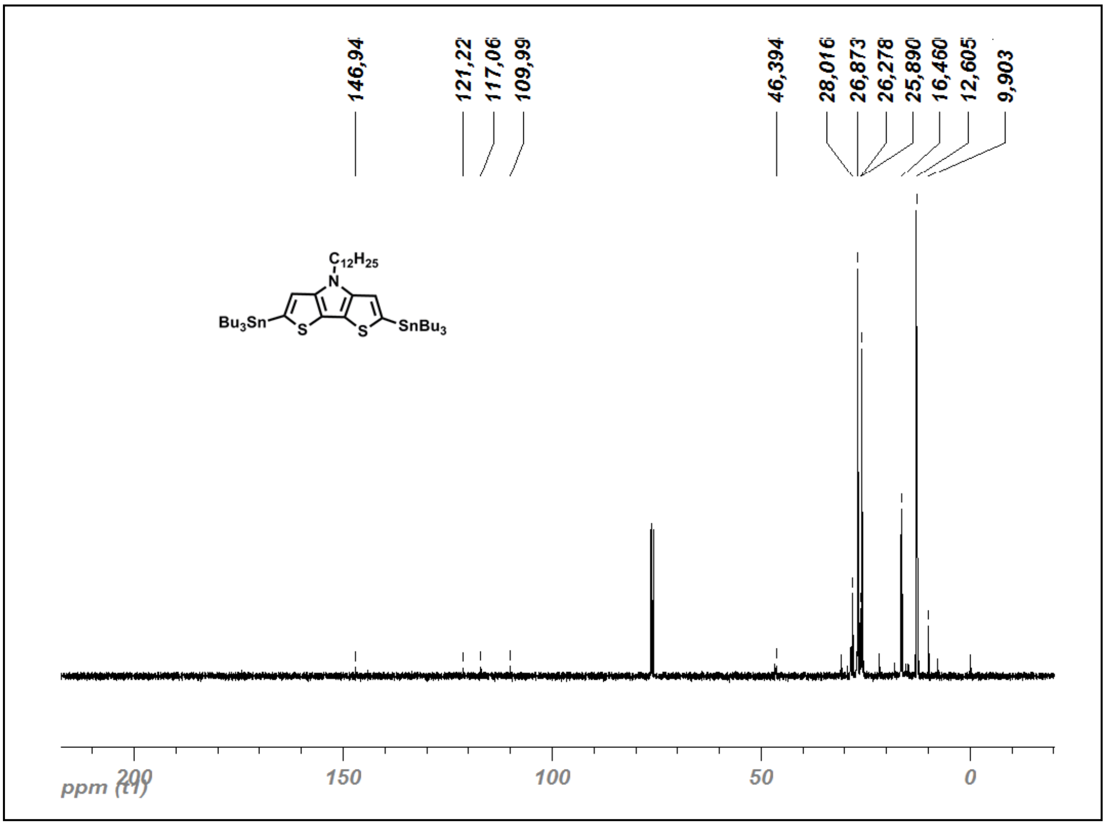

Figure A.13 ^{13}C-NMR spectrum of of 4-dodecyl-2,6-bis(tributylstannyl)-4H-dithieno [3,2-b:2´,3´-d]pyrrole

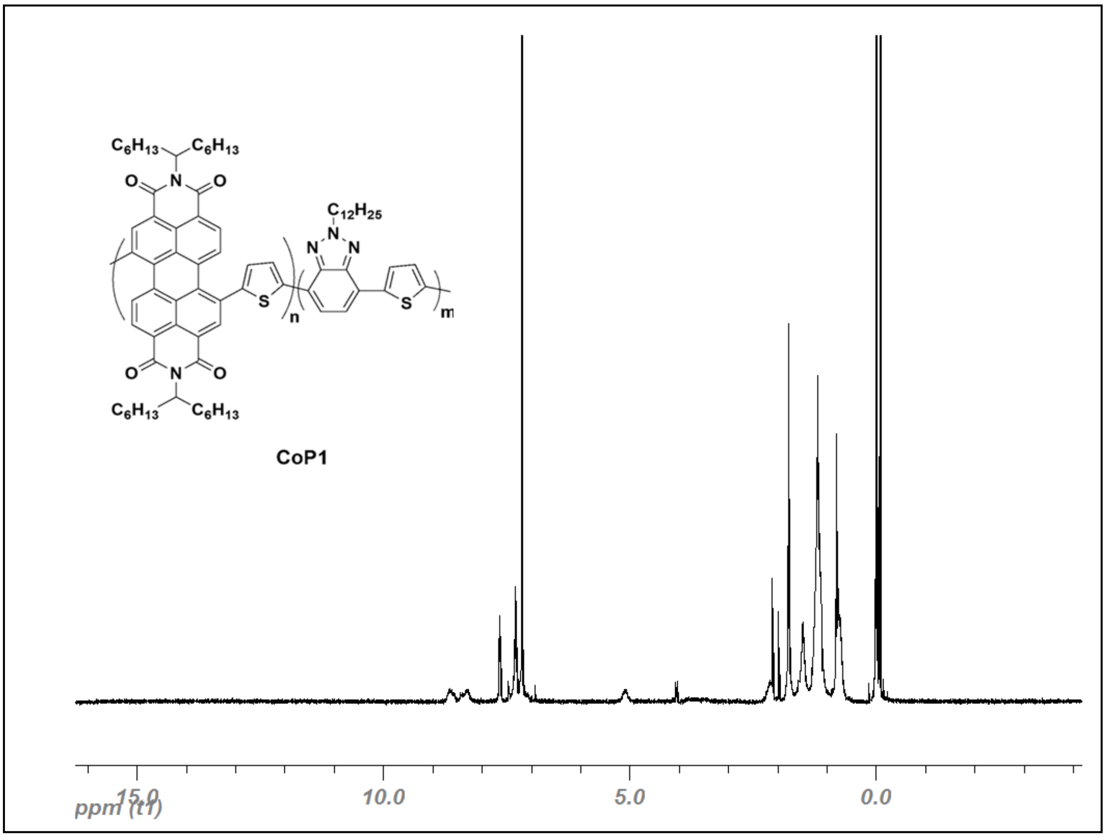

Figure A.14 ^{1}H-NMR spectrum of CoP1

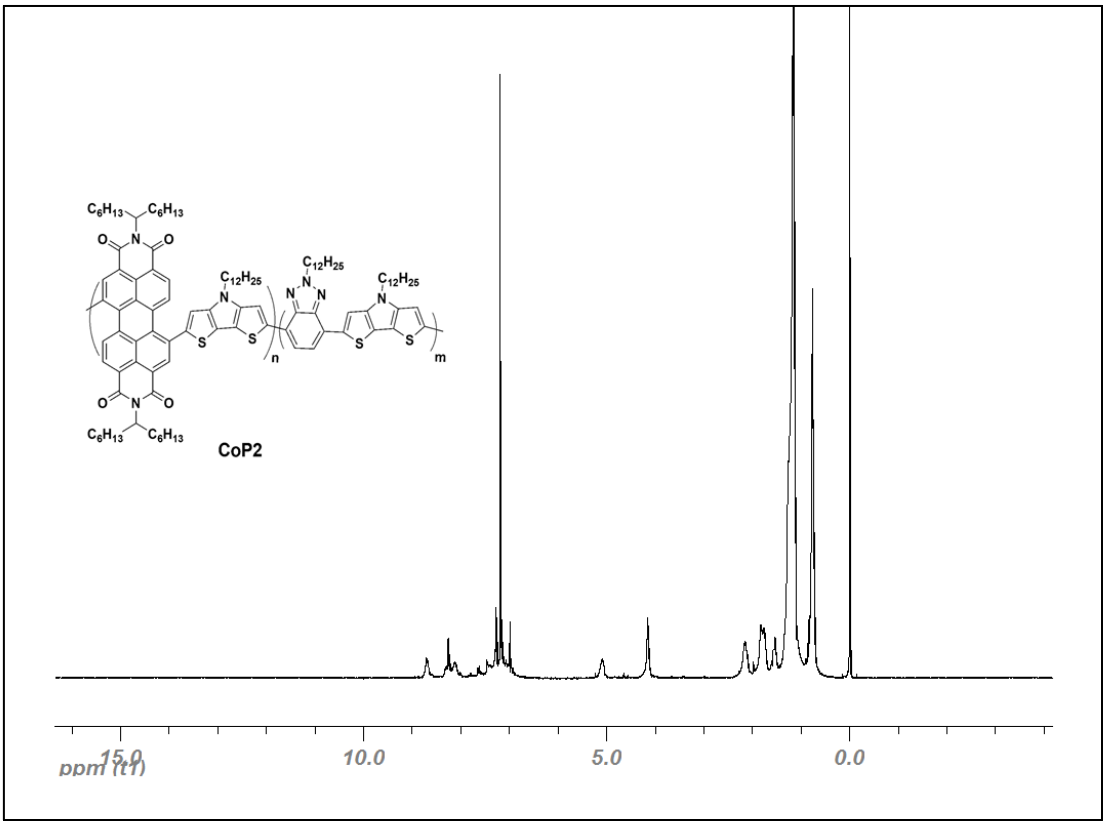

Figure A.15 ^{1}H-NMR spectrum of CoP2