Chapter 1

Introduction

1.1 Conjugated materials

Conjugated polymers/molecules offered the promise of achieving a new generation of materials which exhibit the electrical and optical properties of metals or semiconductors and which retain the attractive mechanical properties and processing advantages of polymers [1]. In conjugated polymers, the chemical bonding leads to one unpaired electron (the π electron) per carbon atom. Moreover, π bonding, in which the carbon orbitals are in the sp2pz configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer [2]. This electronic delocalization provides the "highway" for charge mobility along the backbone of the polymer chain.

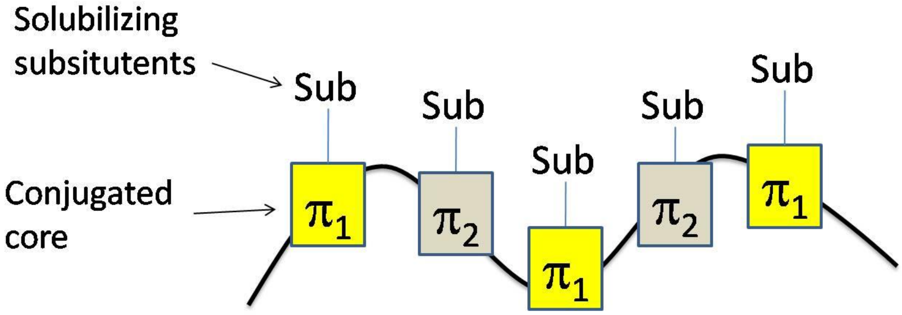


Figure 1.1 Schematic representation of conjugated polymer

The electronic structure in conjugated polymers is determined by the chain symmetry (i.e. the number and kind of atoms within the repeat unit), with the result that such polymers can exhibit semiconducting or even metallic properties. π-Conjugated backbone composed of linked unsaturated units resulting in extended π–orbitals along the polymer chain, thus enabling proper charge transport and optical absorption. Solubility and processability are important features of conducting material. These are quite essential for inexpensive manufacturing processes. This feature can be achieved by functionalization of the polymer core with solubilising substituent. In typical conjugated polymer, the π band is divided into π and π^* bands. Since each band can hold two electrons per atom (spin up and spin down), the π band is filled and the π^* band is empty. The energy difference between the highest occupied state in the π band and the lowest unoccupied state in the π^* band is the $\pi \pm \pi^*$ energy gap, Eg. Because Eg depends upon the molecular structure of the repeat unit, synthetic chemists are provided the opportunity and the challenge to control the energy gap by design at the molecular level.

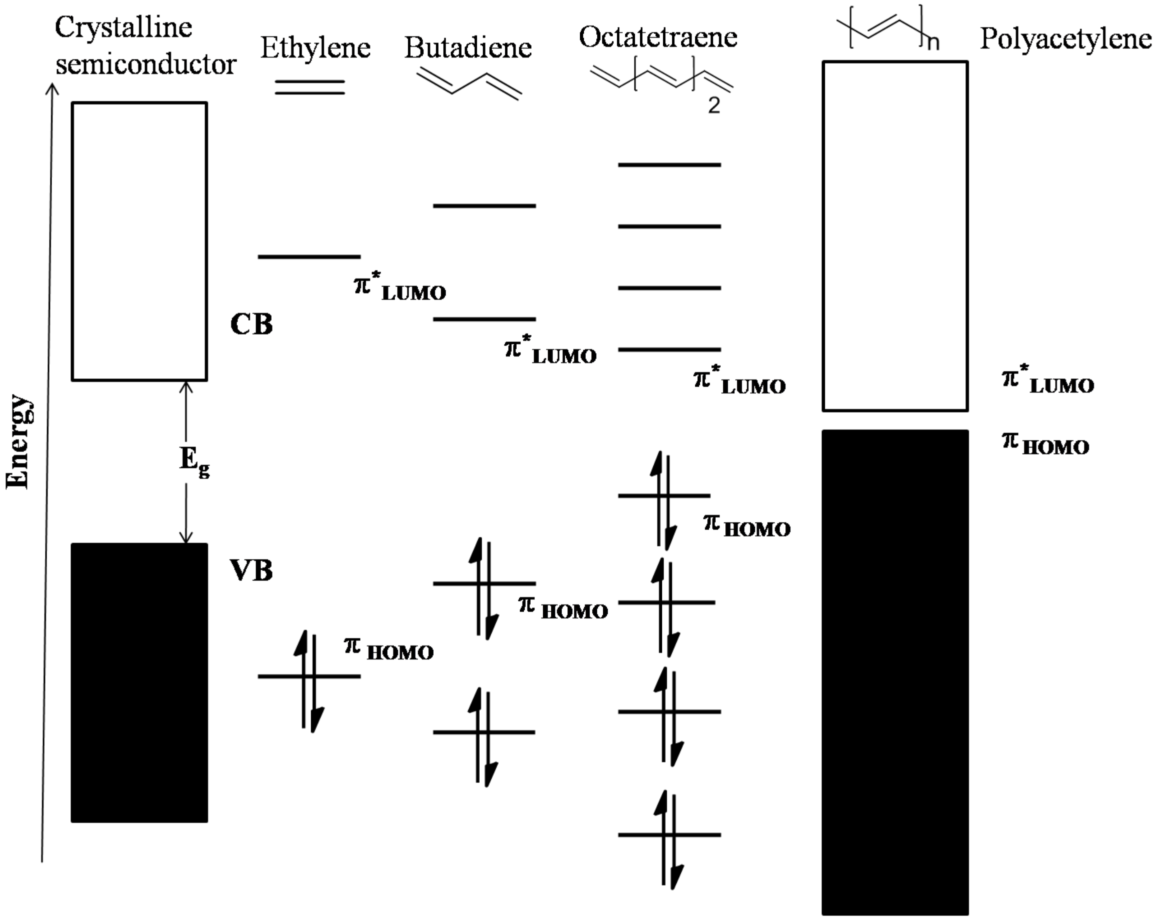


Figure 1.2 HOMO-LUMO and bandgap representation

Conjugated polymers possess large numbers of repeating units, which gave rise to two energy levels valance band and conduction band [3]. The top of the valance and conductance bands in conjugated polymers corresponds to HOMO energy levels and LUMO energy levels of polymers, respectively. Charge carrier properties depend on the positions of HOMO and LUMO energy levels. Organic semiconductors are classified in to three type a) p-types (hole conducting) b) n-types (electron conducting) and c) ambipolar types (both hole and electron conducting).

Conjugated polymers have played a pivotal role in the development of field of organic electronics. Organic electronics is a field of materials science concerning the design, synthesis, characterization and application of organic small molecules or polymers that show desirable electronic properties such as conductivity. The organic electronic is also called by other names such as polytronics (polymer electronics), printed electronics, flexible electronics and plastic electronics. When compared to classical electronics which is usually Si-based, organic electronic have several advantages over them, at the same time organic electronic also have disadvantages compared to the classical one. The solubility and processability over a large area are one of prime benefits achieved from organic electronics. These are quite essential for inexpensive manufacturing processes. Another advantage of the organic electronics is that molecules and polymers can be tailored for specific electronic and optical properties. However, the biggest disadvantage faced by the organic electronic is low carrier mobility when compared to their counterparts.

Table 1.1 Comparison between organic electronics and classical electronics

Organic Electronics	Classical Electronics
reduced costs	high manufacturing costs
simple process	complex process
flexible substrates	rigid substrates
large area	small areas
small integration density	extremely high density
high switching times	switching times very small
reduced performances	high performances

Conjugated polymers-based materials have found application in the field of organic electronic devices such as organic photovoltaic cells (OPVs) [4], organic light emitting diodes (OLEDs) [5] and organic thin film transistors (OTFTs) [6].

1.2 Types of conjugated polymers

The first generation of conducting organic materials witnessed predominantly carbon-based molecular structures such as linear acenes, polyacetylene, and poly(p-phenylene vinylene) derivatives (PPV). Polyacetylene was simplest linear conjugated polymers. Pristine polyacetylene were typical semiconductors, and their conductance were increased by doping [7]. Poly(*p*-phenylene vinylene) derivatives (PPV) possesses good solubility unlike polyacetylene based polymers. PPV are also well known for their luminescent properties, in fact they were first class of conjugated polymers which demonstrated electroluminescence and were among the first commercial polymer light emitting diode (LED) [8].

The polypyrrole were class of conducting polymers which possessed high electrical conductivity and good environmental stability which have gathered significant attention. Polypyrrole showed potential applications such as electrodes for rechargeable batteries [9], supercapacitors [10], solid electrolytes for capacitors [11], field effect transistors [12] and electrochemical actuators [13].

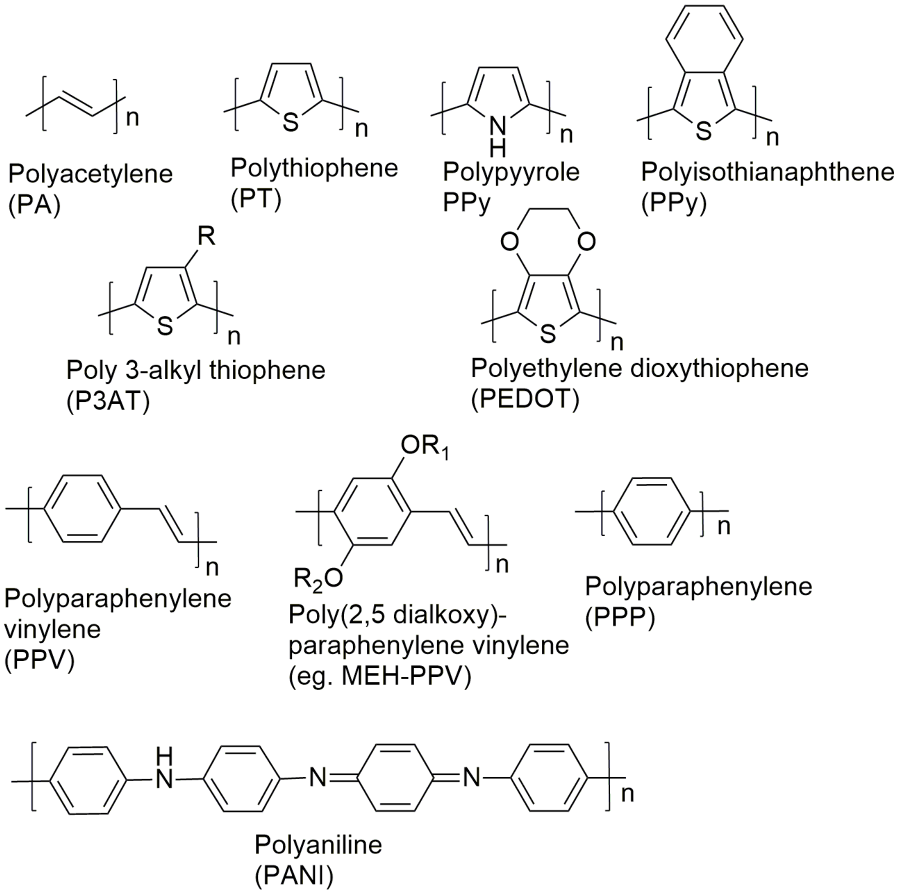


Figure 1.3 Structures of common conjugated polymers [14]

1.2.1 Polythiophenes

The 3rd generation involved the widespread incorporation of heterocycles into the conjugated backbone, culminating in the popularization of the thiophene unit as a molecular building block, as in the well-known material poly(3- hexylthiophene) (P3HT). The donor-acceptor concept has been greatly exploited in the conjugated polymers. Donor–acceptor polymers bear a striking resemblance to inorganic semiconductors compounds in terms of bandgap manipulation. In inorganic semiconductors compounds, an atom (or atoms) of low valence is paired with another atom (or other atoms) of higher valence to allow tuning of the bandgap of the resultant compounds. In case of donor–acceptor polymers, bandgap tuning is achieved through the choice of donor and acceptor moieties, with the donor typically determining the energetic positions of the highest occupied molecular orbital (HOMO) and the acceptor, the lowest unoccupied molecular orbital (LUMO), respectively [14].

The physical properties of conducting polymers were depending on the structure of the monomers. Due to this much of research directly focused on the synthesis and the functionalization of molecules. The removal of structural defects and extension of conjugation in the molecule can be achieved through the synthesis. Dimensionality and overlapping of chains are determined by solid state assembly. The dual effect of planarity in backbone of polymer combined with molecular assembly in form of π stacks lead to enhanced performance of device. Thus, to develop the material with excellent electronic and optical properties, essentially depends on the synthesis of the polythiophenes. Due to these reasons, numerous researchers are involved in the field of synthesis of novel materials and their applications in fabrication of devices.

Polymers having band-gap lower than 2 eV are classified as low band gap polymers. The electron donating and electron withdrawing properties of alternating monomer efficiently increases the intramolecular charge transfer setting up the push-pull effect which narrows the band gap of the conjugated polymer.

Polythiophenes are most important classes of π-conjugated polymers, as they meet the essential requirements of solubility and processability and a wide variety of functionalities can be incorporated through substituent modifications. Functional oligo/poly thiophenes are synthesized by generally metal catalyzed C-C coupling reactions such as Suzuki, Stille, Sonogashira, Negishi and Kumada reactions. Polythiophenes containing bulky alkyl groups at the β-position have been employed in the preparation of light-emitting diodes (LEDs). The emission of such polythiophenes ranges from red to blue depending on the extent of conjugation.

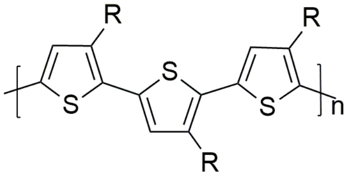
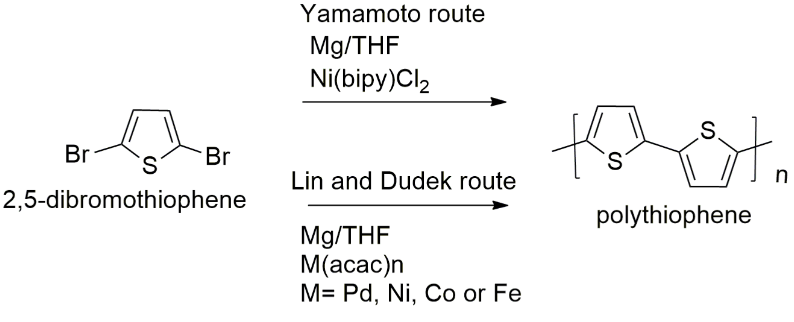


Figure 1.4 Structure of poly 3-alkyl thiophene

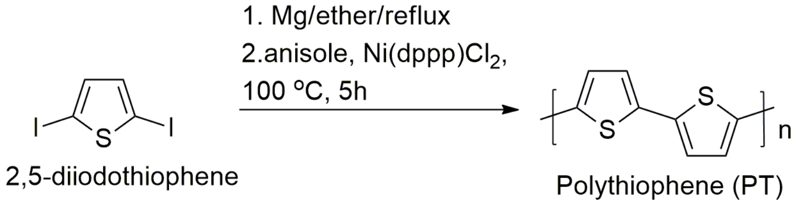
Oligothiophenes are electron rich systems which enables them to possess positive charge and to transport it through self-assembled monolayer or thin films. The conjugation length depends on the amount of main chain distortion due to the substituent on the backbone. The regioregularity of the polythiophene chains for mono/di-substituted polymers in particular, as well as the nature of the substituent play a fundamental role in determining the properties of the materials such as solubility, conductivity, optical properties etc.

Synthesis of unsubstituted polythiophene (PT) was first reported in 1980 by Yamamoto *et al* and Lin *et al* [15]. Both groups synthesized polythiophene using metal catalyzed polymerization of 2,5-dibromothiophene. Yamamoto *et al* were utilized 2,5-dibromo thiophene with Mg in THF in presence of catalyst nickel(bipyridine) dichloride [Ni(bipy)Cl_2]. Lin and Dudek *et al* have synthesized polythiophene by polymerization of 2,5-dibromo thiophene in presence of Mg in THF and using Pd$(acac)_2$ or Ni$(acac)_2$ or Co$(acac)_2$ or Fe$(acac)_3$. Both methods yield low molecular weight polythiophene (scheme 1.1).



Scheme 1.1 Synthesis of polythiophene from 2,5-dibromothiophene

Later on Wudl *et al* have developed new method of polymerization in which highly purified 2, 5-diiodothiophene was first reacted with Mg in ether at reflux temperature to form iodomagnesiumiodothiophene, which was isolated and dissolved in anisole with catalytic amount of Ni(dppp)Cl_2 to yield polythiophene (Scheme 1.2). The synthesized polythiophene possess impurity of Mg and Ni of barely 50 ppm and its conductance in doped form (AsF_5 doped) was about 10 S cm^{-1} [16].

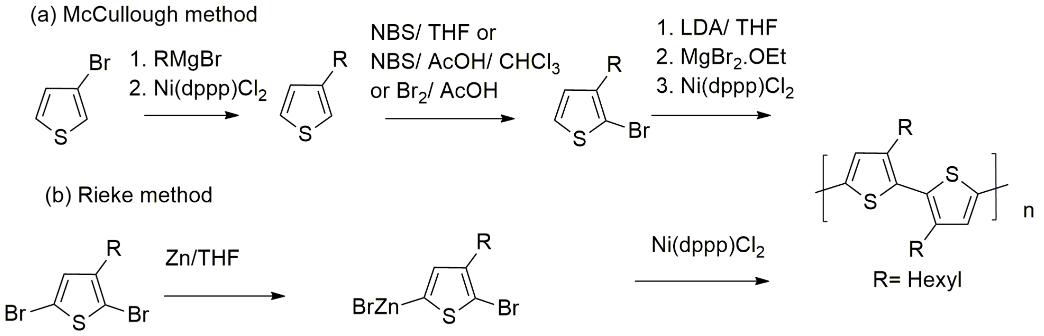


Scheme 1.2 Synthesis of polythiophene from 2,5-diiodothiophene

1.2.2 Regioregular polythiophenes

In early 1992, McCullough group reported synthesis of head to tail [HT] coupled poly(3-alkylthiophene) (Scheme 1.3). The synthesized polythiophene was almost 100% head to tail-head to tail coupling. In this approach typical polythiophenes were prepared in yield of 44-69%. The molecular weight of obtained polythiophenes were in the range of 20-40 *KDa* (PDI = 1.4) [17].

Another approach for synthesis of HT coupled polythiophenes was reported by Reike group [18]. Reike method involves reaction of 2,5-dibromo-3-alkylthiophene with Rieke zinc to form 2-bromo-3-alkyl-5-(bromozincio)thiophene which was further reacted in presence of Ni(dppp)Cl_2 as a cross-coupling catalyst to yield regioregular HT polythiophene (Scheme 1.3).



Scheme 1.3 Synthesis of regioregular head to tail coupled polythiophenes reported by (a) McCullough group and (b) Rieke group.

Alkoxy derivatives have several advantages over alkyl substituted polythiophenes [19]. Alkoxy polythiophene having oxygen bonded directly with thiophene ring results in the lower of band gap of the resultant conjugated polymer as well as stabilizes the conducting state of polymer [20]. The first reported synthesis of mono- and dialkoxysubsituted thiophene derivatives were reported by Leclerc group [21] and by industrial scientists at Hoechst AG [22]. Though most of reported mono- and dialkoxy thiophenes based polymers exhibited low conductivity in oxidized, doped state, the major development achieved through synthesis of bicyclic 3,4-ethylenedioxythiophene (EDOT) and its derivatives which were electrochemically polymerized by Heinze *et al* while Jonas *et al* synthesized by chemical polymerization [23].

3-Substituted and 3,4-disubstituted thiophene have been used as monomers for the preparation of π-conjugated oligomers and polymers exhibiting interesting electric and electronic properties.

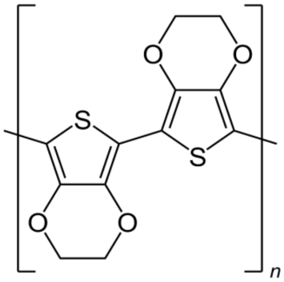


Figure 1.5 Structure of poly(3,4-ethylenedioxythiophene) (PEDOT)

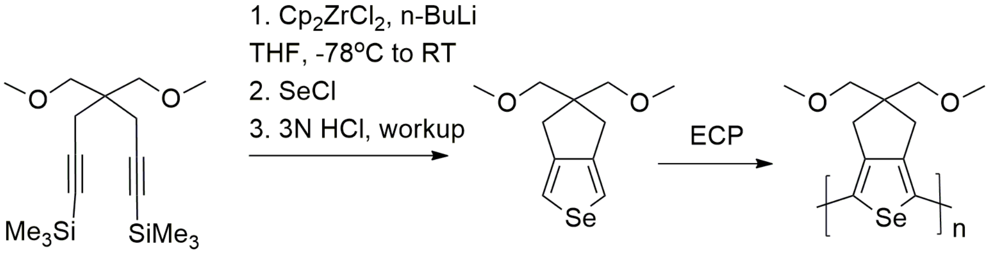
The discovery of the symmetrical poly(3,4-ethylenedioxythiophene) (PEDOT) (Figure 1.5) as a new modified polythiophene with a high chemical stability, and a high electrical conductivity in the doped form, launched numerous investigations into the development of new regiosymmetrical thiophene-based polymer systems.

The properties of conjugated polymers are modified by addition of functional groups on the thiophene units of the polymer backbone. Increase in the dimensionality of conjugated systems contributes to different superstructures in the solid states and gives rise to the multi-directional charge-transport nature. When compared to thiophene units, fused ring or annulated thiophenes shows an extended π-conjugation and more rigid structures. These features lead to the lowering of the polymer bandgap and increase the intermolecular interactions in solid films. The fused ring system is often applied in a copolymer in which electron acceptor unit coupled with an electron donor unit. This is advantageous as it enhanced double bond character between the donor and acceptor unit and stabilizes the quinoid structure of the fused ring system is stabilized [24].

The energy level of the HOMO of the donor can be increased by attaching electron donating groups (EDG), such as thiophene and pyrrole and LUMO of the acceptor is lowered, when electron withdrawing groups (EWG), such as nitrile, thiadiazole and pyrazine units are attached or introduced. This will result in decrease in the band gap of the polymer [25]. Conjugated polymers synthesized by polymerization of simple monomers often results polymers having lesser-defined molecular structures which results in the less defect-free films. To overcome this disadvantage defined conjugated oligomers are synthesized through multiple steps and are processed by more advanced techniques like evaporation to obtain well defined and more defect-free films.

1.2.3 Cyclopentaselenophene based conjugated polymers

S. Das *et al* in 2010 reported novel bis methoxy methyl substituted cyclopenta[*c*] selenophene (CPS) based conjugated polymer (Scheme 1.4). The monomer was synthesized by new approach involving reaction of 1,7-bis(trimethylsilyl)-4,4-bis(methoxymethyl)-1,6-heptadiyne with bis(cyclopentadienyl)-zicronium(IV) dichloride and *n*-butyllithium in dry THF, followed by reaction with *in situ* prepared selenium dichloride ($SeCl_2$). The polymer, polycyclopenta[*c*]selenophene (PCPS) was synthesized by electrochemical polymerization. Obtained polymer was low band gap (1.65 eV) and had good stability in oxidized state [26].



Scheme1.4 Synthesis of PCPS

In 2013, A. Bedi *et al* reported two new copolymers **P1** and **P2** having dodecyloxymethyl substituted cyclopentathiophene (DCPT) units and DCPT-based thiophene trimer coupled with dibutyl substituted bithiazole (BTz) [27]. Both polymers were synthesized by chemical polymerization using Stille coupling reactions. Both polymers **P1** and **P2** showed *p*-type character and their *p*-type mobility were measured as 0.03 and 0.052 cm^2 V^{-1} s^{-1} with current on/off ratio (Ion/Ioff) in the order of 104 and 103 respectively (Figure 1.6).

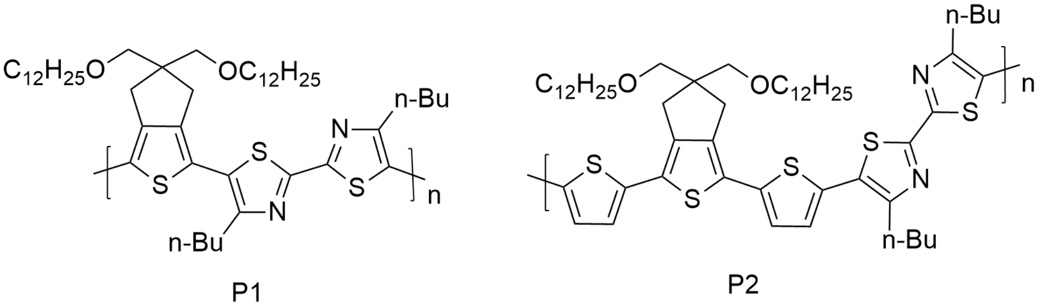


Figure 1.6 Structure of co-polymers **P1** and **P2**

1.2.4 Thieno[*3,4-c*]pyrrole-4,6-dione based polymers

Thieno[*3,4-c*]pyrrole-4,6-dione (TPD) is one of the most explored and quite promising building block used for synthesis of π-conjugated polymers [28]. The fused ring system in the TPD units contributes to the rigidity and yields favourable arrangement in the solid state. The *N*-alkylation allows good solubility and TPD consisted polymers and their material have low energy band gap which is arise from the stabilization energy acquired from the formation of quinoidal-thiophene-maleimide structure during the excited state [29]. The imide functional group of TPD effectively pulls up the electron from the thiophene ring making TPD molecules as an acceptor unit. Due to this attribute TPD is often used as co-monomer coupled with electron-rich unit forming D-A type polymers showing push-pull effect in the backbone of π-conjugated polymers [30].

The first TPD based conjugated homopolymers were reported by Nielsen *et al* [31] in 2004. The synthesized *N*-alkylated TPD and dihydro TPD polymers were relatively low molecular weight. In 2012, Leclerc group reported several TPD based homopolymers which were synthesized by using direct heteroarylation polymerization (DHAP) using 2% Herrmann's Pd alongwith tris(*o*-methoxyphenyl) phosphine [32].

In 2011, X. Guo *et al* reported TPD units based polymer [33]. The synthesized thiophene flanked TPD polymers showed good processability and exhibited low band-gap properties (1.66 eV). The synthesized polymers were used to prepare organic thin-film transistors (OTFTs) and showed remarkable hole mobility of ~0.6 $cm^2\ V^{-1}\ s^{-1}$ (Figure 1.7).

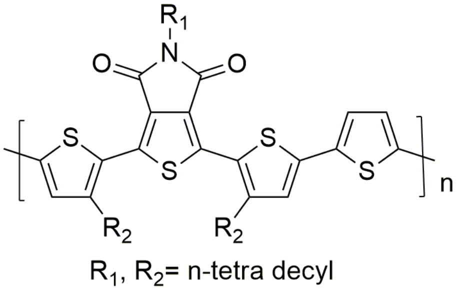
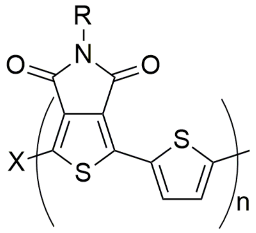


Figure 1.7 Structure of thiophene flanked TPD based conjugated polymer

T. Umeyama *et al* in 2012, reported series of novel polythiophene copolymer having *N*-alkylated TPD units coupled with thiophene units. The polymers were synthesized by Stille coupling reaction and showed (Figure 1.8). [34].



PnTPDT **n = 11, 12, 13, 18.**

Figure 1.8 Structure of TPD and thiophene based copolymer

T. Chu *et al* in 2011, reported synthesis of novel copolymer based on dithienosilole units coupled with TPD units (Figure 1.9). The synthesized polymers possess low band gap nature (1.73 eV) and showed a deep highest occupied molecular orbital energy levels (HOMO) (5.57 eV). The polymers were used as an active material in bulk heterojunction (BHJ) photovoltaic cell fabricated by blending with $PC_{71}BM$ and showed high PCE of 7.3% [35].

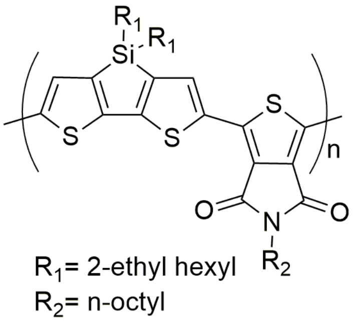


Figure 1.9 Structure of co-polymers having dithienosilole units coupled thienopyrrole-4,6-dione units

1.2.5 Benzo[*1,2-b:4,5 b'*]dithiophene (BDT) based conjugated polymers

Benzo[*1,2-b:4,5 b'*]dithiophene (BDT) based materials have numerous applications in organic electronics [36]. BDT possess large planarity coupled with its symmetric structure. These properties contribute to increases charge transportation and the rigidity of overall structure. The increase in charge mobility accounted by the facial π-π stacking of planar conjugated BDT units. Along with these solubilising subsitutents such as long alkyl chains at 4th and 8th positions not only improve the solubility of polymer but also avoids steric hindrance caused for adjacent units [37].

N. Allard *et al* reported new push-pull conjugated polymers based on BDT units and thieno[*3,4-d*] thiazole (TTz) derivatives (Figure 1.10). The polymers were synthesized by chemical polymerization using Stille coupling reactions between distannyl BDT and dibromo TTz leading to two polymers namely, PBDTTTz-1 and PBDTTTz-2. Synthesized polymers were low band gap, 1.8 and 1.7 eV respectively. Polymer PBDTTTz-1 based bulk heterojunction (BHJ) solar cells showed PCE of 1.4 % where as PBDTTTz-2 based BHJ solar cells demonstrated PCE of 1.7% [38].

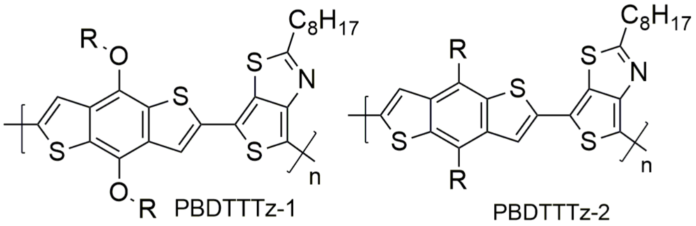


Figure 1.10 Structure of polymers, PBDTTTz-1 and PBDTTTz-2.

P. Morvillo *et al* reported synthesis of a novel copolymer (PolyS) having BDT units and alkylsulfanyl-bithiophene units. The polymer was synthesized by Stille coupling reaction and obtained polymer possesses low band gap character (1.9 eV). The synthesized polymer was used to fabricated BHJ polymer solar cells (PSCs) in combination with $PC_{60}BM$ and $PC_{70}BM$ (electron acceptors). The devices showed PCE of 2.3% (Figure 1.11) [39].

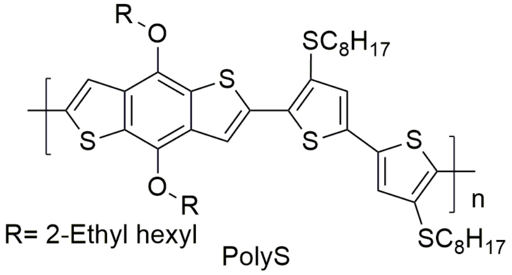


Figure 1.11 Structure of BDT and alkyl sulfanyl-bithiophene based co-polymer

D. Lee *et al* reported the synthesis of new polymer having dialkylthiobenzo[*1,2-b:4,5-b*]dithiophene (S-BDT) (Figure 1.12). The polymer S-PBDT was synthesized by chemical polymerization using Stille coupling reaction of S-BDT. Polymer possessed optical bandgap of 2.08 eV. Polymer solar cell (PSC) was fabricated using S-PBDT showed PCE of 2.75% with open-circuit voltage (V_{oc}) up to 1 V [40].

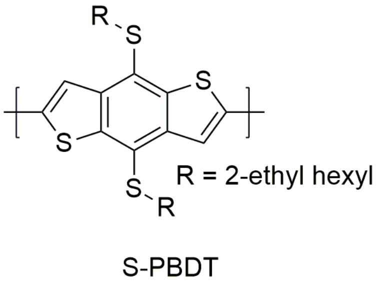


Figure 1.12 Structure of S-PBDT

1.2.6 Dithienopyrrolobenzothiadiazole (DTPBT) based conjugated polymers

In 2012, Y. Cheng *et al* reported six new copolymers having fused donor-acceptor dithienopyrrolobenzothiadiazole (DTPBT) and dithienopyrroloquinoxaline (DTPQX) units (Figure 1.13). The rigid and coplanar units of DTPBT and DTPQX were copolymerized with fluorine (F), carbazole (C) and cyclopenadithiophene (CPDT) units by chemical polycondensation using Suzuki and Stille coupling reaction to yield six polymers namely PFDTPBT, PCDTPBT, PCPDTDTPBT, PFDTPQX, PCDTPQX and PCPDTDTPQX, respectively. The BHJ device having PFDTPQX/PC$_{71}$BM (1:4, w/w) showed PCE of 3.40% [41].

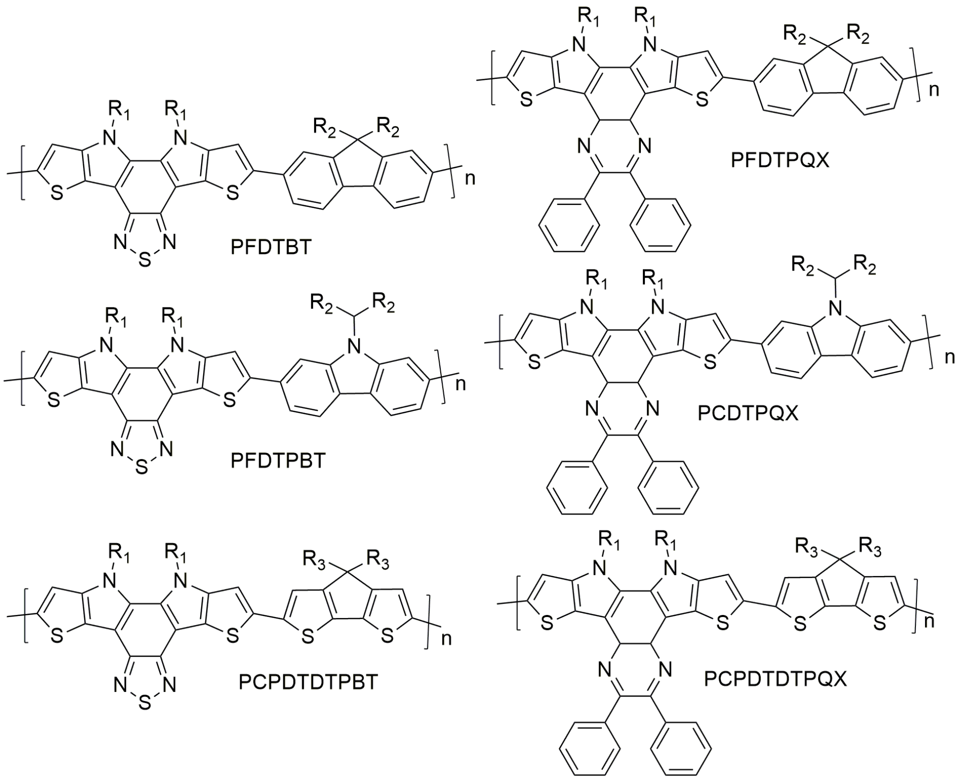


Figure 1.13 Structures of copolymers based on dithienopyrrolobenzothiadiazole (DTPBT) / dithienopyrroloquinoxaline (DTPQX) units coupled with fluorine (F), carbazole (C) and cyclopenadithiophene (CPDT) units

K. Kass *et al* in 2016, reported donor–acceptor-type ladder polymers containing *N*-dialkylated benzothiadiazolodithienopyrrole (BTDTP) units coupled with terephthalophenone derivative (Figure 1.14). Polymer was synthesized by coupling of dibromo BTDTP (BTDTP-Br) and diboronic ester-substituted terephthalophenone derivative by Suzuki reaction. Post polymerization reduction was carried out by methyl lithium and $LiAlH_4$ while ring closure was achieved in presence boron triflouride in chloroform. The obtained ladder polymers, Me-LBTDTPP and H-LBTDTPP, showed an increased Stokes shift when compared phenylene-based ladder polymers (Me-LPPP) [42].

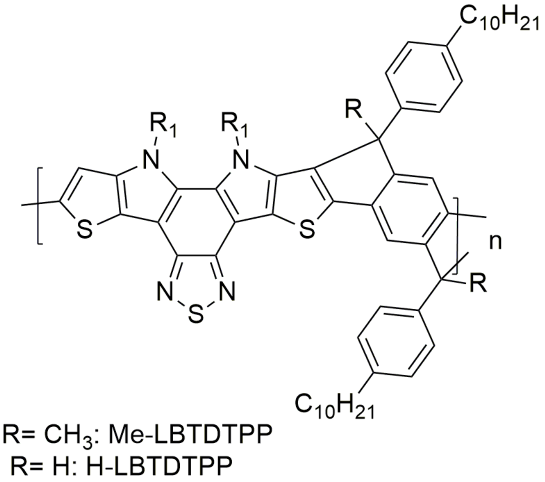


Figure 1.14 Structure of donor–acceptor-type ladder polymers

In 2017, S. Ghosh *et al* reported three polymers having dithienopyrrolobenzothiadiazole, diselenopyrrolobenzothiadiazole and dithienopyrrolobenzoselenodiazole units (Figure 1.15). Polymerization were carried out by electrochemical method and obtained polymers showed low band gap (1.36-1.67 eV) [43].

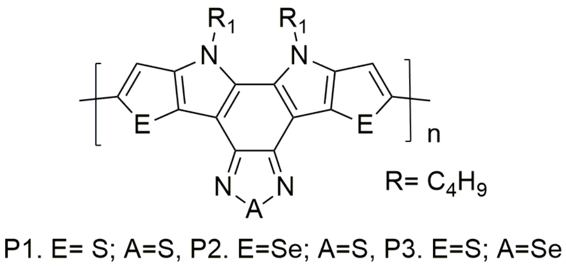


Figure 1.15 Structure of dithienopyrrolobenzothiadiazole, diselenopyrrolobenzothiadiazole and dithienopyrrolobenzoselenodiazole based polymers

1.2.7 Small conjugated molecules

Small conjugated molecules possess unique optical and electronic properties, due to which significant research interest has been focused on them across the world. Small conjugated molecules have a peculiar advantage of well-defined molecular structure. Along with this small conjugated molecules have advantages such as its simple synthesis, high purity, batch to batch reproducibility and its solubility in organic solvents which makes their effective application in organic electronics.

Fused ring system based conjugated molecules having more planar and rigid structure give them greater crystallinity. The extended conjugation acquired by fused conjugated rings system improves charge mobility [44]. Incorporation of alternating donor (electron rich units) – acceptor (electron deficient units) (D-A) units in the π-conjugated small molecules generates "push-pull" effect which have been proved extensively advantageous [45]. This push-pull effect generates intramolecular charge transfer (ICT) interaction which lowers the overall band-gap of the π-conjugated molecule. Thus, the tuning of bandgap of π-conjugated molecules can be modulated by varying a suitable donor, acceptor and linking moiety to yield desired result.

P. Pati *et al* reported synthesis of a series of D-A-D type conjugated molecules having benzooxadiazole and benazothiadiazole units symmetrically coupled with two aromatic heterols (furan, thiophene and selenophene) at 4th and 7th positions (Figure 1.16). OFET device developed from these molecules showed hole mobility about 0.08 $cm^2V^{-1}\ s^{-1}$.

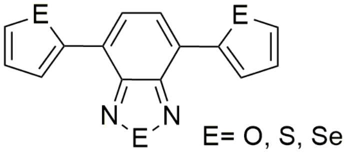


Figure 1.16 Structure of D-A-D type conjugated molecules having benzooxadiazole and benazothiadiazole units

J. Mikroyannidis *et al* reported synthesis of new small conjugated molecules having benzoselenadiazole as core unit (Figure 1.17). Synthesized conjugated molecule was low band gap (1.67 eV). BHJ solar cells based on synthesized molecule showed PCE of 3.16% [46].

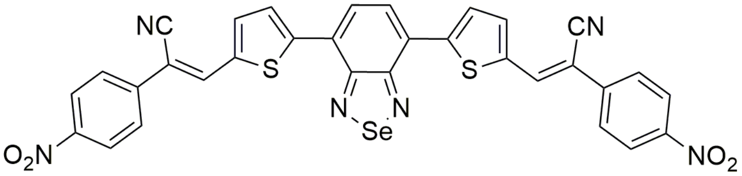


Figure 1.17 Structure of benzoselenadiazole based conjugated molecule

The wide applications of thiophene-based materials in the field of organic electronics, encourage us to synthesize conjugated molecules and to develop new methodology for the synthesis of thiophene based monomers as well as to utilised such molecules for the synthesis of conjugated polymers.

Aim and Objective

- To develop a new synthetic methodology for the synthesis of donor and acceptor molecules.
- To develop fused conjugated molecules/monomers that can be subjected to polymerization without costlier transition metal catalysts and harsh conditions in terms of temperature and pressure.
- To develop conjugated polymers having a push-pull effect and having a better matched energy levels (for efficient electron/hole transfer between all layers and the electrodes of the device), that can compete favorably with other available materials for organic electronics.
- To develop conjugated small molecules having donor-acceptor concept.

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