1.1. Introduction

In twenty-first century, conducting polymers have emerged as one of the vital materials owing to their useful optical, electronic, energy storage and mechanical properties. Initially, organic polymers have been considered as insulators. The importance of this class of materials was realized by the world scientific community when A. J. Heeger, H. Shirakawa and A. G. MacDiarmid won the Nobel Prize in Chemistry in 2000 for their research in halogen doped polyacetylene. This was the real breakthrough in the evolution of organic conducting polymers. After their pioneering work, a number of conjugated polymers were developed including polythiophene, polypyrrole, poly(paraphenylene), polyaniline, poly(phenylene vinylene), polyfluorene etc. These polymers exhibited unusual electronic properties like good conductivity, low ionization potentials, high electron affinities and low energy optical transitions, due to the delocalization of the \( \pi \) electrons over the conjugated backbone. Band theory reasonably explains the electronic structure of materials. The electronic properties of conducting polymers cannot be described well by the standard band theory, because, they are unusual and they don’t transport electrons via the same mechanism that are used to define classical semiconductors. In a conducting polymer,
mobile carriers introduced into the π conjugated backbone via doping results in electrical conductivity. This electronic phenomenon can be explained by the existence of soliton, polaron or bipolon formation. Now a days, polymeric non-linear optical (NLO) materials have attracted considerable research interest and have been the subject of intensive investigations. Polymeric NLO materials possess large second and third-order NLO properties, transparency over a broad wavelength range, ultrafast response time, high optical damage threshold, and capability to be easily processed into good optical quality thin films, offer significant advantages over the traditional inorganic materials. These properties enable them for applications in fabricating integrated optical devices, such as waveguides, electro-optic (EO) modulators and optical frequency doublers, optical signal processing devices and in holography. The thesis presents the synthesis of donor-acceptor copolymers and the experimental investigations on the photoconductivity and third-order NLO properties of the synthesized polymers.

This introductory chapter describes some fundamental principles of photoconducting polymers and NLO polymers. This chapter includes six sections. The first section, illustrates the tool box for band gap engineering to produce low band gap conjugated polymers. In the next section, different polymerization methods for obtaining the D-A copolymers are included. In the third section, the use of quantum chemical tools for designing the active layer polymers is described. Special emphasis is given to the use of Density Functional Theory. In the fourth section, fundamental principles of photoconducting polymers are included. In the fifth section, NLO effects in molecular systems are described. In the final section, aim and scope of the thesis is explained.
1.2. Band-Gap Tailoring: ‘the Tool Box’ for Low Band Gap Polymers

The considerable development of research on solar cells,14-19 light-emitting devices20-22 and organic field-effect transistors (OFETs),23-26 paved the way for the development of π-conjugated polymers with tailored optical properties. The crucial challenge in developing an ideal p-type material is to design a conjugated polymer with requisite properties. The design should be in such a way that, the polymer should possess suitable HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energy levels, high hole mobility, strong absorption ability and good film forming properties simultaneously.27 Band gap is the most important property as far as the other properties are concerned. For a linear π-conjugated system, band gap ($E_g$) can be expressed as the sum of five contributions28 (equation (1)):

$$E_g = E_{BLA} + E_{Res} + E_{Sub} + E_\Theta + E_{Int} \quad \text{................. (1)}$$

Bond length alternation (BLA), resonance effect (Res), introduction of electron-withdrawing or electron-releasing substituents (Sub), mean dihedral angle ($\Theta$) between consecutive units and intermolecular interactions (Int) are the factors offering major contribution to the magnitude of band gap (Fig. 1.1).

![Structural factors that determine the band gap of materials in linear π-conjugated systems.](image)
1.2.1. Structural Factors and Band Gap

Synthetic approaches by structural modifications (Fig. 1.2) can be expected to produce a polymer with reduced HOMO-LUMO gap. In a simple polyene system, BLA offers a major contribution, $E_{BLA}$, to the magnitude of band gap. The combined effects of electron-electron correlation and electron-phonon coupling results in the delocalization of $\pi$ electrons that can lead to a low band gap of $\sim 1.50$ eV. Therefore, a decreased BLA can lead to a reduction in HOMO-LUMO gap, i.e., rigidification of the conjugated system resulting in a fully planar conjugated structure with significantly lowered band gap values in comparison with the parent open chain system.29

The energy required for switching of aromatic form to the quinoid form is called aromatic stabilization or resonance energy. This resonance effect traps the $\pi$ electrons within the aromatic unit preventing them from delocalizing through the entire conjugated polymer backbone.30 This effect can be represented by a quantity, $E_{Res}$. For example, the insertion of double bonds into the polymeric backbone reduces the overall aromaticity of the material resulting in the reduction of band gap.31 A mean dihedral angle, ‘$\Theta$’ between consecutive units limits the delocalization of $\pi$ electrons through the conjugated polymeric backbone, leading to a high band gap. This effect can be represented by a quantity, $E_{\Theta}$. The insertion of electron-donating (donor) or electron-withdrawing (acceptor) substituents is the simple way to control the HOMO and LUMO gap of a $\pi$ conjugated system.28 This can be represented by a term, $E_{Sub}$. In the case of thiophene unit, the insertion of acceptor groups like cyano, carboxy or nitro at the 3-position of the thiophene unit results in an increased oxidation potential.32 In addition, the insertion of electron releasing groups to a conjugated system also yields
a higher energy HOMO level with reduction in band gap. It was reported that the inductive effect of simple alkyl groups lowered the oxidation potential of the thiophene ring by \( \sim 0.20 \text{ V} \).\(^{33}\) The Fifth contribution (\( E_{\text{int}} \)) to band gap involves intermolecular interactions, which have great impact on the magnitude of band gap. For example, intramolecular sulphur-oxygen interactions in EDOT-thiophene conjugated system, lead to a self-rigidification of the conjugated structure and thereby a low band gap.\(^{34}\)

![Fig. 1.2: Band gap engineering strategies in conjugated polymers.](image)

### 1.2.2. Alternating Donor-Acceptor (D-A) Groups

The D-A concept was first introduced by E. E. Havinga et al., in 1992.\(^{35}\) A regularly alternating donor-acceptor patterns in conjugated polymer results in broadening of the valence and conduction bands and hence reduction in band gap. Very low optical band gaps (\( \sim 0.5 \text{ eV} \)) have been reported for combinations of different donor groups with different
acceptors like croconic or squaric acid. For a given conjugated polymer, the HOMO, LUMO energy levels and band gap have a major role in determining the electrical and optical properties. Lowering of band gap is possible either by increasing the HOMO level or decreasing the LUMO level of the polymer or by compressing the two levels closer together simultaneously. The reduction in the band gap in D-A copolymer is explained by the hybridization concept, i.e., the HOMO level of the donor will interact with the HOMO level of the acceptor unit and the LUMO level of the donor will interact with LUMO level of the acceptor to yield two new HOMOs and two new LUMOs. The electrons rearrange themselves from their original non interacting orbitals in to the new set of hybridized orbitals of the polymer, i.e., a high lying HOMO level and a low lying LUMO level (Fig. 1.3). This results in lowering of the band gap in a D-A copolymer.

Fig. 1.3: Orbital interactions of donor and acceptor units in D-A copolymer.

1.3. Polymerization methods for D-A copolymers

A good choice of the D-A combination permits the fine tuning of band gap to the desired magnitude. Now a days, several synthetic strategies are
available for the preparation of conjugated copolymers. Most used polymerization techniques include chemical oxidative polymerization, electrochemical polymerization, Suzuki polymerization and Stille polymerization. Among the different techniques, transition metal-catalyzed cross-coupling reactions have been used as powerful synthetic strategy in copolymer synthesis. The most generally used transition-metal catalysts are palladium or nickel based complexes. The organometallic nucleophiles supported reactions are Stille (stannyl), Kumada-Corriu (grignard reagents), Suzuki-Miyaura (boron reagents) or Sonogashira (copper). Catalytic cycle of transition-metal catalyzed reactions is shown in Fig. 1.4. The first step is the formation of organo palladium species by the oxidative addition of palladium to the halide. Second step is the formation of an intermediate via transmetallation reaction with the organometallic nucleophiles. Final step is the reductive elimination of the desired product which restores the original palladium catalyst and completes the catalytic cycle. These polymerization mechanisms normally follow a step-growth mechanism, and are still the most suitable choice for the synthesis of alternating copolymers.

![Fig. 1.4: Catalytic cycle of transition-metal catalysed reaction.](image)
1.3.1. Kumada-Corriu reaction

Most of the D-A polymers are synthesized through metal-catalyzed polycondensation reactions based on Suzuki, Kumada or Stille coupling reactions. These polymers usually possess broad molecular weight distribution, in which all the end groups of the monomers and oligomers in the reaction mixture react equally with one another. To attain better properties of the polymers, synthesis of polymers with controlled molecular weight and low polydispersity is very important. Compared to step-growth method, the catalyst-transfer Kumada coupling polymerization can often be used to afford polymers with high molecular weight and narrow molecular weight distribution under relatively undemanding conditions.

![Scheme 1: Synthesis of polycarbazoles (P1 & P2) by catalyst transfer Kumada coupling.](image)

Recently, H. Wen et al., have prepared well-defined polycarbazoles with moderate molecular weight and low polydispersity index of 1.18 via catalyst-transfer Kumada coupling polymerization (Scheme 1).
Scheme 2: Synthesis of P3HT-b-PCPDT block copolymer (P3) by catalyst transfer Kumada coupling.45

Also, a one-pot synthesis of P3HT-b-PCPDT (P3) block copolymer by Kumada catalyst transfer polymerization was reported by P. Willot et al., (Scheme 2).45 F. Pammer have synthesized poly(4-alkylthiazole), highly head-to-tail regioregular material with a number average molecular weight significantly greater than 3.0 kDa via Kumada-coupling polycondensation of reversed monomers (Scheme 3).46

Scheme 3: Synthesis of poly(4-alkylthiazole) (P4) by Kumada-coupling polycondensation.46

1.3.2. Suzuki-Miyaura Coupling Reaction

Suzuki reaction is a C-C coupling reaction where the coupling partners are a boronic acid with a halide catalyzed by a palladium (0) complex.47-49 It was first reported in 1979 by Akira Suzuki and he shared the Nobel Prize in Chemistry in 2010 with R. F. Heck and Ei-ichi Negishi for their efforts for the discovery and development of palladium-catalyzed cross-coupling reactions in organic synthesis.50
Scheme 4: Synthesis of poly(fluorene-co-quinoxaline) by Suzuki coupling.  

Recently, S. Jo et al., have reported the preparation of poly(fluorene-co-quinoxaline), via conventional Suzuki cross-coupling polymerization as shown in Scheme 4. S. Song et al., have synthesized new conjugated polymers with 1,4-diphenylpyrrolo[3,2-b]pyrrole-2,5-dione, thiophene and carbazole using Suzuki polymerization (Scheme 5). A photovoltaic device was fabricated using a blend of these polymers with PCBM and showed 1.42 % efficiency.

Scheme 5: Synthesis of copolymer with 1,4-diphenylpyrrolo[3,2-b]pyrrole-2,5-dione, thiophene and carbazole.
Also, S. M. Park et al., have synthesized low band gap polymers with dithienylquinoxaline moieties and 6H-phenanthro[1,10,9,8-cdefg]carbazole via the Suzuki coupling reaction (Scheme 6).\(^5\)

![Scheme 6: Synthesis of dithienylquinoxaline-phenanthro[1,10,9,8-cdefg]carbazole copolymer using Suzuki coupling.\(^5\)](attachment:Scheme_6.png)

**1.3.3. Stille Cross-coupling Reaction**

The Stille coupling is a versatile C-C coupling reaction between stannanes and halides or pseudohalides in organic synthesis. Recently, W. Cheng et al., have reported new low band gap conjugated copolymers bearing benzo[1,2-b:4,5-b']dithiophene as donor moiety and tetrazine as acceptor by Stille cross-coupling polymerization (Scheme 7).\(^5\)
Chapter 1

Scheme 7: Synthesis of benzo[1,2-b:4,5-b']dithiophene-tetrazine donor-acceptor copolymers by Stille coupling. \(^{54}\)

Similarly, T. -L. Wang et al., have used Stille coupling reaction to copolymerize dithienothiophene and fluorenone (Scheme 8). \(^{55}\)

Scheme 8: Synthesis of dithienothiophene-fluorenone copolymer by Stille coupling. \(^{55}\)

1.3.4. Sonogashira Reaction

The Sonogashira coupling reaction is one of the most widely used methods for the cross-coupling of vinyl or aryl halides with terminal alkynes. The Sonogashira cross-coupling reaction was first reported by K. Sonogashira, Y. Tohda, and N. Hagihara in 1975. \(^{56}\)
Introduction

Scheme 9: Synthesis of benzodithiophene based poly(aryleneethynylene)s by Pd-catalyzed Sonogashira coupling reaction.

Scheme 10: Synthesis of thienopyrazine based poly(heteroaryleneethynylene)s by palladium catalyzed Sonogashira reaction.
Recently, S. Wen et al., have synthesized benzodithiophene-based poly(aryl-eneethynylene)s via Pd-catalyzed Sonogashira coupling reaction (Scheme 9). Bulk heterojunction solar cell with PCBM showed power conversion efficiency of 0.85 and 2.40 %. R. S. Ashraf et al., have also reported thienopyrazine based low band gap poly(heteroaryl-eneethynylene)s, synthesized via palladium catalysed Sonogashira reaction (Scheme 10). The polymers showed about 2 % efficiency under illumination.

1.3.5. Heck Coupling Reaction

The palladium-catalysed Mizoroki-Heck reaction is one of the most successful routes for the vinylation of aryl/vinyl halides. The first intermolecular Heck reaction was reported by Heck in 1972. S. J. Chen et al., synthesized alternating copolymers of electron-rich 1,4-divinyl-2,5-dioctyloxybenzene and electron-deficient 5,8-(2,3-dipyridyl)-quinoxaline through Heck reaction (Scheme 11).

Also, L. Huo et al., have reported the synthesis and photovoltaic properties of alternating copolymers of electron-rich arylamine/dialkoxyphenylene and electron-deficient 2,1,3-benzo thiadiazole using palladium acetate as catalyst by Heck reaction (Scheme 12).
1.3.6. Direct Arylation Reaction

Generally, reductive polymerization via GRIM (grignard metathesis) is more expensive method compared to oxidative polymerization. It requires stringent polymerization conditions; it is irreversible and sensitive to functional groups. Although the reductive polymerization is having major disadvantages compared to oxidative polymerization, it yields better quality materials in terms of their electrochemical properties. Recently, A. Kumar et al., have reported a new single step reductive polymerization method via direct C–H arylation which uses less stringent polymerization conditions, inert to the presence of functional groups and is economically viable. They have reported single step reductive polymerization of ProDOT derivatives which is amenable for scale-up and is compatible with functional side chains (Scheme 13).
More recently, M. Wakioka et al., have introduced another highly efficient catalyst for the synthesis of alternating copolymers with thieno[3,4-\(c\)]pyrrole-4,6-dione units via direct arylation polymerization method (Scheme 14).\textsuperscript{63}

Scheme 13: Synthesis of ProDOT copolymers using direct arylation.\textsuperscript{62}

Scheme 14: Synthesis of alternating copolymers with thieno[3,4-\(c\)]pyrrole-4,6-dione and thiophene copolymers.\textsuperscript{63}
S. J. Choi et al., have reported microwave-assisted polycondensation via direct arylation of 3,4-ethylenedioxythiophene with 9,9-dioctyl-2,7-dibromofluorene (Scheme 15).\textsuperscript{64}

\textbf{Scheme 15: Synthesis of EDOT-fluorene copolymer using direct arylation.\textsuperscript{64}}

\textbf{Merits of direct arylation}

This method has several advantages,\textsuperscript{62} some of which are

1) Avoids the use of tributyl tin and boronate esters
2) Economically viable
3) No need of dry solvent
4) Relatively high yield
5) Inert to the presence of functional groups
6) Less stringent polymerization conditions

\textbf{1.4. Quantum-chemical calculation of electronic structure of conjugated polymers}

The most important task of conjugated polymer research is to find a suitable low band gap polymer which possesses optimal property for device applications. Normally, polymers are synthesized and their properties are measured. This procedure is obviously very expensive. Economically viable and safe procedure is to calculate the electronic structure with a good approximation using quantum chemistry tools and eliminate unsuitable
molecules before synthesis. However, such calculations require large CPU time; they are certainly much cheaper than the conventional experimental research. Theoretical studies will help to establish the structure-property relationship of conjugated polymers. Hence it plays a major role in better understanding of the structure dependent variables and helps to identify the strategies for effective band gap control. Two kinds of theoretical approaches are available to calculate the electronic structure and properties of a conjugated polymer. The first approach is called the oligomer approach. Several researchers have used this oligomer approach to find band gaps of conjugated polymers. The important feature of this method is to assess the physical properties of the oligomers as a function of progressively increasing size, until convergence is reached. The second one is based on the standard solid state methods using Born–Karman PBC (periodic boundary condition), bloch functions, and translational symmetry called periodic boundary condition approach. The PBC-DFT method was implemented in the Gaussian 03 and Gaussian 09 quantum chemical codes. In order to get good agreement with experimental data, hybrid exchange correlation functional is widely used in the PBC/DFT formalism. Commonly employed hybrid DFT methods include Becke’s three parameter hybrid functional using the Lee-Yang-Parr (LYP) correlation functional (B3LYP). Recently, B. G. Janesko et al., have reported good agreement between B3LYP and experimental band gaps for semiconducting polymers in the theoretical study of organic polymers. More Recently, C. -K. Tai et al., have demonstrated the use of PBC-DFT method to determine geometric and electronic structures and the corresponding energies of polythiophene (PTH) and its derivative systems (PTs). They used B3LYP functional, and the
6-31G(d) basis set in their studies and the results showed good agreement with experimental data. T. M. Pappenfus et al., have performed DFT calculations on a series of D-A copolymers using the oligomer approach and periodic boundary conditions. They have demonstrated that the two methods agree well with one another and correlated with experimental data in a nearly identical manner. Recently, Heyd-Scuseria-Ernzerhof (HSE06) functional incorporating a screened Hartree-Fock interaction has been introduced which is more computationally effective than traditional hybrid functional, B3LYP. In the present work, we have used Local Spin Density Approximation (LSDA), B3LYP and HSE06 in combination with 6-31G basis set for calculating the properties of the D-A conjugated polymers.

1.5. Photoconductivity

An increase in electrical conductivity when a material is irradiated with electromagnetic radiation of appropriate energy is termed as photoconductivity. Photogeneration of carriers in polymers is carried out by a multi-step process. The initial process is the absorption of photon and this absorbed energy leads to the formation of excited state, which is stable for a specific life time. The excited state has high electric dipole moment due to charge separation; this is called charge transfer (CT) state. If undisturbed, the excited species may relax back to initial state together with the release of absorbed energy as photon of light. It can also undergo a non-radiative relaxation as thermal energy dissipation within the material. The bound pair can be either separated by thermal environment or by an applied electric field. The Goliber and Perlstein model described the creation of the CT state through the generation and diffusion of exciton. An exciton
can also be considered as a species with absorption spectrum different from the molecule in the ground state and show fluorescence and stimulated emission. The exciton dissociates at interfaces, impurity sites with asymmetric ionization potentials or it can be dissociated by application of strong electric field.

The second requirement for photoconductivity is the transport of generated charge carriers through the medium. In organic semiconductors, charge transport proceeds via hopping within a positional disorder and energetic disorder system of localized states. The terms positional and energetic disorder implies that the distance between hopping sites and the energy required to hop from one localized state to the other, vary significantly. Usually the carrier mobility is low and is in the range $10^{-2}$ to $10^{-8} \text{ cm}^2/\text{Vs}$ and carrier mobility in polymers can be determined using the time of flight (TOF) technique. According to Gill's model, the temperature and field dependence of mobility must be $\log \mu \propto 1/T$ and $\log \mu \propto E^{1/2}$. Whereas, according to Bassler model, the temperature dependence has the form $\log \mu \propto 1/T^2$ and field dependence $\log \mu \propto E$. In polymers, addition of molecules with low ionization potential than the polymer host will lead to hole trapping. Holes will remain trapped at these locations until an electron from a neighbouring electron rich unit gains sufficient energy and move to following trap. At moderate number densities of sensitizers, such trap states can form alternate transport levels.

In photoconductors, electrons and holes are produced by the irradiation of light, which can be separated under an electric field of required magnitude and permit transport towards the appropriate electrode.
In most amorphous organic media, hole transport is most significant. A hole (an electron vacancy) can move through the material while the negative charge remains trapped and bound to the site of creation, which is therefore an anion. When a photoconductor is irradiated with suitable radiation, carrier generation and recombination will take place. After reaching equilibrium, the resultant photoconductivity is given by equation (2):$\sigma_{ph} = G \tau e \mu$ .................................................. (2)

where, ‘G’ is the rate at which carriers are photogenerated within the photoconductor, ‘\( \tau \)’ is the average time between generation and recombination of a carrier (recombination time), ‘e’ is the electronic charge and ‘\( \mu \)’ is the mobility, the velocity of the carrier in unit electric field. Thus, the steady state photocurrent density is given by equation (3):$J_{ph} = \sigma_{ph} E = G \tau e \mu E$ ................................................ (3)

where, ‘E’ is the electric field applied to the photoconductor.

Photoconductive sensitivity, change in conductivity per incident light intensity is given by equation (4):$S = \frac{i_{ph} L}{P_0 A V}$ .................................................. (4)

where, ‘\( i_{ph} \)’ is the photocurrent, ‘L’ is the thickness of the sample, ‘\( P_0 \)’ is the light power density, ‘A’ is the illuminated area and ‘V’ is the applied voltage. Mostly used photoconducting polymers absorb only in the ultraviolet region and thus suitable sensitizers are required to extend their spectral sensitivity to the desired region.
1.5.1. Role of Sensitizer

Most of the polymers do not absorb strongly near the operating wavelength region owing to their wide band gap. A wide gap between HOMO and LUMO energy levels leads to optical absorption near the ultraviolet region of the spectrum. So in polymers, charge generation at the wavelength of interest is brought about by the addition of small concentrations of molecules with appropriate HOMO and LUMO levels compared to the host polymer. Lower HOMO and LUMO levels than the host matrix are chosen for this purpose. Sensitizer molecules are used to extend the photocurrent generation ability of a given polymer to longer wavelengths. Generally used sensitizers include azo dyes, perylene dyes, squaraines, phthalocyanines, and thiapyrylium salts. The charge-transfer (CT) complexes formed between a donor like polymer and an acceptor like sensitizer leads to longer wavelength absorption. The well-known complex, PVK:TNF is shown in Fig. 1.5.

![Fig. 1.5: The most well-known charge transfer complex, PVK:TNF system.](image)

The commonly employed electron acceptors are summarized in Fig. 1.6. Among the different electron acceptor molecules, the most important and soluble sensitizer, PC61BM ([6,6]-phenyl C61-butyric acid methyl ester) has been subjected to intense studies. The HOMO and LUMO energy level
values of PC$_{61}$BM are -3.7 and -6.1 eV, respectively. Different optoelectronic devices have been demonstrated based on PC$_{61}$BM-semiconducting polymer heterojunctions together with better device performance.$^{95-102}$

1.5.2. Steady state photocurrent measurement

Steady state photocurrent measurement involves measuring the steady state direct current (DC) developed within sandwich cell in the presence of light and in the dark. In this, a Keithley 236 Source Measure Unit is used. A DC voltage is applied to the sandwich cell placed in the dark and the current is measured with respect to time. After the stabilization of dark current developed in the cell, light is allowed to fall on the ITO surface. As a result of photoinduced change in conductivity, the current rises suddenly and approaches a steady state. After reaching the steady state, light is cut off and the measurement of current is continued. If $I_D$ and $I_L$ are the steady state current values, before and after illumination, respectively, the photosensitivity of the device can be calculated using the equation (5):

$$I_{ph} = \frac{(I_L - I_D)}{I_D}$$

(5)
The experimental arrangement is shown schematically in Fig. 1.7.

![Experimental setup schematic](image)

**Fig. 1.7**: The experimental setup for steady state photocurrent measurement.

### 1.6. Non-linear Optical Effects

Non-linear optical (NLO) processes in $\pi$-conjugated molecular systems have attracted considerable research interest because of their wide applications in opto-electronic devices. As the field progressed towards technological applications, research started to focus on developing high-performance materials that comply with device applications. Davydov et al., have first reported the second harmonic generation (SHG) in organic molecules in 1970. This discovery led to a new concept of molecular engineering, i.e., to synthesize new organic materials for NLO studies. NLO research is mainly focused on the second and third-order properties. Of which third-order NLO property of donor-acceptor conjugated copolymer is the current area of interest. An ideal NLO material should have fast optical response time, wide phase matchable angle, large non-linear figure of merit, flexibility for molecular design and morphology, processability into crystals or thin films, ease of
fabrication, nontoxicity, optical transparency, good environmental stability and high mechanical and thermal stability. Organic NLO materials can fulfil many of these primary requirements in comparison with inorganic materials. Third-order NLO effects in organic molecules is mainly due to strong donor-acceptor intramolecular interaction, i.e., strong delocalization produces NLO properties. The optical non-linearities of organic materials are governed by the nature of $\pi$-bonding sequence and the conjugation length. The non-linear response of a material when the material interacts with the electric field of light is termed as NLO effect. In the presence of intense light such as laser, the charge distribution in a medium gets modified under the influence of strong electric field, and the medium gets polarized. At the microscopic level, dipole moment dependence on the electric field (E) is given by equation (6):

$$\mu_i = \mu_i(0) + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \ldots \ldots \ (6)$$

where, ‘$\alpha$’, ‘$\beta$’ and ‘$\gamma$’ are the polarizability, first hyperpolarizability and second hyperpolarizability respectively, which determines the strength of the NLO effects in molecular systems.

Organic materials possessing a large third-order NLO response have attracted significant attention for the past two decades, because of their potential applications in optical switching, optical limiting, three-dimensional (3D) lithographic microfabrication, 3D fluorescence imaging and 3D optical data storage. In 1989, M. S. Bahae et al. have introduced z-scan method to determine third-order non-linear optical coefficients of materials. Here, the transmittance of the material is measured as the material is moved along the propagation path of a Gaussian beam in
z-direction using an aperture or without an aperture.\textsuperscript{120} In this method, sign as well as magnitude of non-linear coefficient can be easily deduced from transmittance curve. This technique can be used for measuring both non-linear absorption and non-linear refraction coefficients.\textsuperscript{120}

1.6.1. Non-linear Absorption

Here the absorption process involves the change in absorption of a material as a function of input fluence.\textsuperscript{122} At higher intensities, the probability of absorption of more than a single photon before relaxing down to the ground state can be increased. Non-linear absorption can be due to two phenomena; firstly, the reverse saturable absorption (RSA), which leads to increase in absorption of the material with increase in laser intensity and secondly, the saturable absorption (SA); which leads to decrease in absorption of a material, as the laser intensity increases.\textsuperscript{123,124} SA is observed when excited state absorption is lower than the ground state absorption, which leads to an increase in the transmission through the material as the input intensity is increased. While, RSA is observed when excited state absorption is greater than the ground state absorption, which leads to a decrease in the transmission through the material as the input intensity is increased.\textsuperscript{125} RSA generally represents positive absorption induced either by excited state absorption (ESA) or by a two photon absorption (TPA) process, which requires intensity of the order of $\sim 10^8$ W/cm\textsuperscript{2}.\textsuperscript{106}

1.6.1.1. Two Photon Absorption

This phenomenon refers to the transition of electrons from the ground state to excited state by simultaneously absorbing two photons from the
incident radiation. Here, the non-linear absorption is directly proportional to the square of the intensity of the incident radiation (I) and is shown in equation (7):\textsuperscript{122}

\[
\frac{dI}{dz} = -\alpha I - \beta I^2 \quad \text{.......................................................... (7)}
\]

Here, ‘\(\alpha\)’ and ‘\(\beta\)’ are the linear absorption coefficient, two photon absorption coefficient, respectively.

1.6.1.2. \textit{Multiphoton Absorption}

Multiphoton absorption process involves the simultaneous absorption of ‘\(n\)’ photons from the incident beam. The absorption of (n+1) photons from a single optical beam can be written as equation (8):\textsuperscript{122}

\[
\frac{dI}{dz} = -\left(\alpha + \gamma^{(n+1)} I^n\right) I \quad \text{.................................................. (8)}
\]

where, ‘\(\gamma^{(n+1)}\)’ stands for (n+1) photon absorption coefficient.

1.6.1.3. \textit{Excited State Absorption}

Semiconductors and polyatomic molecules possess a high density state near to their excited states.\textsuperscript{122} Therefore, before the photon relaxes to the ground state, it absorbs more number of photons and gets promoted to excited state. This process is referred to as excited state absorption.\textsuperscript{122}

1.6.2. \textit{Optical Limiting}

Optical limiters are those devices which are transparent to light at low input fluences, but become opaque at higher input intensities. This device finds application in optical pulse compression, pulse shaping and protection of eyes and sensitive optical devices from laser induced damages.\textsuperscript{126,127} The
Chapter 1

criteria required for a material to act as a promising optical limiter is: high linear transmittance throughout the sensor band width, low optical limiting threshold, stability, etc. An ideal limiter should exhibit a linear transmission up to input threshold fluence called optical limiting threshold, which varies from material to material. Optical limiting threshold mainly depends on non-linear absorption coefficient ($\beta$) of a material.

1.6.3. Non-linear refraction

Non-linear refraction (NLR) is the change in refractive index of a medium when a material is exposed to electromagnetic radiation of suitable frequency. This property has been utilized in various applications like optical switching, logic gates, communication systems, data processing, non-linear spectroscopy and optical limiting devices. The dependence of NLR on intensity of illumination ($I$) is given by equation (9):

$$n = n_0 + n_2 I$$

where, ‘$n_0$’ is the linear refractive index and ‘$n_2$’ is non-linear refraction coefficient. The NLR property of a material could be due to Raman induced Kerr effect, electronic polarization, thermal contributions, molecular orientation effects and photorefractive effects.

1.6.4. z-scan technique

This is a simple single beam technique designed and developed by M. S. Bahae et al., to measure the sign as well as magnitude of non-linear absorption and non-linear refraction. Principle used in this technique is spatial beam distortion. It offers high sensitivity and simplicity than non-
linear interferometry, degenerate four wave mixing, ellipse rotation and beam distortion measurements. It allows to determine the third-order NLO properties of solids, liquids as well as liquid crystals. If transmitted light is measured through a finite aperture placed in the far field as the sample is moved in z-direction, is referred to as closed aperture (CA) z-scan technique. However, if the transmitted light is measured without an aperture, then it is referred to as open aperture (OA) z-scan technique. Here the output is sensitive only to non-linear absorption of a material. CA and OA z-scan methods yield the real and imaginary parts of non-linear susceptibility, respectively.120,121

The experimental setup for single beam z-scan is given in Fig. 1.8.

![Fig. 1.8: Schematic representation of the experimental setup for z-scan technique.](image)

1.6.4.1. Open Aperture (OA) z-scan

In this method, non-linear absorption of a material is measured. If the material is exhibiting NLO absorption like two photon absorption, the material can behave as either reverse saturable absorber (transmission is
minimum at focal point) or saturable absorber (transmission is maximum at the focal region).\textsuperscript{120}

1.6.4.2. Closed Aperture (CA) z-scan

The basis of CA z-scan is the self phase modulation and self refraction effects. In CA z-scan technique, sample behaves like thin lens of variable focal length due to change in refractive index at each position ($n = n_0 + n_2 I$).\textsuperscript{122} If the material with negative non-linear refractive index is brought closer to focus, the beam irradiance enhances, which lead to self-lensing in the sample. A negative self-lensing prior to focus will tend to collimate the beam, resulting in beam narrowing at the aperture which causes an increase in transmission (peak). As the sample passes the focal plane to the right in $z$-direction, the same self-defocusing enhances the beam divergence causing a beam broadening at the aperture, and thus a decreased transmission (valley). A peak in the transmittance curve followed by valley in the transmittance curve reveals the negative non-linearity of a material. Whereas, positive non-linear refraction gives valley-peak configuration.\textsuperscript{120}

**Advantages and disadvantages of z-scan technique:**\textsuperscript{120}
This technique has several advantages, like:

a) Simplicity and ease of interpretation.

b) Possibility of isolating the refractive and absorptive parts of non-linearity.

c) Similarity between z-scan and optical limiting geometry.

d) Sign and magnitude of non-linearity can be measured simultaneously.
Introduction

- Can resolve a phase distortion of $\lambda/300$ indicating a high degree of sensitivity.

Disadvantages are,

a) Stringent requirement of high quality Gaussian TEM$_{00}$ beam for absolute measurements.

b) Determination of the non-linear coefficients is entirely dependent on energy content, spatial and temporal profiles, and laser source stability.

1.7. Aim and Scope of the Thesis


2) Synthesis of the copolymers using direct arylation and Suzuki coupling methods.

3) Explore the application of conjugated polymers as active layer in photoconducting devices.

4) Explore the application of conjugated copolymers in non-linear optical devices.
Chapter 1

References


Chapter 1


Introduction

[50] Nobelpri... The Nobel Prize in Chemistry 2010. Nobel Prize


Electronics, 2013, 14, 2124.


[58] R. S. Ashraf, M. Shahid, E. Klemm, M. Al-Ibrahim, S. Sensfuss,


Chem., 2007, 45, 3861.


Chapter 1


Introduction


Chapter 1


