Chapter 1

Introduction


1.1. **Introduction to Organic Semiconductors**

Ever since the discovery of synthetic polymers in early 1900's, polymers are emerging as important class of materials, just after steel and widely find applications from household items to frontier high technologies. In general, commercial polymers are belonging to engineering thermoplastics and they can be easily processed into desire objects via melt or solution processing techniques. Polyethylene, polyesters, polyamide, polystyrene and polyacrylcs are some classical examples for the commercially important engineering thermoplastics. Generally, most of the polymers are insulators and largely employed as switches, encapsulating materials for metal wires or body panels of electronic items such as computers, transistors and washing machine to prevent from electrical shock in daily life. According to band theory, materials are classified into three types - conductors, semi-conductors and insulators depending upon the energy gap between their valence and conduction bands.\(^1\)

The band formation occurs when the bonding molecular orbitals or \(\pi\)-orbitals merge to form the valence band (VB) and the antibonding molecular orbitals or \(\pi^*\)-orbitals form the conduction band (CB). When electric field is applied, the free electrons get excited and move from the VB to the CB, and hence passage of electrical current occurs. The highest occupied orbital of the VB is known as HOMO and the lowest unoccupied orbital of CB is known as LUMO. In conductors, the VB and CB bands are virtually mixed and there is almost no energy gap. Metals such as Copper and Aluminum are good example for conductors and largely employed as electricity transmitters. Silicon and Germanium are good examples for intrinsic semi-conductors and they possessed a small band gap of less than 2 eV. They can be converted to active semi-conductors by giving thermal energy or chemical doping process using either tri- or penta-valent elements. These semiconducting materials are widely employed as diodes and for other applications in electronic industry. Polymers are belonging to the third category, i.e. insulators, due to the presence of large energy gap (more than 10 eV).\(^2\) Therefore, neither thermal effect nor chemical
doping can induce any transition of electrons from VB to CB for conducting electricity, polyethylene and polyvinylchloride (PVC) are good examples.

The incredible discovery of electrical conductivity in polyacetylene by three eminent scientists Alan J Heeger, Alan MacDiarmid, and Hideki Shirakawa in 1977 has led to the exploration of conjugated polymers for variety of electrical and opto-electronic applications. They were awarded Nobel Prize for Chemistry in 2000 for their discovery and development of conducting polymers. The doping of polyacetylene (prepared from the hydrocarbon acetylene) using iodine can be represented as in scheme 1.1. This accidental discovery provides insights into the nature of conjugated polymers and their electrical conductivity, and opened up new fields of chemical and physical research.

\[
\text{Scheme 1.1. Doping of polyacetylene using iodine}
\]

Shortly after the discovery of conductive polyacetylene, \(\pi\)-conjugated systems were explored in different area of applications. Among the two major groups of applications, one category considers the conductivity as the main property while the second group give importance to their electro-active properties. The first set of applications includes diodes, transistors, aircraft structures, printed circuit boards, artificial nerves conducting adhesives, electromagnetic shielding etc. The second classification gave way to molecular electronics, displays, sensors, rechargeable batteries etc. where electro-optical properties of the polymers play the major role. The extended \(\pi\)-conjugation in conducting polymers is highly susceptible to chemical or electrochemical oxidation or reduction that will alters the electrical and optical properties of the polymer chain. Because of the reversibility of these processes one can control
Chapter 1

Introduction

the opto-electric properties with a great deal of precision. By doing this way it is able to switch the polymers from a conducting state to an insulating state.

Among the above mentioned applications, conducting polymers for electroluminescent (EL) device applications is an active area of research. Since this thesis is mainly determined to produce polymers with good photoluminescence and electroluminescence property, it is necessary to understand the basic phenomenon of electroluminescence (EL) and also about the electroluminescence polymers. Therefore, this chapter mainly describes the electroluminescence in conjugated polymers, especially in poly(phenylenevinylene)s, their luminescence properties and different approaches to enhance the luminescence behaviours.

1.2. Electroluminescent Polymers

Electroluminescence is an electro-optical phenomenon—"the generation of light by electrical excitation"—is widely seen in a range of semiconductors. The first report of organic electroluminescence was from Pope et al. in the 1960's who prepared an electroluminescent device using single crystals of anthracene. Helfrich and Schneider were made similar studies with liquid electrodes which also require high voltages for device emission. After that, there have been numerous reports of electroluminescent phenomena in a range of conjugated materials.

The early studies were completely based on molecular crystals; however their limited application due to the high voltage for charge injection and the reactivity of some metals used as the negative electrodes urged the researchers to think about devices with thin films. Robert et al., Vincett et al. and many others have manifested that more sophisticated device structure can be constructed by the use of vacuum deposited non-crystalline films of conjugated molecules that can work with high efficiency. In 1987, Van-Slyke and Tang demonstrated electroluminescence from a two-layer sublimed molecular film devices comprising of an aromatic diamine and an emissive layer of 8-hydroxyquinolinealuminium (Alq3). Since then a great deal of developments

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of these devices occurred and high performance devices were explored by several researchers including Tang et al. and Adachi et al.\textsuperscript{18-22} Subsequently, after the success of fabricating small conjugated molecular devices, in 1990 Richard Friend and Andrew Holmes have discovered the first polymer based electroluminescent device from poly (p-phenylene vinylene), when spin casted on an indium tin oxide (ITO) coated glass.\textsuperscript{23-26} For a polymer to be electroluminescent, it should satisfy the following two conditions, that is, (i) it should be fluorescent and, (ii) it should conduct electricity (see scheme 1.2).

\begin{center}
\textbf{Scheme 1.2. The conditions for a polymer to show electroluminescence.}
\end{center}

Studies have shown that the phenomenon of electroluminescence requires three processes, (i) injection of electrons from cathode, (ii) injection of holes from the anode and, (iii) the capture of holes and electrons at the emissive layer (so-called recombination). The final step is the radiative decay of the excitation energy resulting in luminescence process.\textsuperscript{7} The basic structure and mechanism for a polymer light emitting (electroluminescent) device is given in scheme 1.3.

\begin{center}
\textbf{Scheme 1.3. Typical design of a PLED}
\end{center}
Chapter I

Introduction

The basic device architecture consists of a light emitting polymer film, an optically transparent anode and a metallic cathode, together with an AC or DC power source, which may be operated in a continuous or intermittent mode. The anode is most often indium/tin oxide (ITO) coated glass, while the cathode is typically a low work function metal such as aluminium, calcium or magnesium. The polymer may be deposited on the ITO by spin or dip coating from solution, and is of the order of 100 nm thick. The cathode metal is evaporated onto the polymer film in vacuum.

The working of PLED can be better explained by the band scheme represented in scheme 1.4. The cathode injects electrons in the conduction band of the polymer ($\pi^*$ state), which corresponds to the LUMO, and the anode injects electrons to the valence band ($\pi$ state), which corresponds to the HOMO. The injected charges (polarons) can travel from one electrode to the other, be annihilated by certain processes such as multiphonon emission, Auger processes, or surface recombination.

Scheme 1.4. Band scheme of a single layer light emitting diode

The physics of organic LEDs involves the formation of a neutral species called excitons which occurs mainly by the recombination of electrons and holes. The injection and charge transport through the emissive layer is easier when the difference between the work function of the electrodes and the polymer layer is very small. The balance of the charge carriers is very
important for high efficiency device. Due to the difficulty in attaining the current balance in single-layer device (with one emissive layer, as shown in scheme 1.4), double-layer structures has been used widely. In this case, either a hole transporting or electron transporting layer is used in addition to the semiconducting emissive layer. The next crucial step in the device operation is the electron – hole recombination process which occurs by the injection of electrons into the conduction band and holes into the valence band. The recombination produces excited state species and the excitons formed can be in the singlet or triplet state according to the spin statistics. Because only singlets can decay radiatively and there is only one singlet for three triplet states, the maximum quantum efficiency (photons emitted per electrons injected) attainable with fluorescent polymers is theoretically 25%.

The growth of LED technology was very rapid after the discovery of polymer based LEDs. The survey showed that inorganic and organic crystals were given way to polymeric materials since they have a lot of significant properties like colour tuning ability, low cost, mechanical stability, environmental stability, and flexibility etc.28 (see scheme 1.5).
In addition to the color tuning ability of these π-conjugated systems, they have the added advantages such as brightness, wide viewing angle, high contrast and thin film forming property etc. Even though, they have very significant properties, low electroluminescence efficiencies and short operating lifetime are important issues to be addressed. Therefore the main challenges in the area of optoelectronics are the development of highly luminescent and amorphous polymers with good photo and thermal stability.

The search for new polymeric emitters having improved thermal stability, high photo stability and longer luminescence lifetime is currently an active area of research in PLEDs. Some examples of π-conjugated polymers used in electroluminescent devices with different emission colors are given in scheme 1.6.

Among all these conducting systems, poly(p-phenylenevinylene)s (PPVs) and their derivatives are the well-studied class of electroluminescent polymers because of their good processability, solubility and potential use in opto-electronic applications. Nowadays, the PPV family serves as a typical

Scheme 1.6. Polymers with different emission colors (or π-π*band gaps).

Among all these conducting systems, poly(p-phenylenevinylene)s (PPVs) and their derivatives are the well-studied class of electroluminescent polymers because of their good processability, solubility and potential use in opto-electronic applications. Nowadays, the PPV family serves as a typical
conjugated polymer for different kinds of applications and also for the primary understanding of the electronic and optical processes. The properties of PPVs can be improved by different solubilising groups like alkyl, aryl, alkoxy chains etc. Depending on the method of synthesis and choice of substituents, the emission color of PPVs can also be tuned in the entire visible region.

1.3. Poly(Phenyleneynyl)ene)s (PPVs)

The discovery of electroluminescence in PPV by the Cambridge group has made tremendous growth in PLEDs which gave inevitable importance to PPV and its derivatives. There are many basic methods for the synthesis of PPV derivatives which include polymerization through quinodimethane intermediates (Wessling’s route), polycondensation reactions; transition metal mediated coupling reactions, metathesis polymerizations, chemical vapour deposition techniques etc. Some of them are explained below.

1.3.1. Wessling and Gilch route

In the early 1960’s Wessling’s and Zimmerman developed a thermo-conversion procedure for PPVs. It is based on the aqueous solvent synthesis of poly (p-xylylene-a-dialkylsulfoniumhalides) from a, a’-bis(dialkyl sulfonium salts), followed by thermolytic formation of the final conjugated polymer. The sulfonium precursor formed will solubilise the polymer and it can be eliminated as hydrogen halide and tetrahydrothiophene. The mechanism of this reaction was believed to be according to a chain growth polymerization, via the formation of a p-quinodimethane like intermediate. Another synthetic procedure for PPVs was introduced by Gilch and in this polymerization a bis-halomethyl monomer was converted directly into the polymer by the treatment with excess of base. As in the case of Wessling route, Gilch route also believed to proceed through quinodimethane intermediate by radical or anionic pathway. The basic mechanism of Wessling and Gilch polymerization is given in scheme 1.7. In both mechanisms, the possibility of the formation of tolane bis-benzyl (TBB) defects cannot be ruled out which are formed by the coupling of the monomer biradicals.
Several modifications were made for the Gilch polymerization and two important routes among them are chlorine (halo) precursor route and non-ionic route. In the first route, 1,4-bis (chloromethyl) arenes by treatment with about one equivalent of potassium-tert-butoxide in nonhydroxylic solvents like tetrahydrofuran. This methodology was first introduced by Swatos and Gordon in 1990, as one of the most successful early PPV synthesis. In the second route, which was developed by Vanderzande et al., one of the chlorine atoms in the monomer was substituted with non-ionic sulfinyl groups in the ethylene moiety; therefore the precursor polymer would not contain any chlorine atoms. This precursor showed better thermal stability and was soluble in organic solvents. The Cl⁻ ions of the precursor polymer were replaced by F⁻, Br⁻, I⁻ or acetate ions through ion exchange via dialysis to give the corresponding precursor polymer. The sulfinyl groups can be removed by simple heating of the monomer for a few hours. Due to the presence of small amounts of halogens, the efficiency of the devices with these polymers was found to be low than that obtained from the conventional Gilch route.

1.3.2. Polycondensation Reactions (Knoevenagel and Wittig Reactions)

Knoevenagel reaction includes the reaction of an aldehyde group with an active methylene group (see scheme 1.8). Generally it requires a strong electron accepting group in the methylene unit (for eg., CN) and both the
monomomers (aldehyde and nitrile compounds) can be easily synthesized from the bishalomethyl compound.

**Knoevenagel route**

\[
\text{Base} \quad \begin{array}{c}
\text{OHC} - \text{CHO}^+ \\
\text{NC} \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{NC} \\
\end{array}
\]

**Wittig route**

\[
\begin{array}{c}
\text{(RO)OP} \\
\text{R}_1 \\
\text{R}_2 \\
\end{array} + \text{OHC} - \text{CHO} \\
\text{Base} \quad \rightarrow \quad \begin{array}{c}
\text{PPV} \\
\text{R}_1 \\
\text{R}_2 \\
\end{array}
\]

*Scheme 1.8. Knoevenagel and Wittig polycondensation reactions*

The polycondensation reactions between aryl-bis-aldehydes with aryl bisphosphonium salts or bisphosphonates are known as Wittig reactions (see scheme 1.8). They are widely used for the synthesis of alternating copolymers containing different substituents in the adjacent phenylene units. The significance of this method is that they avoid the formation of the TBB defects and allow the synthesis of alternating copolymers which is not possible by other methods.

1.3.3. Other Routes for PPV Synthesis 30,32

Heck coupling reaction is another route for PPV synthesis which involves the coupling between aromatic dihalides with divinylbenzene with a transition metal mediated route. 30,32 It is a Pd-catalyzed polymerization reaction with fewer side effects and both PPV homo and copolymers can be prepared (scheme 1.9).

*Scheme 1.9. Synthesis of PPV via Heck coupling reaction*
Among the transition metal mediated polymerizations, Stille coupling of halo-arenes with bisstannyl ethene is also very important. Chemical vapour deposition technique can also be used for the PPV synthesis which requires high heating at 500-700 °C. This route will produce by-product impurities and results in the production of an ill-defined polymer by the elimination of halogen in the final stage. Metathesis polymerization reactions are another type of synthetic method for phenylenevinylene, which can be done either by a transition metal mediated reaction or by a catalytic reaction to produce the precursor polymer, as introduced by Grubbs and coworkers (called ring opening metathesis polymerization (ROMP)). In the second reaction, a molybdenum carbine moiety is usually used as the catalyst.

1.4. Luminescence in PPVs

We have seen that PPV was the first electroluminescent polymer reported, and its photoluminescence and electroluminescence spectra are found to be consistent (see figure 1.1) which shows the similar emitting species with light or electric current as excitation source.

![Figure 1.1. Absorption, PL and EL spectra of PPV (Adapted from the ref. 27)](image)

To achieve efficient electroluminescence, highly photo luminescent emitting material is necessary in which the recombination of the charge carriers will take place within the layer rather than escaping to the opposite electrodes. After the discovery of electroluminescence in 1990, devices with soluble PPVs
were fabricated to improve the performance. Soon after this preliminary stage of research, the rapid development of these prototype devices met specific applications in different fields. However, these developments demand high understanding of the design and synthesis of materials.

Among the poly(phenylenevinylene)s, poly(2-methoxy-5-(2-ethylhexyloxy))-1,4-phenylenevinylene (MEH-PPV) (see scheme 1.10) and its copolymers are one of the most thoroughly studied π-conjugated polymers because of their potential applications in polymer light emitting diodes and plastic solar cells.\textsuperscript{27,30} Even though a lot of improvements have been made for improving the luminescence efficiency of PPV based polymers, low electroluminescent efficiency, short operating lifetime, poor environmental stability are some of the issues to be solved.\textsuperscript{27,32}

For a device with better performance and response time, high charge carrier mobility plays an important factor. Balanced charge injection from both the electrodes is necessary for achieving a device with high efficiency.\textsuperscript{33,34} It can be attained by many methods, either by the introduction of an additional charge transporting layer between the polymer emissive layer and the electrodes or by the use of an emissive polymeric layer which has a charge transporting group.\textsuperscript{35-38} In PPV derivatives, the second method was achieved by the structural modification of the emissive layer by electron withdrawing or electron donating groups in the polymer backbone. By this method the energy bands of the polymers can be adjusted and make comparable with the work function of the electrodes. For example in a single layer device, consisting of PPV as the emissive layer has a drawback of high LUMO energy with high work function cathode due to its poor electron accepting nature.\textsuperscript{27} To improve this electron injection ability, electron withdrawing groups such as cyano, trifluoromethyl, methyl sulfonyl phenyl, oxadiazole, triazole etc. are attached to the arylenne or vinylene group of the polymers (see scheme 1.10).\textsuperscript{39-42}
In general, the π-conjugated polymers have high tendency for π-π-stacking which gives rise to molecular aggregated domains in the polymer matrix in the solution as well as in the solid state. These molecular aggregates influence on the luminescence properties of conjugated materials (for example, PPVs) and it diminishes the long-term performance of luminance materials in electronic devices. Therefore, the control of molecular aggregation in the π-conjugated systems is one of the major task for attaining highly luminescent materials for optoelectronics.

1.5. Molecular Aggregation in PPVs

Aggregation is an important and widely seen phenomenon in π-conjugated polymers which makes the domains of polymer chains aggregated with distinct properties compared to the isolated chains. The aggregation properties are different in solution and solid state. The solution aggregation properties mainly arises when the polymer chains tend to aggregate after the critical concentration, which depends on several factors such as molecular weight, chemical structure, solvents and temperature. Since most of the
Chapter 1

Introduction

applications are depend on the uniformity and morphology of the polymer films used, the preparation of the same needs more attention. The association of the polymer chains in the solid state was found to have a major effect on the luminescence properties mainly due to the formation of inter and intra chain excited state species.\textsuperscript{47} Eventhough the formation of these species is still under discussion, there are clear reports of these species in different \(\pi\)-conjugated polymers like polythiophenes, polyflourenes, ladder type polyphenylenes, polyphenyleneethynylenes etc.\textsuperscript{47-51} Generally, the formation of interchain excited state species is very common in \(\pi\)-conjugated polymers which are responsible for the low luminescence quantum yield in the solid state.\textsuperscript{43, 52}

MEH-PPV is one of the most extensively studied electroluminescent polymer and its structure is designed based on the concept that the branched ethylhexyloxy unit and the methoxy units enhances the solubility and improves the luminescence properties by reducing molecular aggregation.\textsuperscript{53} In MEH-PPV also, the presence of excimers was observed and the research works in this area have demonstrated the necessity of modification in the synthetic, structural and processing methods of the polymers for the highly efficient conjugated PPV derivatives. Since the molecular aggregates are ground state species formed by the close contact of the \(\pi\)-conjugated segments of the polymer chains, their absorption and emission positions are lower in energy than the independent chain segments.\textsuperscript{52, 54} As mentioned above, the polymer chain organization in PPVs is highly dependent on the solvent quality also, that is, poor solvents forces the isolated chains to form highly associated aggregated particles.\textsuperscript{44} The efficiently packed conjugated backbones will get red shifted electronic properties, whereas the isolated part remains unaltered. For example, depending upon the conformations adopted by the polymer chains in solution, different types of associations or chain organizations are possible (see scheme 1.11). The large polymer chains can be associated to give aggregated and agglomerated species in which the first causes change in electronic properties compared to the latter.

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In a good solvent

**Scheme 1.11. Schematic representation of association and the collapse of isolated chains in poor solvents (Adapted from ref. 44).**

In general, the molecular aggregation could be prevented by controlling the inter- and intra-chain interactions which can be achieved by different methods like thermal annealing, confinement in conjugation length, synthesis of polymer blends and copolymers and introduction of bulky pendants etc.\textsuperscript{27,55-58} In a very recent paper, Becker et al. have reported that all the major properties for a highly luminescent material such as the extent of conjugation length, suppression in aggregate formation and tuning of emission color can be achieved in polyfluorenes by the attachment of indenofluorene, bulky dendron groups, and perylene dye respectively in the main chain or as side chains.\textsuperscript{59} The formation of aggregated species in polyfluorene copolymers are found to decrease the photoluminescent quantum yield in the solid state very drastically to 7 % compared to their solution quantum yield ($\phi_{\text{FL}} = 45-60$ %). Therefore, understanding and controlling the factors affecting the formation of intra and interchain excited state species is a challenging task for optimizing the efficiency of $\pi$-conjugated polymers in electroluminescent devices.
Chapter 1

1.6. Investigation on Molecular Aggregation in \( \pi \)-Conjugated Polymers

The molecular aggregation properties are generally monitored by absorption or emission spectrometers, time resolved photoluminescence techniques, electron microscopic studies etc. In solution state the molecular aggregation can be traced by a number of methods which includes using a good solvent/poor solvent combination, concentration or temperature dependant studies etc.\(^{60-63}\) In the first method, the polymer chains were allowed to fully disperse in a good solvent (in which it is fully soluble), to which a poor/bad solvent is slowly added to induce aggregation. Upon addition of the poor solvent noticeable color change will be observed indicating the formation of aggregates. The main possibility of this change may be because of the conformational change of the \( \pi \)-conjugated chains by chain folding. In bad solvents, the polymer forms rigid and stable structures and the excitation of which will result in lower energy emissive species. The concentration dependant studies are based on the formation of aggregates by self-coiling of the polymer chains.

Scheme 1.12. Schematic representation of polymer chains in good and bad solvent

A lots of works were done on the congeners of PPVs poly(phenyleneethynylene)s, (PPEs) based on the above discussed concept. Usually THF, CHCl\(_3\) etc. are used as the good solvents, whereas methanol (MeOH) act as a bad solvent in most cases.\(^{64,65}\) Bunz group are the pioneers in PPE-based polymers and their study based on the above concept showed the
development of a red shifted peak corresponding to the aggregation in the solvent/temperature induced studies. The studies on the well-known MEH-PPV have shown that the solvents like toluene, xylene, chlorobenzene etc. assist the aggregation phenomena by π-stacking, whereas THF, chloroform etc. hinders the same. Therefore, noticeable changes will be there in the absorption and fluorescence spectra by the presence of the molecular aggregates. The red shift observed in the absorption and emission spectra has known to be caused by the interchain aggregation, but there still exists debates about this process. One reason for this red shift was explained due to the delocalization of the π-electrons over multiple stacked segments of different chains in the aggregated state because of the close proximity. Another factor for the red shift is attributed to the collapse of isolated chains and planarization of the phenyl rings due to confinement in conjugation. But in brief, the molecular aggregates formed in the presence of high amount of poor solvent, in highly concentrated polymer solution or in low temperature conditions, resemble like the polymers in the solid state. The segmental association of the polymer chains also found to be different in various solvents and it was demonstrated by Li et al. that in a good solvent the PPV chains forms looser network aggregates whereas in a poor solvent tightly packed aggregates are formed. These interchain aggregations are mainly driven by aromatic π-π interactions. Fakis and coworkers have studied the influence of aggregates and solvent aromaticity on the photophysical properties of the PPV derivatives.

The molecular aggregation in the solid state can also be followed by many methods like time-resolved decay measurements, SEM, TEM, etc. including the absorption and luminescence measurements. Recently Chen et al. have shown that the molecular aggregation in MEH-PPV results in the nematic textures which causes a red shift in the emission maxima. In this case the molecular aggregation is assumed to be driven by the aromatic π-π interactions in which the small methoxy unit is unable to provide necessary shielding for the polymer backbone. In another report, Chen et al. has given the direct
evidence for the morphological characteristics from the SEM and TEM studies, and they got lamellar mesophasic (worm-like) textures (see scheme 1.13).\textsuperscript{71} For both the PPVs they studied, MEH-PPV and poly(2,5-di-octyloxy-1,4-phenylenevinylene) (DO-PPV), the nematic or lamellar textures obtained were explained on the basis of a schematic model as shown in scheme 1.13.

\begin{scheme}
\centering
\includegraphics[width=0.5\textwidth]{scheme1_13.png}
\caption{Worm-like TEM image and schematic model for the representation of hierarchical features of DO-PPV aggregate (Adapted from ref.\textsuperscript{71})}
\end{scheme}

de Boer et al.\textsuperscript{72} have reported self organization in PPV based block copolymers in which complete evaporation of the solvents produce honeycomb patterns as reported in rod-coil block polymers and amphiphiles (see scheme 1.14).\textsuperscript{73,74}

\begin{scheme}
\centering
\includegraphics[width=0.5\textwidth]{scheme1_14.png}
\caption{Optical transmission and AFM (a), fluorescence and SEM (b) images of honeycomb structured film from PPV based rod-coil block polymers obtained by drop casting from CS\textsubscript{2} (Adapted from ref. 72).}
\end{scheme}
In the optical microscopy, the bright spots correspond to the cavities and the fluorescence microscopic images showed that the honeycomb patterns are uniformly distributed in the solid films. These highly ordered micrometer size structures are solvent dependent and they find applications in opto-electronic devices, thermal insulation materials and membranes. With a newly developed scanning probe technique, Kemerink et al. have studied the inter and intra chain aggregations in a series of symmetrically and unsymmetrically substituted PPV polymers which showed different morphological characters based on the polymer concentration and solvent used for film casting. All these morphological characters leads to a change in properties like charge carrier transport, charge mobility etc. which are believed to be due to the differences in the molecular packing in the aggregated state.

Recently, Deepa et al. from our research group had developed a solvent induced self-organization in polyurethane-oligo-phenylenevinylene random copolymer for the various morphologies and sizes ranging from micron to nano-meter sized pores, hexagons, vesicles and solid luminescent spheres. Using detailed photophysical studies, they have shown that molecular aggregation via \( \pi \)-conjugated segments play a major role in the random block polymers for these types of morphological features.

Scheme 1.15. Self-organization of Polyurethane-oligophenylenevinylene Block Copolymers for Micro or Nano-structures (Adapted from ref. 76).
In short, PPVs are highly luminescent class of conducting polymers that are found countless applications in optical and electronic industry. The above discussions are mainly pointed on towards the necessity of structural modification and control of molecular aggregation for the designing of highly luminescent and efficient materials.

1.7. Approaches to Control Polymer Aggregation

There are various approaches to control the molecular aggregation in the \( \pi \)-conjugated systems, among them, thermal treatments, synthesis of polymer blends, confinement in conjugation length, and bulky approach are worth mentioning. The next section explains this concept of controlling molecular aggregation in conjugated polymers (especially in PPVs) for enhanced luminescence properties.

1.7.1. Thermal Annealing

Recently, Lee et al. has reported the enhancement of EL efficiency by thermal treatments in which the highly amorphous and emissive polymer MEH-PPV was subjected to heat treatment above the glass transition temperature (\( T_g \)).\(^{55a} \) As the thermal annealing temperature increases, the smoothness of the film surface improve due to the better chain movements of the polymer chains above the \( T_g \) (see scheme 1.16). This thermal annealing process found to decrease the quantum yield, however, this method was recommended because the excimer formation was highly reduced and enhances the EL efficiency of the devices. Besides these methods Chou et al. demonstrated that the thermal treatment of the well-known MEH-PPV can enhance the photoluminescent quantum yield about 6.5 times than that of the untreated one.\(^{77} \) Even though there is a slight increase in the turn-on voltage is observed for MEH-PPV compared to the unsubstituted one, the EL and PL efficiencies were found to be increased with a device configuration ITO/PPV/Al. Hence they have shown that the PL and EL efficiencies are highly influenced by the heating time and temperature.
As temperature increases, more smoothens

Scheme 1.16. Thermal annealing increases the EL efficiency by smoothening the surface (Adapted from ref. 55a).

1.7.2. Polymer Blends

Polymer blends are very promising part of opto-electronic industry since they can offer a combination of different optical and electronic properties in the same material because of the presence of multiple units having different properties. In blends, these interchain interactions can give rise to different supramolecular properties like energy transfer processes between the blended components. In order to enhance the luminescence properties, small organic molecules are blended with the polymers and the energy transfer mechanism between both systems will enhances the photoluminescence quantum yield. One such interesting observation was reported by Marchioni et al. which describe the twofold increase in the absolute quantum yield of MEH-PPV when blended with a small organic molecule triphenylfluoranthene (scheme 1.17, 3PF). This enhancement in the photoluminescent quantum yield was ascribed due to the direct sensitization of the intra-chain emitting state in MEH-PPV by energy transfer from 3PF. Another way of improving the luminescence properties is by the fabrication of multilayer devices for efficient and balanced charge transport. An alternative way to attain this is by making single layer devices with the blends of conjugated polymers and charge transporting materials. The external quantum efficiency of the devices was found to be improved by several orders of magnitude than the one with multilayered systems. In a recent report Ahn et al. have shown such a blending approach in
which MEH-PPV is blended with an electron transporting layer DFD (see scheme 1.17). As the weight percentage of the electron transporting material varied from 20 % to 95 %, the efficiency of the device increased to two orders of magnitude in which the emission (orange/yellow) is observed only from the PPV backbone.

Polymers bearing polar groups can be also blended with MEH-PPV for enhanced device properties. Kim and coworkers have synthesized a blend of MEH-PPV with PSS which is having a polar sulfonate group (see scheme 1.17). Due to the presence of this polar ionomer unit, the electron injection has been improved from the cathode to the emitting molecules and thus, the luminescence efficiency. This enhancement was much higher than that of a device without a polar group (for example, MEH-PPV/Polystyrene blend). In short, blending studies have demonstrated that the improved PL/EL efficiency is attributed mainly to the interrupted conjugation and lower packing of the PPV chains.

1.7.3. Confinement Approach

A defined conjugation is very interesting since it gives a sharp emission peak and a well-define absorption spectrum. Confinement in conjugation length can be achieved by introducing cis/meta-linkages or non-conjugated spacers in the conjugated polymer backbone. The two approaches for
controlling molecular aggregation by breaking the conjugation length are schematically represented as shown in scheme 1.18.

*Scheme 1.18. Representation of conjugation control in PPVs*

In the first approach introducing a meta-linkage or cis-vinylene linkage, the conjugation length of the polymer can be broken whereas in the second approach, non-conjugated segments were incorporated in the polymer backbone. Both methods will hinder the perfect $\pi-\pi$ stacking of the polymer chains resulting in the reduction of intra/interchain interactions. The introduction of meta-linkages or non-conjugated unit’s makes a twist in the polymer backbone which often shifts the emission wavelength to the blue region. Few examples of confinement approach are shown in scheme 1.19. Karasz and coworkers pioneered a lot in the area of meta-substituted phenylenevinyles and have shown the effect of substitution on the optical properties.\(^82\)-\(^87\) They have made a significant contribution in making highly luminescent polymers and are able to produce PPVs with high EL efficiency. In one report they explained a meta-phenylenevinylene polymer which has an improved electroluminescence efficiency of 0.05% than the unsubstituted PPV (0.006 %) (see scheme 1.19, m-PPV).\(^82\) Studies on polymers with non-emitting blocks in the PPV backbone have demonstrated that the luminescence efficiency of these polymers highly depend upon the length of the non-conjugated block. These segments enhance the solubility of the polymer backbone and can emit in any region in the visible spectrum (see examples in scheme 1.19, alkyl-PPV and MOB-DEO)\(^88\)-\(^92\).
To achieve large band gap polymers for blue emission, Zheng et al. have reported a new polymer with the introduction of a non-conjugated rigid adamantane spacer in the polymer backbone to control the chromophore conjugation. The polymers possess unusual thermal stability ($T_g \approx 150 ^\circ C$) and photo physical properties due to the incorporation of the rigid and spherical adamantyl moiety. The fabrication of a single layer device with a structure ITO/polymer/MgAg showed blue emission for Ad-PPV-1 (with a low turn-on-voltage of 5.5V) and bright green emission for Ad-PPV-2 (see scheme 1.19). They demonstrated that the adamantane group is an efficient π-conjugation interrupter which produces polymers that can perform better in devices with low turn-on-voltages.

*Scheme 1.19. Examples of conjugation control in PPVs.*

In addition to the introduction of cis/meta linkages and non-conjugated segments, it was shown that the incorporation of conjugated systems (other
than phenylenevinylene units) in the aromatic backbone can also break the polymer packing. Zheng et al. showed the twisting mechanism in PPVs by binaphthyl group (Scheme 1.19, binaphthyl-PPV). The binaphthyl copolymer exhibits blue-green emission and a device of the polymer with ITO anode and Al cathode showed an external quantum efficiency of 0.1% and a low driving voltage of 6V. After that a similar observation was reported in a biphenyl copolymer of PPV by Sarker et al. in which green-blue emission was achieved in a device with configuration ITO/PEDOT/polymer/Ca/Al (Φ_{ext} = 0.17 %) (Scheme 1.19, biphenyl-PPV). In both cases mentioned above, the interruption in conjugation of the PPV backbone by the binaphthyl or biphenyl substitution increases the non-radiative decay which resulted in a blue shifted emission with low external quantum efficiency. Ramakrishnan and co-workers have demonstrated the control of conjugation length by synthesizing PPVs with suitable precursor polymer in which the amounts of acetoxy and methoxy substituents was varied. It was found that the fluorescence quantum yields of samples decreases with increase in the extent of conjugation. This was explained due to the presence of a distribution of conjugation length within a single polymer chain which facilitates energy transfer processes.

\[
\begin{align*}
\text{Scheme 1.20. Precursor route to PPVs containing randomly placed acetoxy and methoxy groups to attain polymers with control in conjugation length (Adapted from ref. 57a).}
\end{align*}
\]

Therefore, the introduction of meta-substitution or non-conjugated segments in the conjugated backbone is a very efficient approach for both the color tuning as well as the improved solubility by controlling the molecular aggregation. Eventhough, this method allow the polymers to bend and twist effectively and control the chain packing in the solid state, the difference in HOMO-LUMO energies of the confined structures from that of the parent...
polymer causes difficulty in choosing the work function of electrodes and also alter the color of emission. 96

1.8. Bulky Approach in PPVs

As we have seen, quenching of emissive state caused by the interchain interactions is one of the major problems in achieving the high luminescence efficiency. Attachment of bulky side groups is an alternative solution for this problem. Scheme 1.21 describes the influence of side chains on the inter-macromolecular packing, which leads to the formation of micro-aggregates. The rigidity and size of the bulky pendants separates the polymer chains more efficiently; reduce the molecular aggregation which prevent luminescence quenching. Therefore, incorporation of bulky substituents into the polymer backbone for making highly luminescent polymers is an active area of research.

There are a lot of reports of bulky PPVs which can be divided into different types according to the nature of the pendants attached, like aromatic, inorganic, cyclic etc.

1.8.1. Bulky PPVs with Aromatic Pendants

The introduction of the bulky pendant group improves the photo luminescent and electroluminescent efficiency of the devices by inhibiting the intermolecular interaction between the polymer chains. Among the aromatic bulky pendants phenyl, naphthyl, biphenyl, etc. are very important. Hsieh et al. and Peng et al. have synthesized fully conjugated and highly luminescent PPVs with 2,3-diphenyl or 2-biphenylyl side substituents that exhibited emission

Scheme 1.21. Aggregation behaviour of \(\pi\)-conjugated polymeric emitters
peaks at 488 and 490 nm, respectively (see scheme 1.22, DP-PPV and Biphenyl-PPV). The improvement of luminescent behavior of the PPV polymers was also studied by varying the substituent positions by Jin et al. They introduced 3,7-dimethyloctyloxy groups into the ortho-, meta-, and para-positions of the phenyloxy group (as shown in scheme 1.21, DMO-PPV) in the PPV for improving the EL characteristics and control the emission colors. Reports by Liang et al., suggested that in addition to the suppression of molecular aggregation, the triphenylamine (TPA) moiety can contribute to the hole-transporting, solubilising and energy transfer properties. The results demonstrated that the introduction of hole-transporting TPA units can improve the brightness and device efficiency (see scheme 1.22, TPA-co-PPV). Earlier, Pu et al. also reported triphenylamine substituted PPV, which has high hole transporting ability with high fluorescence efficiency. The PL and EL efficiency of the PPVs was further improved by the bulky phenylanthracene pendant as reported by Chung et al. The three polymers prepared (given in scheme 1.22, Polymer 1-3) were found to be highly soluble and the large interchain separation caused by the bulky units in polymer 1 enhances the PL emission quantum yield. The efficiency of the devices using these polymers increased in the order polymer 3 < polymer 2 < polymer 1. The presence of ethylhexyl and phenylanthracene pendants found to increase the interchain distances which suppresses the formation of interchain excitons resulting in the improved EL efficiency by decreasing the rate of exciton state decay.

Chang and Lee et al. independently reported naphthyl substituted PPVs (see scheme 1.22, DDN-PPV, 2N-PPV, 4N-PPV and NAP-PPV) which were mainly focused on improving the thermal stability and glass transition temperature or rigidity of the polymer chains by the bulky substitution. The electrical and optical properties of the polymers were also found to be very promising with this bulky naphthyl group. The intramolecular energy transfer processes were also found to be a reason for the enhanced luminescence properties as shown by Shin et al. in (2,2-diphenylvinyl)phenyl substituted
bulky-PPV derivative (scheme 1.22). High electroluminescent efficiency was achieved with yellow emission for this polymer.

The intermolecular aggregation and excimer formation can be further minimized by introducing branched π-conjugated systems, such as conjugated dendrimers which will prevent the close packing of the polymer chains three dimensionally.\textsuperscript{106-111}

\textit{Scheme 1.22. Bulky PPVs with aromatic pendants}
Jakubiak et al. have utilized the steric crowding and liquid crystallinity of dendritic side groups for the fewer polymer chain aggregation by three dimensional separations leading to high photoluminescent quantum yield (see scheme 1.23). Bulky side chains are used to enhance the main chain separation to reduce the aggregation properties in the solid state and the thermotropic liquid crystalline behaviour obtained can be used to form highly ordered photoluminescent films for generating polarized light.

Scheme 1.23. Bulky PPVs with aromatic dendritic pendants

Dendritic phenyl group-substituted PPVs were also reported by Dinakaran et al. which shows high photoluminescence in the solution and in the solid state. With the increase in bulkiness of the copolymer, they could observe the increase in the rigidity of the polymer backbone which is evidenced from the high $T_g$ values. The bulky homopolymer, DEN-PPV (see scheme 1.23) has a $T_g$ value of 243 °C which is much higher than that of MEH-PPV. The bulky group also transfer its excitation energy to the polymer backbone which will lead to the enhancement of photoluminescent quantum efficiency. The electroluminescence of the copolymer MEH-PPV/DEN-PPV (molar ratio: 25/75) was found to be 70 % higher than that of MEH-PPV. Tang and co-workers also achieved a device with low operating voltage by using PPV
derivatives bearing dendritic groups.\textsuperscript{111} The highly phenylated bluest light emitting PPVs were reported by Mikroyannidis which showed limited solubility and reduced chromophoric length due to steric effect.\textsuperscript{112} They are found to be highly amorphous and possess glass transition temperature in the range of 158-176 °C which will be very promising for the lifetime of the electroluminescent devices (Ph-PPV-1 and Ph-PPV-2 in scheme 1.23). A lot of works were reported by Mikroyannidis and co-workers in highly phenylated and alkoxyphenyl-PPVs which possess high glass transition temperatures.\textsuperscript{112-115} The above discussion summarizes the fact that conjugated dendrimers minimizes the tendency of molecular aggregation with defined color of emission and enhances the luminescent properties.

### 1.8.2. Bulky PPVs with Inorganic Pendants

Other than aromatic PPVs, inorganic pendant groups are also known which are shown to improve many other properties. Phenylenevinylene polymer and oligomer have reported by Detert et al. using sulfones as pendant groups (see scheme 1.24).\textsuperscript{116} The impact of the sulfone unit, which is an electron accepting group, was to make PPVs efficient for device applications by their charge transport ability. By the use of this electron accepting pendant group, stabilization of the conduction band occurs, as a result the band gap decreases with an emission in the green-yellow region. Silane and oxadiazole substituted phenylenevinylene are also reported by Detert et al. and they were found to have significant influence on the aggregation and emission properties.\textsuperscript{117-120} Recently Chou et al. introduced polyhedral oligomeric silsequioxane (POSS) units in the PPV backbone in order to improve the thermal stability and electroluminescence properties (scheme 1.24, C).\textsuperscript{121} Copolymers of POSS-PPV with MEH-PPV were synthesized to obtain red emitting, very bright EL device by decreasing the interchain interactions between the polymer chains. The copolymer with 10 % POSS showed a low turn-on-voltage of 2.5V and a 4-fold increase in the device brightness

NIIST
compared to pure MEH-PPV in a double layer device with ITO/PEDOT/polymer/Ca/Al configuration.

Scheme 1.24. Sulfone (A and B), silsequioxane (C), and silyl (D, E and F) substituted phenylenevinylene

Silyl and alkoxy substituted PPV copolymers containing flourene and carbazole units were reported by Ahn et al. (scheme 1.24, D and E) which gives highly photoluminescent (PL_{eff.} = 0.81) and blue-green electroluminescent polymers.\textsuperscript{122} The fabrication of a single layer device of these copolymers with a configuration ITO/polymer/AI suggested that the EL efficiency could be improved by 13-32 times in comparison with MEH-PPV. The structure-property relationships of a series of silyl substituted PPVs were investigated by Chen et al. by varying the alkyl chain length from C1 to C18 as

NIIST 32
shown in scheme 1.24, F.\textsuperscript{123} The molecular weight and thermal stability of the polymers found to increase with the alkyl chain length whereas the electrochemical stability decreases. Also, the single layer (ITO/PPV/Mg:Ag) and double layer (ITO/PEDOT:PSS/PPV/Mg:Ag) device construction indicated that the hole injecting layer in the latter enhances the current efficiency and power efficiency by 7 times with a lower turn-on voltage.

1.8.3. Bulky PPVs with Cyclic Pendants

Apart from the aromatic and inorganic bulky pendants, a few reports of cyclic systems is also known which can serve as good bulky units for controlling the interchain aggregation in PPVs.\textsuperscript{124-133} Choo et al.\textsuperscript{131} and Jeong et al.\textsuperscript{129} have investigated the effect of size and rigidity of the pendant groups attached to the polymer backbone by incorporating cyclohexyl and adamantyl substituents (see scheme 1.25). It was noticed that the mono-adamantyl systems (MAE-PPV) shows an enhancement in the PL intensity about 4 times greater than that of MEH-PPV. This can be explained due to the reduction in interchain interactions by the bulky adamantyl group. They have demonstrated the performance of the polymer by making a single layer device with a structure ITO/MAE-PPV/Al, but the operating voltage required for the efficient current flow was very high.

It was noticed that the rigid bulky substituents mentioned above decreases the solubility of the resulting polymers which makes difficulty in the film processing. In order to improve this, instead of the methoxy group in MAE-PPV, Lee et al. reported ethylhexyl-adamantyl PPV (EH-AE-PPV, scheme 1.25) which also exhibits good solubility and enhancement in PL intensity as result of reduction in interchain aggregation by the steric effect of the bulky group.\textsuperscript{130} A device was constructed to prove the electroluminescent properties of the polymer with a configuration Al/LiF/EH-AE-PPV/PEDOT/ITO where PEDOT is used as a hole transporting layer. Another important example for the bulky pendant is cholesteryl group (see scheme 1.25) which showed an improvement in PL efficiency in the solid state.\textsuperscript{132} The NIIST
symmetrically substituted cholesteryl PPV showed a PL efficiency of 53% and good EL properties in single and double layer devices with configuration ITO/PPV/Ca and ITO/PVK/PPV/Ca respectively. Recently Ko et al. and Talaie et al. independently reported cyclohexyl substituted PPVs that are highly soluble and highly luminescent for opto-electronic applications.\textsuperscript{124, 125} They have shown that the ring size and alkyl chain length has significant effects in improving the photoluminescent and electroluminescent properties (scheme 1.25).

\textbf{Scheme 1.25. Bulky PPVs with cyclic pendants}

From all the previous discussions it was demonstrated that one of the main challenging issue in the production of highly luminescent conjugated materials is the molecular aggregation phenomenon. It is therefore, necessary to understand and analyze the factors affecting the molecular aggregation and the nature of aggregates formed. Among the approaches to control the aggregation and reduce the interchain interactions, introduction of bulky substituents were proven to be very hopeful since the emission color can be retained.
1.9. Aim of the Thesis

In this introduction chapter, more effort has been paid to discuss the luminescent properties of poly(p-phenylenevinylene)s (PPVs) which are found to be an essential component in the opto-electronic industry. The modification of its chemical structure, solubility etc. are also highlighted that are crucial factors in determining the device performances. The history of these polymers started from 1990 after the discovery of light emitting phenomena by the Cambridge group and a summary of the research works from that period is explained. However, more importance has been given to explain the approaches which are used to improve the luminescence properties of PPV polymers, such as confinement approach, thermal treatments, bulky approach etc. The advantages of the bulky anchoring groups are that they increase the glass transition temperature ($T_g$) of the PPV and high $T_g$ is an important parameter for long operating lifetime of devices. Though the bulky approach has been demonstrated earlier, most of the promising candidates such as adamantyl or cholesteryl PPV were found insoluble which hampers their complete structural characterization as well as processability. It is important to design new bulky polymer (or oligomer) structures to overcome the above limitations for better understanding the molecular aggregation process $\pi$-in the conjugated backbone. Therefore, developing low cost and highly luminescent new bulky PPVs through easy synthetic routes (similar to MEH-PPV) from commercially available low cost material is an attractive and essential requirement for futuristic application, in general for the bulky $\pi$-conjugates. The overall ramifications of important development in improving the luminescence intensity and trace the factors behind the molecular aggregation in the highly luminescent bulky-PPVs for optoelectronic applications is a challenging problem to be addressed.

In the search for new derivatives or substituents for the synthesis of highly emissive freely soluble PPVs to address the above-issues, we have come across a new rigid cycloaliphatic alcohol, tricyclodecanemethanol (TCD). TCD
Chapter 1

Introduction

is a very attractive bulky anchoring group for \( \pi \)-conjugated polymers because of its tri-cyclic rigid bulky structure; also it is sluggish to crystallize, has low cost and has commercial availability. However up to our knowledge, there are no reports of conducting polymers based on TCD in the literature. This thesis work is focussed to develop novel highly luminescent “bulky \( \pi \)-conjugated poly\((p\)-phenylenevinylene)\)s and their oligomers” based on new tricyclodecane (TCD) pendants. Additionally, efforts were also put to probe the molecular interaction in bulky \( \pi \)-conjugated polymers using spectroscopic techniques to trace the factors behind the aggregation phenomena.

The three major aspects discussed in the thesis are:

(i) Design and development of novel tricyclodecane substituted poly\((p\)-phenylenevinylene)\)s and their copolymers for enhanced solid state luminescence.

(ii) Probing the molecular aggregation in the bulky \( \pi \)-conjugated materials and their blends by detailed spectroscopic studies in solution as well as in the solid state.

(iii) Development of supramolecular ring banded liquid crystalline bulky oligo-phenylenevinylenes.

The second chapter gives a detailed discussion on the ‘Bulky TCD-based Poly\((p\)-phenylenevinylene)\)s, Oligomers and Copolymers’, their synthesis, structural characterization and copolymerization effect on the thermal and photophysical properties. Structurally similar OPVs were utilized for correlating the structural and photo-physical properties of the polymers. The effect of bulky substituents on the polymerization reactions and the molecular weights were also investigated. Highly rigid PPV-structures showed photoluminescence enhancement 4-5 times higher than that of MEH-PPV, and were further supported by the increased solid state quantum efficiency of the bulky substituted OPVs. Since the bulky unit can improve the luminescence properties, the factors affecting the enhanced luminescent behaviour should be followed and that studies (‘Aggregation properties of the bulky PPVs’)

NIIST 36
constitutes the third chapter. Absorption and photoluminescence (PL) spectroscopic techniques were employed as tools to trace the aggregation properties in solution as well as in the solid state. Chapter four hold interest on the discussion of 'Bulky TCD-based oligo-phenylenevinylene with a highly supra-organized structure'. The liquid crystalline properties of the OPVs were investigated in detail with the help of thermal, X-ray diffraction and other microscopic studies. Photophysical experiments revealed that strong π-π interaction in the film as well as in the liquid crystalline frozen stage is the main driving force for the supra-ring structure formation. The melt crystallization process demonstrated here is a new tool for the production of ring banded patterns in π conjugated materials and could be useful for application in opto-electronics.

Finally, overall conclusion of the thesis is summarized as chapter 5.
Chapter 1

1.10. References


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Chapter 1

Introduction

Chapter 1

Introduction


Chapter 1

Introduction


Chapter 1

Introduction


NIIST 45
Chapter 1

Introduction

