Synopsis

The study of conjugated polymers, in particular PPV derivatives, continues to fascinate researchers both from the standpoint of developing new routes to control their structure and photophysical properties; this is also driven by the immense potential since this class of polymers has demonstrated in the context of various devices, such as LEDs, photovoltaics, FETs, etc. Also, there has been great interest in utilizing conjugated polymers in developing sensory devices. This thesis has examined a few interesting aspects that could be used to control the structure and consequently the photophysical properties of PPV derivatives. The first chapter of this thesis provides a brief introduction to conjugated polymers, with an emphasis on PPV based polymers, different synthetic methodologies for their preparation, previous attempts to obtain PPV with controlled conjugation length, and also a brief discussion of conjugated polymer nanoparticles (CPNs) and their preparation by various methods.

The second chapter deals with the preparation of conjugated polymer (MEHPPV) nanoparticles by reprecipitation method and utilization of these nanoparticles in detection of nitro explosives in aqueous medium. Nanoparticles of MEHPPV with different sizes were prepared by a simple precipitation method from a THF solution into water. Although these nanoparticles were prepared from very hydrophobic MEHPPV, these nanoparticles were reasonably stable in aqueous medium, especially when their sizes were relatively small; their UV-visible and fluorescence spectra could be readily recorded using simple solution methods. The sizes could be controlled by varying the concentration of the polymer solution used. The CPNs are spherical particles as confirmed by atomic force microscopy (AFM). The emission maximum of the nanoparticles is red shifted compared to a solution of the polymer. The fluorescence spectrum of this aqueous nanoparticle dispersion exhibited very high sensitivity to electron-deficient aromatic compounds, in particular the explosive TNT; the CPNs were able to sense nanomolar concentrations of the explosives. Stern-Volmer constant (K_{SV}) is higher for 2,4,6-trinitro toluene (TNT) than any other analytes studied. Among the different sized nanoparticles studied the

bigger one showed highest quenching efficiency. Electron-deficient aromatic molecules were shown to quench the fluorescence of the nanoparticles, possibly by excited state electron transfer mechanism; this hypothesis was supported by quenching experiments carried out using a variety of nitro-aromatic molecules with varying reduction potentials, in addition to a few electron-rich aromatic molecules. A fairly good correlation between the quenching efficiency of the analyte and its reduction potential was noticed; however, in a few instances this correlation failed. This suggested that a second factor, namely the solubility of the analyte in water (its hydrophobicity) also is a key factor as this governs the tendency of the analyte to adsorb on the nanoparticle surface, which clearly is the first step in the quenching process.
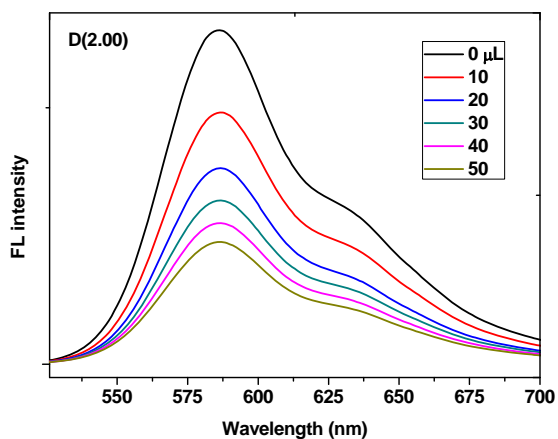

Fluorescence quenching of CPNs by TNT
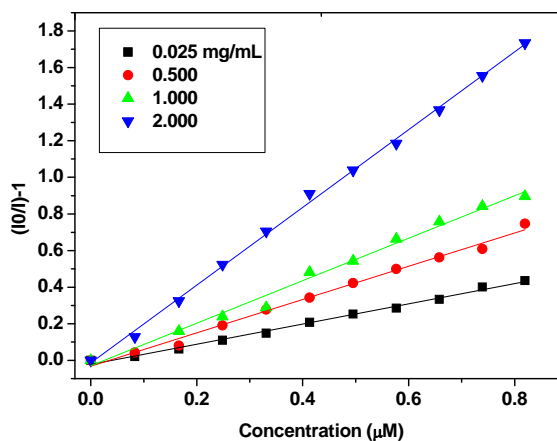
Stern-Volmer plot for different sizes of the nanoparticles with 2,4,6-trinitrotoluene (TNT)

In the third chapter synthesis and characterization of MEHPPV with reduced conjugation length by utilizing the concept of conjugation breaking using non-coplanar entities are presented. MEHPPV with reduced conjugation length was prepared by incorporating non-coplanar entities, such as biphenyl and binaphthyl units, along the polymer backbone. Both Gilch and Witting-Horner methods were successfully utilized to prepare copolymers; the former approach permitted the variation of the level of the twisted comonomer incorporation, whereas the latter approach only provided an alternating copolymer. Although biphenyl based monomers could not be homopolymerized by Gilch method, it was possible to prepare

copolymers using xylylene type comonomers. The polymers prepared by the Gilch method are random copolymers; the solubility decreases with increase in the amount of biphenyl incorporation, which was ascribed to the presence of a substantial fraction of longer conjugated segments in such random copolymers. The non-coplanar entities cause truncation of conjugation length in MEHPPV, as evident from their absorption spectra. The copolymers prepared via the Gilch method exhibited a blue shift of about 57 and 20 nm in the absorption and emission, respectively; while the alternating copolymers prepared by Wittig-Horner-Emmons method exhibited a larger blue-shift of about 84 and 54 nm clearly implying a significantly larger reduction in the conjugation length. The copolymers prepared by Wittig-Horner-Emmons method are alternating in nature and therefore leads to a greater reduction in conjugation length; this was evident from the substantially higher blue-shift in the absorption and fluorescence spectra. An interesting feature in the alternating copolymers is the distinct difference in the relative changes in the absorption and emission spectra of the biphenyl and binaphthyl containing copolymers, which appear to suggest in the latter case there is a greater extent of planarization of the excited state. Both these systems provided some useful insights into the various factors that govern the photophysical properties of this class of truncated conjugated polymers. Further examination of this aspect could reveal some other unique features of these copolymers.
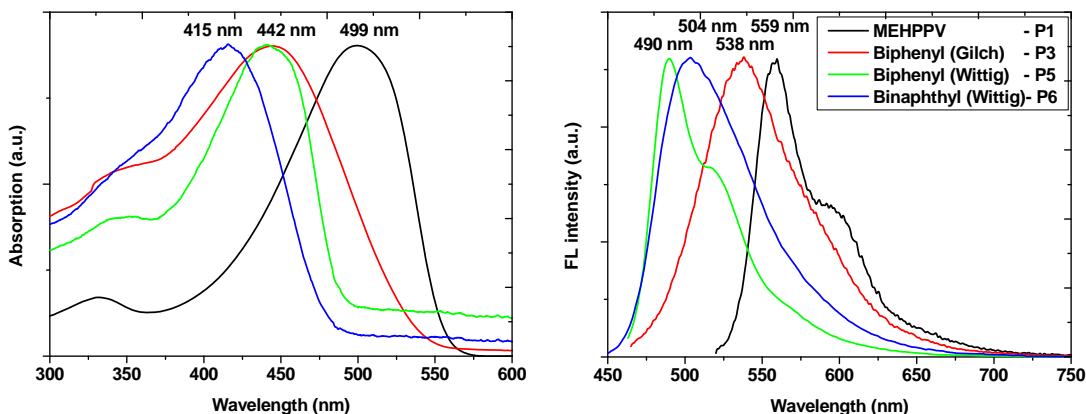
Comparison of absorption (left) and fluorescence (right) spectra of the biphenyl and binaphthyl containing copolymers synthesized by different methods, with MEHPPV.

In the fourth chapter, an approach to prepare copolymer precursors to unsubstituted PPV that holds the potential to control conjugation length is described. The precursor copolymers were prepared by changing the monomer feed ratio of the two monomers, viz. dithiocarbamate (DTC) and xanthate, using the Gilch copolymerization to generate the precursors having varying extents of DTC and xanthate groups. The percentage composition of the precursor copolymers was calculated using ^{1}H NMR and compared with the values calculated from thermogram; the copolymer composition varies linearly with monomers feed suggesting that any desired composition can be readily accessed. Thermogravimetric analysis (TGA) of the precursors, as a preliminary study to examine the possibility of selective elimination of one of these groups to generate conjugated polymers with varying conjugation lengths, demonstrates that a certain level of selectivity in thermal elimination can be achieved because of the distinctly different thermal labilities of the xanthate and DTC groups. These studies clearly suggest that fine-tuning of the thermally eliminatable groups, specifically using xanthate and DTC, could serve as a useful approach to vary the conjugation length of unsubstituted PPVs, which could have important implication in device fabrication. Clearly further work is needed to characterize the selectively eliminated polymers using other spectroscopic methods, such as UV-visible and fluorescence, before device work could be taken up.