CHAPTER 5

Conclusion and future scope of the present investigation


5.1 Conclusion

Conjugated polymers are attractive materials for optoelectronic applications such as light-emitting diodes, sensors and solar cells. They offer advantages with respect to traditional inorganic semiconductors regarding processability (they require simple techniques such as spin coating, printing) and functionality (modification of the molecules offers enormous variety in functionalization). Rapid progress is being made in the development of polymers for electronic devices. The use of polymer in electronic devices for large scale applications requires high performance, reliability and stability, longer lifetime, good control and reproducibility. A large number of different classes of conjugated polymers have been developed such as poly(N-vinylcarbazole)s, poly(fluorine)s (PFS), poly(p-phenylene vinylenes) (PPVs), and poly(thiophenes) (PTs). Polythiophenes and its derivatives are very unique among other polyconjugated systems due to their solubility, environmental stability, fusibility, processibility. Now-a-days, soluble polythiophene derivatives are of great importance due to their easy processing purpose. The tuneable emissive properties are particularly attractive for lighting and display applications. The wavelength of emission depends on the extent of conjugation, and can be controlled by modification of the chemical structure. This can be achieved by the attachment of functional groups, which alter the electronic structure of the polymer. So, light emission is possible over the entire visible range of the visible spectrum, by “chemical” tuning of the HOMO-LUMO energy gap of the polymer.

The purpose of this thesis is to provide an insight into the synthesis, characterization and electrochemical, photoluminescence and electroluminescent properties of π-conjugated 3-ester substituted polythiophene derivatives for the polymer-based light emitting diode devices.

The findings of the thesis are described below

1. Synthesis and characterization of ester substituted polythiophenes

A series of ester substituted thiophene monomers has been synthesized by esterification reaction. The yield of the monomers is 60-80%. The formation of monomers was confirmed by FTIR, $^1$H NMR spectroscopy. The polymers have been prepared by the oxidative polymerization using ferric chloride. The polymerization process is slow and yield of the
polymer is 42-66%. The polymers show good solubility in THF, CHCl₃, DMF, DMAc, and DMSO. The number average molecular weights of polymers are in the range of 3154 to 22260 g / mole. The soluble part of the polymers is found to be oligomer. The Absorption maximum in UV-Vis spectra of the polymers is in the range of 307-392 nm. All the polymers show red shift of absorption maximum with respect to their monomers. Optical band gap of the polymers is found to be 2.1-2.47 eV. XRD analysis reveals that polymers are amorphous in nature. Polymers possess good thermal stability with the onset decomposition temperature around 300-350 °C under nitrogen atmosphere. Thermal stability increases with the increase in molecular weight of polymers. The polymers exhibit a glass transition temperature (Tg) in the range of 63-154 °C. It is observed that Tg of the polymers decreases with the increase in length of side chain.

2. Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Cyclic voltammetry study indicates that the oxidation potentials of polymers are high (2.45V) and there is no significant change with substituents. At the same time, change in side chain plays a significant role for altering the reduction potential of polymers. The reduction potential of the polymers is in the range of -0.84V to -2.25 V. It is observed that quinolinyl containing polymer PQTA have the least reduction potential amongst ester substituted polymers due to large molecular weight compared to others. All the polymers seem to be stable under cyclic oxidation and reduction potential (up to 10 cycles). The phenyl and quinolinyl containing polymers have higher band gap and HOMO energy level than alkyl and cyclohexyl derivative polymers. LUMO energy level is same for all the polymers. The electrochemical band gap of the polymers is in the range of 1.57 -2.365 eV and the value is lower than the optical band gap.

The fluorescence emission maximum of the polymers is found to be in the range of 530nm for PPDCHTA to 547 nm for PHTA. The light emission is in the yellow-green region. Stokes shifts of the polymers are in the range of 148 nm for PQTA to 230nm for PPDCHTA. The PL intensity increases with increasing the degree of polymerization. It is found high for PQTA and low for polymer PPDCHTA. It is consistent with their degree of polymerization. The enhanced fluorescence efficiency of polymers is achieved at the cost of their solubility. Here, ester spacer weakens the direct effect of side chain on polythiophene backbone. Also,
PL intensity increases with dilution and the limiting value of the concentration is 0.0125 wt%
for all polymers except PQTA which is 0.006 wt%. The PL intensities increase with
dilution which indicates fluorescence quenching at higher polymer solution concentration.
Polymers in solid state show emission band at 553-564 nm. The fluorescence of polymers in
solid state shows red shift in comparison to their solution. The relative fluorescence quantum
yield of polymers in THF solution is in the range of 0.237 to 2.481 with respect to
Rhodamine B dye. The high fluorescence quantum yield of PQTA polymer is due to the
presence of quinoline moiety in the polythiophene backbone.

The polymers show yellowish colour in EL spectra. The turn on voltage of devices is in
the range of 5.4V to 7V for current injection. Turn on voltage of POTA is low (5.4 V) and is
high (7 V) for PPDPTA. The emission maxima of EL devices based on POTA and PQTA are
536 and 540 nm respectively, which are similar to their corresponding photoluminescence
maximum. Light emission of the EL device was too weak to be measured for PHTA, PDTA,
and PDDTA and no emission was observed for PPDPTA and PPDCHTA. This may be due to
the weak film forming capability and low intensity of PL in solid state of oligomer
compound. This results in poor interaction of interfaces for charge transport of carrier in LED
device.

3. Fluorescence quenching of ester substituted polythiophenes and their application as
chemical sensor

Only quinolinyl containing polymer PQTA shows fluorescence quenching behaviour in
the presence of HCl and other polymers do not show any significant fluorescence quenching
in the presence of HCl. The fluorescence quenching of PQTA polymer in acids is due to the
protonation of imine nitrogen in quinolinyl group. The PQTA polymer can trace the small
concentration of acid and metal ions in solution. The Stern-Volmer quenching coefficient for
HCl is calculated and found to be 141 M⁻¹. Moreover quenching depends on concentration of
HCl. The detection limit of HCl acid by PQTA polymer is found to be 0.08 -10 mole L⁻¹. The
PQTA polymer can be reusable after treatment with alkali for acid detection purpose. The
fluorescence of PQTA polymer is quenched by copper, cadmium and lead metal ions and
quenching is sensitive to concentrations of metal ions. The Stern-Volmer quenching
coefficients are 2.285×10³ M⁻¹ for Cu²⁺ ions, 2.287×10³ M⁻¹ for Cd²⁺ ions and 3.7×10⁴ M⁻¹
for Pb²⁺ ions. In the case of Cu²⁺ ions, the overall detection range is 2.5 × 10⁻⁶ - 100 × 10⁻⁶
mole L⁻¹, while for Cd²⁺ ions the overall sensing range is 5 × 10⁻⁶ - 100 × 10⁻⁶ mole L⁻¹, and
for Pb\textsuperscript{2+} ions overall detection range is \(4 \times 10^{-6} - 100 \times 10^{-6}\) mole L\textsuperscript{-1}. The fluorescence of PQTA polymer is exorbitantly increased in the presence of Al\textsuperscript{3+}, Zn\textsuperscript{2+}, nucleotides and protein (l-proline). The PQTA polymer possesses multi facet fluorescence properties which can sense the wide range of compounds from acids to metal ions and from nucleotides to protein.

The same polymer can be utilized in light emitting diode, chemical sensor and other optoelectronic applications by incorporating the appropriate side chain moiety on the conjugated backbone.

5.2 Future scope of the present investigation

1. Theoretical study of band gap for 3-ester substituted polythiophenes.
2. Interaction of 3- ester substituted polythiophenes and quantum dot and its light emitting diode application.
3. To study the actual mechanism of blue shifting emission of PQTA polymer in the presence of specific copper metal ions.
4. To investigate the exorbitantly enhanced fluorescence of PQTA polymer in the presence of Al\textsuperscript{3+}, Zn\textsuperscript{2+}, nucleotides and proteins.