CHAPTER 3

Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes
3.1 Introduction

Recent advances in the field of electroluminescence of conjugated polymers provide a bright future for LEDs [1-13]. Conjugated polymers offer a number of advantages over conventional inorganic / organic materials. The processibility promises a significant advantage in large-area fabrication and the flexibility promises the fabrication of displays with unusual non-standard shapes [14-19]. In recent years, thiophene based polymers have been particularly exploited due to their structural versatility, solubility upon functionalization and environmental stability [20-28]. The photoluminescence properties of conjugated polythiophenes are of considerable interest due to their potential applications in light emitting diodes (LED), solar cells, chemical sensors and field effect transistor (FET) [29-32]. Solid state luminescence efficiency of polythiophenes is too low. This low efficiency is attributed to internal conversion of exciton through molecular aggregates and the existence of sulphur in the thienyl moiety which promotes intersystem crossing via spin–orbit coupling, i.e. the heavy atom effect [33-36]. The fluorescence efficiency can be enhanced by changing the substitution patterns by replacing a fraction of the thienylene moieties with groups possessing lighter atoms, e.g., phenylene or introducing steric constraints to reduce molecular aggregation of the side chain substituents on the polythiophene backbone [37-39]. Polythiophenes with suitable substituents in the 3-positions have shown tuneable photoluminescence properties [40-42]. The introduction of bulky groups like cyclohexyl, phenyl on polythiophene causes a steric twisting of the backbone and reduces the conjugation gives blue shifted emission [43-44]. Alkoxy side groups on polythiophenes backbone reduce the band gap of the polymer [45]. The incorporation of strong electron-withdrawing groups such as carboxylates is difficult because these substituents increase the potential for oxidation of the monomer and destabilize the resulting radical cation [46-47]. The devastating electron withdrawing effect of the oxygen atom in the vicinity of the thiophene can be neutralized by the intercalation of one methylene groups without any loss of polymer electroactivity. Electron-withdrawing ester groups on the thiophene ring are of considerable interest, as it may facilitate electron injection, influence electronic properties and promote triplet formation. It may also stabilize the conjugated backbone against oxidation or other unwanted degradative events [48-49]. The ester containing polythiophene derivatives show higher fluorescence quantum efficiency than that of alkyl containing derivatives [50-53].
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

The study of the electrochemical behaviour of polymers as a function of substitution can shed some light on the understanding of the reduction and oxidation process. The reduction and oxidation processes consist of several simultaneous and/or consecutive chemical and physical processes like swelling of the polymer, charge transfer between the electrode and the polymer, insertion of compensating ions into the bulk of the polymer, conformational changes of the polymer chain and change of conductivity [54]. The introduction of side groups will change several properties of the polymer and it may be difficult to confirm that oxidation and reduction potentials are entirely the result of one certain functionality. Nevertheless, some trends can be extracted that may be helpful for design and application of new materials. In addition, the energy position of HOMO and LUMO of conjugated polymers can be determined by cyclic voltammetric method. The relevance and generality of electrochemical characterization of conjugated polymers can be estimated by comparison to other methods. This is frequently done by calculating the electrochemical band gap and comparing it with optical band gap [55-56].

The operation of a light-emitting diode comprises several steps: charge injection, charge transport, charge recombination and decay of the exciton via radiative and non-radiative channels [57-63]. The electroluminescence process is strongly related to photoluminescence. In the majority of cases the same excited states are responsible for both electroluminescence (EL) and photoluminescence (PL). Electroluminescence is a combination of both optical and electrical phenomenon. Electroluminescent properties offer to choose colour for LED application. It also gives the information about quantum efficiency, stability and operating voltage required for LED.

Fabricating the state-of-the-art polymer light emitting diodes (PLEDs) involves achieving balanced and efficient injection of both electrons and holes, and therefore low work function cathodes and high work function anodes are required to minimise injection barriers. The mismatch of work function between the anode/cathode also introduces a fundamental asymmetry in the barrier heights in forward and reverse bias, which in turn leads to diode-like rectifying behaviour. The most widely used anode is indium-tin-oxide (ITO) because of its transparency and low resistivity. However, ITO is not ideal because it is not a well defined system and its physical properties are highly sensitive to the fabrication and preparation process [64]. Furthermore, the work function of ITO is often lower than desired. Improved hole injection and device performance (higher efficiency/lifetime and lower operating voltage) have been obtained by introducing a layer of poly(ethylene-dioxythiophene)/poly(styrene sulphonic acid) (PEDOT:PSS) between the ITO and the emitting polymer [65-
68]. A similar stratagem, based on the incorporation of an interlayer between the electrode and the active layer, has also been successfully employed at the cathode/polymer interface to enhance electron injection. For example, a thin film of LiF can be inserted between an aluminium cathode and the organic emitter [69-70]. This enables fabrication of efficient diodes without resorting to low work-function metal cathodes, such as calcium and magnesium, which are reactive to the environment and detrimental to the lifetime of LEDs. The consensus over the mechanism behind electron enhancement by insulators such as LiF has not yet been achieved. The different mechanisms are enhanced electron tunnelling from the Al following hole accumulation at the polymer/insulator junction or large voltage drops in the insulator, longer electron attenuation length, reduction of interfacial reactions with the metal electrode, reduction of the barrier height to electron injection, and dissociation of the LiF to form a low work function contact [71-74].

In this chapter, electrochemical, photoluminescence and electroluminescence properties of synthesized polymers have been discussed. The oxidation and reduction potential of different ester substituted polythiophenes were determined by cyclic voltammetry method. We have discussed the influence of substituents on the red/ox potentials. Redox stability of polymers was tested by cyclic voltammetry up to 10 cycles. Furthermore, band gap of polymers was measured by electrochemically and compared with optical method. Photoluminescence properties in solution and solid state of polymers were investigated. The relative quantum yield of polymers with respect to Rhodamine B dye was measured. The electroluminescence properties of polymers were studied by fabricating LED device with configuration ITO / PEDOT: PSS / Polymer/ LiF / Al.

3.2 Experiment

3.2.1 Materials

LiClO₄ (Aldrich), Poly(ethylene dioxythiophene): Poly(styrene sulfonate) (PEDOT:PSS) (Aldrich), LiF (Merck, Germany), ITO coated glass (Vin Karola, USA) were used as received.

3.2.2 Instrumentations

3.2.2.1 Cyclic voltammetry

Polymer films for electrochemical studies were spin cast from THF solution on to ITO coated glass. Cyclic voltammetric (CV) experiments were performed with a standard one
compartment three-electrode configuration cell (Figure 3.1) with the polymer films deposited on ITO coated glass electrode as the working electrode, platinum as the counter electrode, and an Ag/AgNO₃ (0.1M) electrode as the reference electrode. The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. All potentials are reported with respect to reference electrode. Acetonitrile containing LiClO₄ (0.1M) was used as the electrolytic medium. The measurements were calibrated using ferrocene as the standard and the scan rate was 50 mV/s. The experiments were conducted on a Sycopel AEW2-10 cyclic voltammeter.

![Figure 3.1: Typical 3-electrode electrochemical cell](image)

### 3.2.2.2 Photoluminescence spectroscopy

Photoluminescence spectra were recorded using a Hitachi F-2500 FL Spectrophotometer, by excitation of the polymer at maximum absorption wavelength. The fluorescence spectrum of polymer at different concentration in THF solvent was recorded. Solid state PL of polymers was measured by preparing the polymer film on the glass substrate.
3.2.2.3 Device fabrication and testing

The electroluminescence (EL) devices (Figure 3.2) were fabricated on indium–tin oxide (ITO) coated glass substrate with sheet resistance of 20 Ω/cm². The substrate was ultrasonically cleaned with detergent, deionized water, acetone, trichloroethylene, and isopropyl alcohol, sequentially each for 20 minutes and then baked for 2h at 110°C. The ITO substrates were treated with UV–ozone for 5 min prior to film coating. Subsequently, onto the ITO glass a layer of poly(ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) was spin–coated at 1500 rpm from its aqueous solution and then vacuum-dried for 2h at 120°C. The polymer layer was spin–coated at 1500 rpm from the corresponding THF solution (1 wt %) on top of the vacuum-dried PEDOT: PSS layer and then vacuum–dried for 2h at 130°C. Under a high vacuum (1×10⁻³ Torr), a layer of LiF (1nm) at a deposition rate 0.5 Å/s was vacuum deposited and a thick layer of Al (150nm) at a deposition rate 1-4 Å/s was deposited subsequently as cathode. Thickness of the deposited layers was controlled by quartz crystal monitor. The cathode was deposited on the top of the structure. The electroluminescence (EL) spectra were measured using a high resolution spectrometer (Ocean Optics, HR-2000CG UV-NIR). I – V characteristic of LED devices were measured by Keithley 2400 programmable current voltage digital source meter.
3.3 Results and discussions

3.3.1 Electrochemical properties of polymers

3.3.1.1 Redox properties of polymers

Electrochemical properties of synthesized polymers can be assessed in cyclic voltammetry method. Cyclic voltammetry (CV) is a suitable way to study the redox states of polymers. The electrode potential at which a polymer undergoes reduction or oxidation can be rapidly located by CV. Cyclic voltammograms of spin cast of polymers film from THF solvent in 0.1 M LiClO$_4$ acetonitrile solution are shown in Figure 3.3 - 3.9. The oxidation and reduction potentials of polymers are listed in Table 3.1. The oxidation potentials of polymers are found to be high 2.45 V and there is no significant change with different side chains. These observations may be attributed to low molecular weight polymers [54] (molecular weight of soluble portion of polymer in THF solvent is low). On the other hand, reduction potential of polymers has been found to be altered with different side chains. The reduction potential of polymers is in the range of -0.84V to -2.25V. The reduction potential decreases with increasing alkyl side chain length and PDDTA has the lowest reduction potential (-1.2V) among alkyl ester polythiophenes. The reduction potential of PPDPTA, PPDCHTA and PQTA is -1.85 V, -1.8 V and -0.84 V respectively. 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.

Table 3.1: Oxidation and reduction potential of polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Oxidation potential (V)</th>
<th>Reduction potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>2.45</td>
<td>-2.1</td>
</tr>
<tr>
<td>POTA</td>
<td>2.45</td>
<td>-2.25</td>
</tr>
<tr>
<td>PDTA</td>
<td>2.45</td>
<td>-2.0</td>
</tr>
<tr>
<td>PDDTA</td>
<td>2.45</td>
<td>-1.2</td>
</tr>
<tr>
<td>PPDPTA</td>
<td>2.45</td>
<td>-1.85</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>2.45</td>
<td>-1.8</td>
</tr>
<tr>
<td>PQTA</td>
<td>2.47</td>
<td>-0.84</td>
</tr>
</tbody>
</table>
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.3: CV of polymer PHTA in thin film, Scan rate 50mV/S

Figure 3.4: CV of polymer POTA in thin film, Scan rate 50mV/S
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.5: CV of polymer PDTA in thin film, Scan rate 50mV/S

Figure 3.6: CV of polymer PDDTA in thin film, Scan rate 50mV/S
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.7: CV of polymer PPDPTA in thin film, Scan rate 50mV/S

Figure 3.8: CV of polymer PPDCHTA in thin film, Scan rate 50mV/S
3.3.1.2 Redox stability of polymers

CV provides information regarding the stability of the product during multiple redox cycles. ITO coated polymers were exposed to cyclic oxidation and reduction up to 10 cycles. Cyclic voltograms after 10 cycles are given in figure 3.10-3.16. It is observed that there is no significant change in redox potentials. Therefore polymers are quite stable under redox potential. This is possibly due to the presence of ester group in the polymer side chains [4].
Figure 3.10: CV (10 cycles) of polymer PHTA in thin film, Scan rate 50mV/S

Figure 3.11: CV (10 cycles) of polymer POTA in thin film, Scan rate 50mV/S
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.12: CV (10 cycles) of polymer PDTA in thin film, Scan rate 50mV/S

Figure 3.13: CV (10 cycles) of polymer PDDTA in thin film, Scan rate 50mV/S
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.14: CV (10 cycles) of polymer PPDPTA in thin film, Scan rate 50mV/S

Figure 3.15: CV (10 cycles) of polymer PPDCHTA in thin film, Scan rate 50mV/S
3.3.1.3 Estimation of energy level of polymers

The energy levels of HOMO and LUMO provide guidelines in selecting the electrode materials when constructing a LED based on these polymers. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are estimated. Levels are calculated using the following empirical equation (3.1) [75].

\[
\text{HOMO} = 4.4 + (E_{\text{ox onset}}^{\text{onset}}) \quad \text{and} \quad \text{LUMO} = 4.4 + (E_{\text{red onset}}^{\text{onset}})
\]  

(3.1)

The charging of the polymer during the doping process is associated with conformational reorganisation and modification of the energy levels of the polymer. From this point of view only onset potential probes injection of charges to neutral polymers in the ground state. Onset is also advantageous when two or more red / ox peaks are not fully resolved. The onset has been evaluated by drawing two tangents for each peak and is assumed to be where the two tangents cross as indicated by the dashed line for \(E_{\text{pa}}^{\text{ox}}\) in Figure 3.17.
The onset of oxidation and reduction potential, HOMO and LUMO of polymers are given in table 3.2. The HOMO energy level of alkyl and cyclohexyl containing polymers are same and is found to be 5.4 eV. The phenyl and quinolinyl polymers PPDPTA and PQTA, HOMO energy level are ascertained to be 5.9 eV and 6.125 eV, respectively. In case of phenyl and quinolinyl containing polymers, HOMO energy level is higher than alkyl and cyclohexyl derivative polymers. This may be due to the presence of aromatic phenyl and quinolinyl group attached to the ester polythiophenes. On the other hand, LUMO energy level of the polymers is almost identical.
Table 3.2: Onset ox/red potentials and HOMO and LUMO energy levels of polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Side chain moiety (R)</th>
<th>Onset of oxidation potential (V)</th>
<th>HOMO (eV)</th>
<th>Onset of reduction potential (V)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>-C₆H₁₃</td>
<td>1.1</td>
<td>5.5</td>
<td>-0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>POTA</td>
<td>-C₈H₁₇</td>
<td>1.0</td>
<td>5.4</td>
<td>-0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>PDTA</td>
<td>-C₁₀H₂₁</td>
<td>1.0</td>
<td>5.4</td>
<td>-0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>PDDTA</td>
<td>-C₁₂H₂₅</td>
<td>1.0</td>
<td>5.4</td>
<td>-0.57</td>
<td>3.83</td>
</tr>
<tr>
<td>PPDPTA</td>
<td></td>
<td>1.5</td>
<td>5.9</td>
<td>-0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td></td>
<td>1.0</td>
<td>5.4</td>
<td>-0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>PQTA</td>
<td></td>
<td>1.725</td>
<td>6.125</td>
<td>-0.64</td>
<td>3.76</td>
</tr>
</tbody>
</table>

3.3.1.4 Comparison of band gap estimated from optical and electrochemical method

The band gap is an important parameter whose magnitude governs the intrinsic electronic and optical properties of conjugated polymers. The existence of a finite band gap in conjugated polymers is considered to originate principally from bond length alternation.

The electrochemical determination of band gap actually leads to the formation of charge carriers. On contrary, optical transitions do not reveal the formation of free charge carriers, as the excited state in conjugated polymers may be viewed as a bound exciton. At the same time, optical transitions cannot be directly compared to the electrochemical doping process [54].

The electrochemical and optical band gap of polymers are given in table 3.3. The band gap of alkyl and cyclohexyl containing polymers determined by optical and electrochemical
method are more or less same and is found to be 1.6-1.7eV for electrochemical method and 2.29-2.38 eV for optical method. The band gap of phenyl containing polymers is found to be 2.1eV (electrochemically) and 2.45eV (optically). The band gap of quinolinyl containing polymer is found to be 2.365 eV (electrochemically) and 2.47 eV (optically). The band gap of phenyl and quinolinyl containing polymers has higher than alkyl and cyclohexyl polymers. It is seen that optical band gap gives higher values of the band gap. However, both the method establishes the same trend of band gap. Substitutes in 3-ester polythiophene have a pronounced effect on the band gap.

Table 3.3: Electrochemical and optical band gap of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Side chain moiety (R)</th>
<th>Electrochemical band gap (eV)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>-C₆H₁₃</td>
<td>1.7</td>
<td>2.36</td>
</tr>
<tr>
<td>POTAX</td>
<td>-C₈H₁₇</td>
<td>1.6</td>
<td>2.36</td>
</tr>
<tr>
<td>PDTA</td>
<td>-C₁₀H₂₁</td>
<td>1.6</td>
<td>2.29</td>
</tr>
<tr>
<td>PDPTA</td>
<td>-C₁₂H₂₅</td>
<td>1.57</td>
<td>2.38</td>
</tr>
<tr>
<td>PPDTA</td>
<td>-N⁺</td>
<td>2.1</td>
<td>2.45</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>-C₁₅H₃₁</td>
<td>1.6</td>
<td>2.31</td>
</tr>
<tr>
<td>PQTA</td>
<td>-Q⁻</td>
<td>2.365</td>
<td>2.47</td>
</tr>
</tbody>
</table>
3.3.2 Photoluminescence behaviour of polymers

3.3.2.1 Photoluminescence in solution

The photoluminescence (PL) of the polymers in THF solution, excited at the maximum absorption wave length is measured. The emission maximum ($\lambda_{PL_{\text{max}}}$) of the polymers has been found in the range of 530 nm for PPDCHTA to 547 nm for PHTA (Table 3.4), indicating difference of effective conjugation length in the relaxed excited state. The emission of light is in the yellow-green region. The Absorption, emission and stokes shifts of the polymers are shown in Figure 3.18-3.24. Stokes shifts of the polymers range from 148 nm for PQTA to 230 nm for PPDCHTA. These large stokes shifts may be attributed to the configuration rearrangement upon excitation [76-77]. Here, it is observed that side chain of ester substituted polythiophenes plays no significant role for changing the colour of fluorescence emission. However, the fluorescence efficiency has been modified with the change in side chain substituents. It is well known that thiophene itself is a non-fluorescent, while oligothiophenes ($T_n$) and oligo(alkylthiophenes) with two or more thienyl moieties are all fluorescent. Bithiophene shows a very weak fluorescence emission band at 360 nm. The fluorescence quantum yield of bithiophene is only about 1%. The emission maxima, fluorescence quantum yields, and fluorescence of oligothiophenes have been found to increase with increasing number of thienylene moieties [78-79].

The PL intensity of the polymers in THF solution excited at 350 nm has been investigated at 0.05 wt % polymer concentration (Figure 3.25). The PL intensity increases with increasing conjugation length. PL intensity is found to be high for PQTA and low for polymer PPDCHTA. It is consistent with their degree of polymerization. Here, ester spacer weakens the direct effect of side chain on polythiophene backbone.

Table 3.4: Absorption, emission and stokes shift of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption (nm)</th>
<th>Emission (nm)</th>
<th>Stokes shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>370</td>
<td>547</td>
<td>177</td>
</tr>
<tr>
<td>POTA</td>
<td>363</td>
<td>533</td>
<td>170</td>
</tr>
<tr>
<td>PDTA</td>
<td>363</td>
<td>545</td>
<td>182</td>
</tr>
<tr>
<td>PDDTA</td>
<td>359</td>
<td>543</td>
<td>184</td>
</tr>
<tr>
<td>PPDPTA</td>
<td>315</td>
<td>542</td>
<td>227</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>307</td>
<td>530</td>
<td>230</td>
</tr>
<tr>
<td>PQTA</td>
<td>392</td>
<td>540</td>
<td>148</td>
</tr>
</tbody>
</table>
Figure 3.18: Absorption, emission and stokes shift of polymer PHTA in THF solution, excited at 370 nm.

Figure 3.19: Absorption, emission and stokes shift of polymer POTA in THF solution, excited at 363 nm.
Figure 3.20: Absorption, emission and stokes shift of polymer PDTA in THF solution, excited at 363 nm

Figure 3.21: Absorption, emission and stokes shift of polymer PDHTA in THF solution, excited at 359 nm
Figure 3.22: Absorption, emission and stokes shift of polymer PPDPTA in THF solution, excited at 315 nm

Figure 3.23: absorption, emission and stokes shift of polymer PPDCHTA in THF solution, excited at 307 nm
Figure 3.24: absorption, emission and stokes shift of polymer PHTA in THF solution, excited at 392 nm

Figure 3.25: Normalized PL spectra of polymers excited at 350nm in THF solution at 0.05 wt% polymer concentration
3.3.2.2 Photoluminescence in dilute solution

The PL characteristics of the polymers in THF have been measured in different solution concentrations (Figure 3.26- 3.32). The limiting concentration of polymers is given in Table 3.5. The PL intensity increases up to 0.0125 wt% of polymers then decreases except polymer PQTA. The PL intensity of polymer PQTA increases up to 0.006 wt% of polymer and shows steady after 0.006 wt%. The limiting value of the concentration is 0.0125 wt % for all polymers except PQTA polymer which is 0.006 wt%. The result indicates that the PL intensity increases with decrease in solution concentration. This is due to fluorescence quenching at higher polymer solution concentration. This can be explained by classical concentration quenching effects due to nonemissive excimer complexes most easily formed in the more planar conjugated structure at higher concentrations [22].

Table 3.5: Limiting concentration of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Limiting concentration (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>0.0125</td>
</tr>
<tr>
<td>POTA</td>
<td>0.0125</td>
</tr>
<tr>
<td>PDTA</td>
<td>0.0125</td>
</tr>
<tr>
<td>PDDTA</td>
<td>0.0125</td>
</tr>
<tr>
<td>PPDPTA</td>
<td>0.0125</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>0.0125</td>
</tr>
<tr>
<td>PQTA</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Figure 3.26: Normalized PL intensity of polymer PHTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

Figure 3.27: Normalized PL intensity of polymer POTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.
Chapter 3:  Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.28: Normalized PL intensity of polymer PDTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

Figure 3.29: Normalized PL intensity of polymer PDDTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.
Figure 3.30: Normalized PL intensity of polymer PPDPTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

Figure 3.31: Normalized PL intensity of polymer PPDCHTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.
3.3.2.3 Photoluminescence in solid state

The PL in solid state of polymers is measured by preparing the polymer film on the glass substrate. The PL emission of polymers films in solid state are broad and intensity is low (Figure 3.33). The fluorescence emission maximum of polymers in solution and solid state is summarized in Table 3.6. The polymers in solid state show emission band at 553-564 nm. The fluorescence of polymer in solid state shows red shift in comparison to their solution. The low fluorescence efficiency of polymers in solid state is attributed to π- stacking [33].

Table 3.6: PL emission maxima of polymers in solution and solid

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Excited at (nm)</th>
<th>Emission maximum of polymer (0.05 wt%) in THF solution (nm)</th>
<th>Emission maximum of polymer in thin film (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>370</td>
<td>547</td>
<td>564</td>
</tr>
<tr>
<td>POTRA</td>
<td>363</td>
<td>533</td>
<td>549</td>
</tr>
</tbody>
</table>
Table 3.2: Normalized PL spectra of polymers excited at 350 nm in thin film

<table>
<thead>
<tr>
<th>Polymer</th>
<th>363</th>
<th>545</th>
<th>553</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDTA</td>
<td>359</td>
<td>543</td>
<td>548</td>
</tr>
<tr>
<td>PDDTA</td>
<td>315</td>
<td>542</td>
<td>557</td>
</tr>
<tr>
<td>PPDFTA</td>
<td>307</td>
<td>530</td>
<td>562</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>392</td>
<td>540</td>
<td>563</td>
</tr>
</tbody>
</table>

Figure 3.33: Normalized PL spectra of polymers excited at 350 nm in thin film

3.3.3 Quantum yield of polymers

The maximum fluorescence of polymers intensity value at 0.0125 wt% in THF was taken for quantum yield calculation. The standard fluorescent sample, Rhodamine B dye was chosen because it emits in a similar region to these polymers. The fluorescence spectrum of Rhodamine B dye at 0.0125 wt% in THF solvent was recorded. The quantum yield value of polymers was calculated using the standard sample Rhodamine B dye. The quantum yield of
a polymer sample in solution $\phi_s$ relative to a reference sample of known quantum yield $\phi_r$ may be related by eqn. (3.2) [80]:

$$\phi_s = \phi_r \left( \frac{A_r}{A_s} \times \frac{I_s}{I_r} \right)$$

(3.2)

Where $A_s$ and $A_r$ are the absorbance of the sample and reference solutions respectively at the excitation wavelength; $I_r$ and $I_s$ are the corresponding relative integrated fluorescence intensities.

The fluorescence quantum yield of polymers is measured and compared with Rhodamine B dye (Table 3.7). The relative quantum yield of polymers is found to be 0.237-2.481 with respect to Rhodamine B dye at 0.0125 wt %. The quantum yield of PQTA is two times higher than the Rhodamine B dye. The presence of quinoline moiety in the polythiophene backbone is responsible for high fluorescence efficiency of PQTA. In PPDPTA and PPDCHTA polymers, possibly inter-chain dispersive interaction exhibits enhanced aggregation which reduces the fluorescence efficiency [81-82].

Table 3.7: Relative fluorescence quantum yield of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Fluorescence Quantum yield of polymer at 0.0125 wt% (relative)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>0.665</td>
</tr>
<tr>
<td>POTA</td>
<td>0.914</td>
</tr>
<tr>
<td>PDTA</td>
<td>0.839</td>
</tr>
<tr>
<td>PDDTA</td>
<td>0.586</td>
</tr>
<tr>
<td>PDDTA</td>
<td>0.586</td>
</tr>
<tr>
<td>PPDPTA</td>
<td>0.26</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>0.237</td>
</tr>
<tr>
<td>PQTA</td>
<td>2.481</td>
</tr>
</tbody>
</table>

* Relative quantum yield with respect to Rhodamine B dye (fluorescence quantum yield taken as 1)
3.3.4 Electroluminescence properties of polymers

3.3.4.1 Electroluminescence of polymers

The LED device was fabricated with the configuration ITO/PEDOT:PSS/polymer/LiF/Al. PEDOT: PSS was used as a hole transporting layer. The electron injection was helped by using a thin 1 nm LiF layer followed by a thick layer of Al. By applying voltage across the thin film of polymer, $h^+$ and $e^-$ charges from electrodes start to move in opposite directions to each other and when they meet each other in polymer chain, they produce an excited state, which subsequently emit radiation i.e. light (Scheme 3.1-3.2). Fig. 3.34 shows the EL spectra of polymers. The polymers exhibit yellowish colour in EL at 15V. The EL maxima of POTA and PQTA are 536 and 540nm respectively, which are similar to their corresponding photoluminescence maxima. 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 [83].

![Scheme 3.1: EL mechanism](image-url)
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Scheme 3.2: Energy level diagram of polymers

Figure 3.34: EL spectra of polymers at 15 V
3.3.4.2 Current - Voltage characteristic of device

Figure 3.35-3.41 shows the current voltage characteristic of the devices. The turn on voltage of the devices is in the range of 5.4V to 7V for current injection (Table 3.8). The turn on voltage is low (5.4 V) for POTA and is high (7 V) for PPDPTA. The current density i.e. charge carrier capacity of POTA and PQTA is higher than the other polymers. This is effective for light emission in LED device.

Table 3.8: Turn on voltage of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Turn on voltage for current injection(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>5.5</td>
</tr>
<tr>
<td>POTA</td>
<td>5.4</td>
</tr>
<tr>
<td>PDTA</td>
<td>6.0</td>
</tr>
<tr>
<td>PDDTA</td>
<td>6.1</td>
</tr>
<tr>
<td>PPDPTA</td>
<td>7.0</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>6.0</td>
</tr>
<tr>
<td>PQTA</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Figure 3.35: I-V characteristic of polymer PHTA
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.36: I-V characteristic of polymer POTA

Figure 3.37: I-V characteristic of polymer PDTA
Figure 3.38: I-V characteristic of polymer PDDTA

Figure 3.39: I-V characteristic of polymer PPDPTA
Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Figure 3.40: I-V characteristic of polymer PPDCHTA

Figure 3.41: I-V characteristic of polymer PQTA
### 3.4 Summary of properties in table

All the properties of polymers are summarized in Table 3.9.

Table 3.9: All the properties of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Side chain moiety (R)</th>
<th>Mn (g/mol)</th>
<th>(DP)</th>
<th>Solubility (%)</th>
<th>Tg (°C)</th>
<th>$\lambda_{max}^{\text{abs}}$ (nm)</th>
<th>$\lambda_{max}^{\text{em}}$ (nm)</th>
<th>PL (nm)</th>
<th>PL (nm)</th>
<th>$E_{\text{on}}$ (V)</th>
<th>$E_{\text{opt}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{\text{g1}}$ (eV)</th>
<th>$E_{\text{g2}}$ (eV)</th>
<th>$\phi$</th>
<th>EL (nm)</th>
<th>Turn on voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>-C$<em>6$H$</em>{12}$</td>
<td>5372</td>
<td>24</td>
<td>24</td>
<td>94</td>
<td>255</td>
<td>370</td>
<td>547</td>
<td>564</td>
<td>2.45</td>
<td>-2.1</td>
<td>5.5</td>
<td>3.8</td>
<td>1.7</td>
<td>2.36</td>
<td>0.665</td>
<td>-</td>
<td>5.5</td>
</tr>
<tr>
<td>POTA</td>
<td>-C$_4$H$_7$</td>
<td>3338</td>
<td>13</td>
<td>27</td>
<td>-</td>
<td>254</td>
<td>363</td>
<td>533</td>
<td>549</td>
<td>2.45</td>
<td>-2.25</td>
<td>5.4</td>
<td>3.8</td>
<td>1.6</td>
<td>2.36</td>
<td>0.914</td>
<td>536</td>
<td>5.4</td>
</tr>
<tr>
<td>PDTA</td>
<td>-C$_5$H$_8$</td>
<td>1589</td>
<td>6</td>
<td>36</td>
<td>70</td>
<td>254</td>
<td>363</td>
<td>545</td>
<td>553</td>
<td>2.45</td>
<td>-2.0</td>
<td>5.4</td>
<td>3.8</td>
<td>1.6</td>
<td>2.29</td>
<td>0.839</td>
<td>-</td>
<td>6.0</td>
</tr>
<tr>
<td>PDDTA</td>
<td>-C$<em>8$H$</em>{15}$</td>
<td>8418</td>
<td>27</td>
<td>37</td>
<td>69</td>
<td>254</td>
<td>359</td>
<td>543</td>
<td>548</td>
<td>2.45</td>
<td>-1.2</td>
<td>5.4</td>
<td>3.83</td>
<td>1.57</td>
<td>2.38</td>
<td>0.586</td>
<td>-</td>
<td>6.1</td>
</tr>
<tr>
<td>PPDPITA</td>
<td>-C$<em>6$H$</em>{12}$</td>
<td>6852</td>
<td>16</td>
<td>87</td>
<td>63</td>
<td>272</td>
<td>315</td>
<td>542</td>
<td>557</td>
<td>2.45</td>
<td>-1.85</td>
<td>5.9</td>
<td>3.8</td>
<td>2.1</td>
<td>2.45</td>
<td>0.26</td>
<td>-</td>
<td>7.0</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>-C$<em>6$H$</em>{12}$</td>
<td>3154</td>
<td>7</td>
<td>90</td>
<td>67</td>
<td>253</td>
<td>307</td>
<td>537</td>
<td>562</td>
<td>2.45</td>
<td>-1.8</td>
<td>5.4</td>
<td>3.8</td>
<td>1.6</td>
<td>2.31</td>
<td>0.237</td>
<td>-</td>
<td>6.0</td>
</tr>
<tr>
<td>PQTA</td>
<td>-C$<em>6$H$</em>{13}$</td>
<td>22260</td>
<td>83</td>
<td>15</td>
<td>154</td>
<td>256</td>
<td>392</td>
<td>540</td>
<td>563</td>
<td>2.47</td>
<td>-0.84</td>
<td>6.125</td>
<td>3.76</td>
<td>2.36</td>
<td>2.47</td>
<td>2.481</td>
<td>540</td>
<td>5.5</td>
</tr>
</tbody>
</table>
3.5 Conclusions

Cyclic voltammetry study indicates that the oxidation potentials of polymers are high (2.45 V) and there is no significant change with substituents. At the same time, change in side chain plays a significance role for altering the reduction potential of polymers. The reduction potential of the polymers is in the range of -0.84 V 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 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 530 nm 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 230 nm for PPDCHTA. The PL intensity increases with increasing the degree of polymerization. It is found to be 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 redshift 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 5.4 V to 7 V 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.

References