Chapter 3

Study of electrochemical and optical properties of conjugated polymers
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3.1. Introduction

Polymers have long been thought of and applied as insulators. The emergence of electronically conducting polymers has resulted a paradigmatic shift in our thinking and has opened up new vistas in chemistry and physics.¹ This story began in the 1970s, when, somewhat surprisingly, a new class of polymers possessing high electronic conductivity in the partially oxidized (or, less frequently, in the reduced) state was discovered. Three collaborating scientists, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa, played a major role in this breakthrough, and they received the Nobel Prize in Chemistry in 2000 “for the discovery and development of electronically conductive polymers”.²⁻⁸ Electrochemistry has played a significant role in the preparation and characterization of these novel materials. Electrochemical techniques are especially well-suited to the controlled synthesis of these compounds and for the tuning of a well-defined oxidation state. The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still at the foreground of research activity in electrochemistry.⁹ After 30 years of research in the field, the fundamental nature of charge propagation is now in general understood; i.e., the transport of electrons can be assumed to occur via an electron exchange reaction (electron hopping) between neighboring redox sites in redox polymers, and by the movement of delocalized electrons through conjugated systems. Many excellent monographs and reviews of the knowledge accumulated regarding the development of conducting polymers, polymer film electrodes and their applications have been published.¹⁰⁻³⁷

Cyclic voltammetry provides basic information on the oxidation potential of the monomers, on film growth, on the redox behavior of the polymer, and on the surface concentration (charge consumed by the polymer). Conclusions can also be drawn from the cyclic voltammograms regarding the rate of charge transfer, charge transport processes and the interactions that occur within the polymer segments at specific sites between the polymer and the ions and solvent molecules. The reduction and oxidation processes consist of several simultaneous and 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
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Changes of the polymer chain and change of conductivity. 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.

Subsequently, optical properties concomitant to conjugated polymers are important as it gives ample idea regarding feasibility of the polymers to be used in electronic devices. The studies of absorption and emission characteristics provide the information of the band gap, range of emissive colours, interaction with the acceptor etc. The optical properties of conjugated polymers generally studied in solid, solution and thin film forms. The polymer conformation in dilute solutions of conjugated polymers is extended so that interconjugation segment interactions are minimized. Generally, a broad unstructured absorption is accompanied by vibronically structured fluorescence in case of dilute solutions of conjugated polymers. The lack of structure in the absorption is originated due to the effects of torsional motion of the aromatic rings on the conjugation length and is primarily a dynamical effect. While, photoluminescence (PL) is structured because of efficient energy transfer, probably via Forster mechanism, allows the fluorescence to emanate from a small subset of the chromophores that have the lowest energy. This correspond to the most highly planarized geometries with the largest conjugation length and lowest HOMO-LUMO gaps.

This chapter reports the electrochemical and the optical properties of synthesized polymers. The oxidation and reduction potential of polymers were assessed by cyclic voltammetry method. Furthermore, band gap of polymers was measured by electrochemically and compared with optical method. The relative PL quantum yield of polymers with respect to Rhodamine B dye was measured. The PL quenching of the polymers in presence of TiO₂ nanoparticles in solution with 1:1 and 1:2 have also been
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observed. This explains the suitability of TiO2 nanoparticles as electron acceptor in hybrid photovoltaic devices indicating ultrafast electron transfer from donor polymer to acceptor.

3.2. Experimental

3.2.1. Materials

LiClO4 (Aldrich), (6,6)-phenyl C61-butyric acid methyl ester (PCBM) (Aldrich), TiO2 nanoparticles (Aldrich), Rhodamine B (Aldrich), ITO coated glass (Vin Karola, USA) were used as received. All the solvents used were purified and distilled according to the standard procedure. The synthesized polymers reported in Chapter 2 were used for electrochemical analyses.

3.2.2. Instrumentations

3.2.2.1. Cyclic voltammetry

Cyclic voltammetry is a dynamic electrochemical method in which the potential applied to an electrochemical cell is scanned and the resulting change in cell current are monitored to yield a cyclic voltammogram of the redox properties of the material under study. The cyclic voltammograms reported here were recorded with a computer controlled Sycopel AEW2-10 potentiostat/galvanostat at a scan rate of 50 mV/S. Measurements 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/Ag+ electrode as the reference electrode. Acetonitrile containing LiClO4 (0.1M) was used as the electrolytic medium. The measurements were calibrated using ferrocene as the standard. Electrochemical oxidation and reduction processes take place when potential is applied in the working electrode with respect to the reference electrode and this process is equivalent to controlling the energy of the electrons within the working electrode.
3.2.2. UV-Visible spectrophotometer

UV-Visible (UV-Vis) spectrophotometer provides information about structure and stability of the materials in solution. Various kinds of electronic excitation may occur in organic molecules by absorbing the energies available in the UV-Vis region. The spectrophotometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance versus wavelength. The intensity of the absorption is proportional to the number, type and location of colour absorbing structures (chromophores) in the molecule. UV-Visible spectra were recorded on a Shimadzu UV-2550 UV-VIS Spectrophotometer using THF solvent.

3.2.2.3. 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.
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3.3. Results and discussion

3.3.1. Estimation of energy level and band gap of the polymer

The energy levels of HOMO and LUMO provide guidelines in selecting the electrode materials when constructing a photovoltaic device based on these polymers. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are estimated from the onset oxidation potentials ($\phi_{\text{ox}}$) and the onset reduction potentials ($\phi_{\text{red}}$) of the polymers. Energy levels and electrochemical band gap ($E_g^{\text{ec}}$) in turn are calculated using the following empirical equations 3.1-3.3.

$$HOMO = -(\phi_{\text{ox}} + 4.71) \text{ (eV)}; \quad (3.1)$$

$$LUMO = -(\phi_{\text{red}} + 4.71) \text{ (eV)}; \quad (3.2)$$

$$E_g^{\text{ec}} = (\phi_{\text{ox}} - \phi_{\text{red}}) \text{ (eV)} \quad (3.3)$$

All the redox potentials are measured against Ag/Ag$^+$ reference electrode and the energy level calculations are based on ferrocene / ferrocenium (Fc/Fc$^+$) redox standard in CH$_3$CN. The HOMO and LUMO levels are calculated from the onset potentials of oxidation and reduction and by assuming the energy level of ferrocene/ferrocenium (Fc/Fc$^+$) to be 4.8 eV below the vacuum level. The formal potential of Fc/Fc$^+$ was measured as 0.09 V against Ag/Ag$^+$.38,47 Hence, the equations (3.1), (3.2) and (3.3) are valid for the calculations of HOMO and LUMO energy levels and electrochemical band gap.

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 dashed line for $E_{\text{pa}}^{0\alpha}$ in Figure 3.2.
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3.3.3. Redox properties of polymers and electrochemical band gap calculation

All the synthesized polymers viz PBTD, PPAET, PPABT, PDDC, PDDCT, PU₁ and PU₂ were used for the electrochemical analyses. The detailed study and findings are discussed below. As the synthesized polymers bear different structural units, hence the electrochemical behaviors of the polymers are compared among the same type of polymers. All the electrochemical parameters are listed in Table 3.1.

Redox behavior and band gap estimation were studied from recorded cyclic voltammogram of the synthesized polymer films in 0.1 M LiClO₄ acetonitrile solution. The peaks in positive potentials are for oxidation whereas the peaks for negative potentials are assigned for reduction of polymer. The voltammogram (Figure 3.3) showed the irreversible oxidation and reduction pattern of the polymer, PBTD. Low oxidation potential value (0.81 V) compared to that of reduction potential (-2.3 V) of the polymer clearly indicates the electron donor nature of the polymer. The onset of oxidation potential and the onset of reduction potential measured for PBTD are 0.46 V and -1.64 V respectively.

Figure 3.2: Measurement of onset in CV
Figure 3.3: Cyclic Voltammogram of PBTD film on ITO coated glass at a scanning rate of 50 mV/S

The cyclic voltammogram (Figure 3.4) for PPAET and PPABT showed single irreversible oxidation and reduction peaks. The turn-on potential for the p-doping (onset oxidation potential) for the polymers PPAET and PPABT are very low compared to the turn-on potential of the n-doping (onset reduction potentials) which in turn indicates that the polymers possess very good donor nature. The electrochemical band gaps for the polymers are 2.19 and 2.14 eV, respectively, for PPAET and PPABT. Thus it can be concluded that PPABT possesses higher effective conjugation length compared to PPAET.
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![Cyclic Voltammogram of PPAET and PPABT films on ITO coated glass at a scanning rate of 50 mV/S.](image)

**Figure 3.4: Cyclic Voltammogram of (a) PPAET and (b) PPABT films on ITO coated glass at a scanning rate of 50 mV/S.**

Cyclic voltammograms of PDDC and PDDCT (Figure 3.5) also reveal useful information regarding electrochemical behavior of the polymers. During anodic scan region of PDDCT, two irreversible oxidation waves are observed. The first oxidation peak at +0.84 V can be attributed to thiophene oxidation, and the second one at +1.96 V can be attributed to carbazole oxidation. On the other hand, PDDC shows single anodic peak at +1.92 V for carbazole oxidation. The reduction potentials observed from the CV curve for PDDC and PDDCT are 1.89 V and 1.95 V respectively. The lower onset oxidation potential for the polymers PDDC and PDDCT indicates that the polymers possess good donor nature. The electrochemical band gaps for the polymers are 2.21 and 1.91 eV, respectively, for PDDC and PDDCT. The thiophene moiety attached to carbazole moiety has the key role in reducing oxidation potential as well as band gap in case of PDDCT.48
Figure 3.5: Cyclic Voltammogram of PDDC and PDDCT films on ITO coated glass at a scanning rate of 50 mV/S

The cyclic voltammograms of PU₁ and PU₂ are shown in Figure 3.6. The difference in energy for HOMO and LUMO energy levels that of PU₁ and PU₂ are the result of different spacers incorporated into them affecting their redox behaviour. The nearly similar onset oxidation potential and band gap observed for PU₁ and PU₂ are resulted due to presence of same binaphthyl chromophore with similar donor ability. The oxidation and reduction potentials measured for PU₁ are 1.51 V and -2.4 V whereas those of PU₂ are 1.52 V and -2.3 V, respectively. The electrochemical band gap for PU₁ and PU₂ found to be 3.19 eV and 3.17 eV.
Figure 3.6: Cyclic voltammograms of polymers (a) PU₁ and (b) PU₂ films on an ITO-coated glass in CH₃CN containing 0.1M LiClO₄ as supporting electrolyte
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Table 3.1: Electrochemical parameters and energy levels of the polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Oxidation Potential/Reduction Potential (V)</th>
<th>( \Phi_{ox} ) (V vs Ag/Ag(^+)/( E_{HOMO} ) (eV))</th>
<th>( \Phi_{red} ) (V vs Ag/Ag(^+)/( E_{LUMO} ) (eV))</th>
<th>( E_{g}^{ec} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTD</td>
<td>0.81/-2.3</td>
<td>0.46/-5.17</td>
<td>-1.64/-3.07</td>
<td>2.10</td>
</tr>
<tr>
<td>PPAET</td>
<td>1.66/-1.92</td>
<td>0.98/-5.69</td>
<td>-1.21/-3.50</td>
<td>2.19</td>
</tr>
<tr>
<td>PPABT</td>
<td>1.59/-1.94</td>
<td>0.91/-5.62</td>
<td>-1.23/-3.48</td>
<td>2.14</td>
</tr>
<tr>
<td>PDDC</td>
<td>1.92/-1.76</td>
<td>1.18/-5.89</td>
<td>-1.03/-3.68</td>
<td>2.21</td>
</tr>
<tr>
<td>PDDCT</td>
<td>0.84, 1.96/-1.95</td>
<td>0.84/-5.55</td>
<td>-1.07/-3.64</td>
<td>1.91</td>
</tr>
<tr>
<td>PU(_1)</td>
<td>1.51/-2.4</td>
<td>1.31/-6.02</td>
<td>-1.88/-2.83</td>
<td>3.19</td>
</tr>
<tr>
<td>PU(_2)</td>
<td>1.52/-2.3</td>
<td>1.41/-6.12</td>
<td>-1.76/-2.95</td>
<td>3.17</td>
</tr>
</tbody>
</table>

From Table 3.1, it is observed that heterocyclic ring (thiophene and carbazole) containing polymers possess lower values of oxidation potential. Moreover, azomethine linkage along the main chain or side chain has also great influence on the redox potentials. PBTD, with azomethine linkage along the main chain has the lowest value of oxidation potential and comparatively matching value of HOMO energy value to inject hole to anode in photovoltaic cells. However, the presence of non-conjugated spacer in case of PU\(_1\) and PU\(_2\) has resulted higher values of oxidation potential which in turn not suitable for easy exciton formation upon irradiation of light onto it.

3.3.4. Scan rate dependencies on peak current

Another important characteristic concomitant to cyclic voltammograms of semiconducting polymer films is the dependence of the peak current \( (i_p) \) on the scan rate \( (v) \). In our study, the plots of anodic peak current \( (i_{pa}) \) vs scan rate \( (v) \) at the rate of 25, 50, 75 and 100 mv/S for polymer films of PBTD, PPAET, PPABT, PDDC and PDDCT are drawn and found straight lines passing though the origin. According to the well established electrochemical treatments, \( i_p \) is proportional to \( v^{1/2} \) for diffusion effect dominated behavior i.e. in solution state. On the other hand, for a material localized on an electrode surface, \( i_p \) is proportional to \( v \) thus indicating the behavior of surface-localized
electroactive surface. The curves showing relation between anodic peak current with scan rate are shown in Figure 3.7-3.9. Anodic peak currents ($i_p$) observed for the polymers synthesized via oxidative coupling reactions, reveal a linear relationship as a function of scan rate ($v$) for p-doping as shown in figures, which indicates that the electrochemical processes are not diffusion limited but surface localized.\textsuperscript{26,49} However, no such characteristic is observed in case of PU\textsubscript{1} and PU\textsubscript{2}. Due to viscous nature of the PUs, relatively thick films are formed onto ITO coated glass. Hence large and sluggish dopant ions with high diffusion coefficients are required to exhibit this surface-localized electroactive behaviour.\textsuperscript{26}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.7.png}
\caption{Anodic peak current density vs. scan rate plot of PBTD}
\end{figure}
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Figure 3.8: Anodic peak current density vs. scan rate plots of PPAET and PPABT

Figure 3.9: Anodic peak current density vs. scan rate plots of PDDC and PDDCT
3.3.5. Optical properties of polymers

3.3.5.1. UV–Vis spectra of polymers

Conjugated polymers possess intensive and broad absorption bands in the UV-visible region, indicating an extensive π- conjugation in the polymer backbone. The $\lambda_{\text{max}}$ depends on the effective π- conjugation of the polymer chain and the aggregation state of the polymer. With increase in π- conjugation length, a red shift to $\lambda_{\text{max}}$ is observed.

Absorption spectra of the polymers also enable to provide important information regarding its optical band gap. Optical absorption in conjugated polymers which are mostly amorphous or semicrystalline may due to the transition of charge carriers, through a forbidden energy gap, called optical band gap. Attempts have been made to determine the optical band gap using the equation 3.4.50

$$E_g^{\text{opt}} (eV) = \frac{1240}{\lambda_{\text{edge}} (\text{nm})} \quad (3.4)$$

Where $E_g^{\text{opt}}$ is the optical band gap of polymers and $\lambda_{\text{edge}}$ is the absorption edge. The optical characteristic exhibited in UV-visible absorption spectra by all the polymers are summarized in Table 3.2.

The UV-vis absorption spectra of the 0.05% PBTD solution in THF is shown in the Figure 3.10. The absorption spectrum shows a broad absorption over the wavelength range of 400-600 nm with the maximum absorption peak at 467 nm ($\lambda_{\text{max}}$). This might be the result of the electronic transition throughout the whole conjugated molecule including both aromatic rings and central azomethine (-CH=N-) linkage i.e. π- π* and n- π* transition. The onset of absorption of the polymer was 587 nm which lead to the optical band gap of 2.11 eV.
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Figure 3.10: UV-visible absorption spectrum of 0.05% PBTD solution in THF.

The UV-vis absorption spectra of the 0.05% of PPAET and PPABT solutions in THF are shown in the Figure 3.11. The absorption spectra display a broad absorption over the wavelength range of 370-580 nm with maximum absorption peak at 407 and 415 nm ($\lambda_{\text{max}}$), respectively, for PPAET and PPABT. This is resulted due to the electronic transition throughout the whole conjugated molecule including both aromatic rings and azomethine (-CH=N-) linkage i.e. $\pi-\pi^*$ and n- $\pi^*$ transitions. The red shift of the absorption maximum of PPABT in comparison to PPAET is due to the influence of side chain alkyl group. More bulky butyl group in PPABT compared to ethyl group in PPAET reduces the torsional strain and increases the coplanarity of the polymer chain. This may help in increase the effective conjugation length of the polymer and absorption ability as well. Therefore, optoelectronic properties of PPABT are superior to that of PPAET. The onsets of absorption of the polymers are 549 nm and 569 nm which lead to the optical band gap of 2.25 eV and 2.17 eV, respectively, for PPAET and PPABT.
The UV-vis absorption spectra of the 0.05% of PDDC and PDDCT solutions in THF are shown in the Figure 3.12. The absorption spectra also show a wide absorption over the wavelength range of 350-590 nm with maximum absorption peaks at 414 and 443 nm ($\lambda_{\text{max}}$), respectively, for PDDC and PDDCT. This is the result of the electronic transition throughout the whole conjugated molecule i.e. $\pi-\pi^*$ conjugation. The presence of thiophene group along with carbazole moiety in PDDCT results in red shift compared to PDDC favoring the quinoidal structure of the polymer. The onsets of absorption of the polymers are 532 nm and 577 nm which lead to the optical band gap of 2.33 eV and 2.15 eV respectively for PDDC and PDDCT.
Figure 3.12: UV-visible absorption spectra of 0.05% of PDDC and PDDCT solutions in THF.

The UV-vis absorption spectra of the polymers, PU₁ and PU₂ for 0.5% solution in DMAc are reported in Figure 3.13. The spectra display the maximum absorption for PU₁ and PU₂ at the wavelength of 339 nm and 340 nm respectively that is due to \(\pi-\pi^*\) transition originating from the binaphthyl moieties. The absorptions of the polyurethanes with conjugated-nonconjugated system are found in near blue region. Effective conjugation length in these polymers is restricted by the presence of nonconjugated spacers and thus results decrease in absorption maximum.
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Fig.3.13: UV-visible absorption spectra of PU₁ and PU₂ in solution.

Table 3.2: Summary of the optical characteristic exhibited in UV-visible absorption spectra

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{edge}}$ (nm)</th>
<th>$E_g^{\text{opt}}$</th>
<th>$E_g^{\text{ec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTBD</td>
<td>467</td>
<td>587</td>
<td>2.11</td>
<td>2.10</td>
</tr>
<tr>
<td>PPAET</td>
<td>407</td>
<td>549</td>
<td>2.25</td>
<td>2.19</td>
</tr>
<tr>
<td>PPABT</td>
<td>415</td>
<td>569</td>
<td>2.17</td>
<td>2.14</td>
</tr>
<tr>
<td>PDDC</td>
<td>414</td>
<td>532</td>
<td>2.33</td>
<td>2.21</td>
</tr>
<tr>
<td>PDDCT</td>
<td>443</td>
<td>577</td>
<td>2.15</td>
<td>1.91</td>
</tr>
<tr>
<td>PU₁</td>
<td>339</td>
<td>365</td>
<td>3.40</td>
<td>3.19</td>
</tr>
<tr>
<td>PU₂</td>
<td>340</td>
<td>366</td>
<td>3.39</td>
<td>3.17</td>
</tr>
</tbody>
</table>
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3.3.5.2. 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. But in our case, we have found nearly matching electrochemical and optical band gaps (Table 3.2) and the similar trend of variation. Only the difference in observed electrochemical and optical band gap is recorded in case of PDDC, PU₁ and PU₂.

3.3.5.3. Photoluminescence and quantum yield of polymers in solution

The photoluminescence (PL) of the polymers in THF solution, excited at the maximum absorption wavelength is measured. The emission maxima (λ_{PL max}) of the polymers have been found in the range of 548 nm for PDDC and 644 nm for PBTD (Table 3.4), indicating difference of effective conjugation length and structural changes in the relaxed excited state. Only, PU₁ and PU₂ exhibited PL in blue region i.e. 379 nm and 380 nm respectively.

A study of photoluminescence (PL) spectra of 0.05% solution of PPAET, PPABT, PDDC, PDDCT, PU₁ and PU₂ in THF with varying amounts of TiO₂ nanoparticles and PCBM (for PBTD) (1:1 and 1:2 ratio to polymer) has also been carried out. The PL spectra are displayed in Figure 3.14-3.18. The PL intensity of blended solutions of polymers got quenched with increasing amount of TiO₂ (PCBM in case of PBTD) compared to that of pristine polymer solution. The quenching of PL emission is 2-20 times for 1:1 and 1:2 ratio of polymer to TiO₂ (or PCBM for PBTD) than that of the pristine polymer solution. This can be attributed to strong photoinduced electronic interactions between polymers and acceptors (TiO₂ and PCBM) indicating efficient
exciton dissociation in the blend by ultrafast electron transfer from polymer to acceptor.\textsuperscript{49,53} This study indicates the possibility of utilizing PCBM and TiO\textsubscript{2} nanoparticles as acceptor along with the synthesized polymers as donor in fabrication of polymer photovoltaic devices.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.14.png}
\caption{PL spectra of 0.05\% PBTD solution and blend of PBTD and PCBM in THF}
\end{figure}
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Figure 3.15: PL spectra of 0.05% PPAET solution and blend of PPAET and TiO$_2$ in THF

Figure 3.16: PL spectra of 0.05% PPABT solution and blend PPABT and TiO$_2$ in THF
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Figure 3.17: PL spectra of 0.05% PDDC solution and blend of PDDC and TiO₂ in THF

Figure 3.18: PL spectra of 0.05% PDDCT solution and blend of PDDCT and TiO₂ in THF
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Figure 3.19: PL spectra of 0.05% PU₁ solution and blend of PU₁ and TiO₂ in THF

Figure 3.20: PL spectra of 0.05% PU₂ solution and blend of PU₂ and TiO₂ in THF
The maximum fluorescence of polymer intensity value at 0.05 wt % in THF is taken for quantum yield calculation. The standard fluorescent sample, Rhodamine B dye has been chosen because it emits in a similar region to these polymers. The fluorescence spectrum of Rhodamine B dye at 0.05 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 equation 3.5.\textsuperscript{54}

$$\Phi_s = \Phi_r \left( \frac{A_r}{A_s} \times \frac{I_s}{I_r} \right)$$ \hfill (3.5)

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 3.3). The relative quantum yield of polymers is found to be 0.113-0.846 with respect to Rhodamine B dye at 0.05 wt %. It is observed that heterocyclic ring containing polymers i.e. PBTD, PPAET, PPABT, PDDCT showed good fluorescent quantum yield compared to others. The effect of azomethine linkage on quantum yield is also found to be pronounced as PBTD, PPAET and PPABT exhibited comparatively higher quantum yield. The presence of non-conjugated spacers with binaphthyl chromophore in PU\textsubscript{1} and PU\textsubscript{2} might have resulted lower relative quantum yields compared to other fully conjugated polymers.
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Table 3.3: Absorption, emission and relative quantum yield values of polymers in solution

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption (nm)</th>
<th>Emission (nm)</th>
<th>Stokes shift (nm)</th>
<th>PL quantum yield (Relative*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTD</td>
<td>467</td>
<td>644</td>
<td>177</td>
<td>0.864</td>
</tr>
<tr>
<td>PPAET</td>
<td>407</td>
<td>582</td>
<td>175</td>
<td>0.436</td>
</tr>
<tr>
<td>PPABT</td>
<td>415</td>
<td>608</td>
<td>193</td>
<td>0.769</td>
</tr>
<tr>
<td>PDDC</td>
<td>414</td>
<td>548</td>
<td>134</td>
<td>0.345</td>
</tr>
<tr>
<td>PDDCT</td>
<td>433</td>
<td>576</td>
<td>143</td>
<td>0.792</td>
</tr>
<tr>
<td>PU₁</td>
<td>339</td>
<td>379</td>
<td>40</td>
<td>0.113</td>
</tr>
<tr>
<td>PU₂</td>
<td>340</td>
<td>380</td>
<td>40</td>
<td>0.146</td>
</tr>
</tbody>
</table>

* Relative quantum yield is measured with respect to Rhodamine

3.4. Conclusion

- Electrochemical properties of the synthesized polymers are studied from recorded cyclic voltammogram. The polymers bear low oxidation potential compared to reduction potential which indicates that they possess good electron donor ability. HOMO and LUMO energy levels are calculated approximately from the onset oxidation and reduction potential and difference of these level gives band gap of the polymers.

- Electrochemical band gaps of these polymers are found to be in the range of 1.93-3.2 eV. The polymers PU₁ and PU₂ with conjugated-non conjugated system exhibit comparatively higher electrochemical band gaps due to limited conjugation length in the polymer chain.
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- The UV-vis absorption spectra of the 0.05% polymer solutions in THF show a broad absorption over the wavelength range of 350-590 nm with maximum absorption peak at 497 nm, 415 nm and 467 nm ($\lambda_{\text{max}}$), respectively, for PPAET, PPABT and PBTD. This is resulted due to the electronic transition throughout the whole conjugated molecule including both aromatic rings and azomethine (-CH=\(\equiv\)N-) linkage i.e. $\pi-\pi^*$ and $n-\pi^*$ transition. PDDC and PDDCT also exhibit absorption maxima at 412 nm and 462 nm. Thiophene moiety attached with 9-dodecyl carbazole unit in PDDCT results in increase of absorption ability.

- The absorptions of the polyurethanes, PU$_1$ and PU$_2$ with conjugated-nonconjugated system are found in near blue region. Effective conjugation length in these polymers is restricted by the presence of nonconjugated spacers and thus results decrease in absorption maximum.

- The calculated optical band gaps from onset of absorption spectra are in the range of 2.1-3.4 eV. The polymers exhibit good photoluminescence characteristics in solution. Relative quantum yield with respect to Rhodamine B dye have been calculated and found to be in the range of 0.113-0.846. PBTD exhibited the highest quantum yield whereas PU$_1$ exhibited the lowest.

- PL characteristic depends on the type of chromophores and conjugation length in the polymers. The PL quenching of the polymers in presence of TiO$_2$ nanoparticles (or PCBM in case of PBTD) in solution with 1:1 and 1:2 have been observed. This explains the suitability of TiO$_2$ nanoparticles as electron acceptor in hybrid photovoltaic devices indicating ultrafast electron transfer from donor polymer to acceptor.
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References

1. Ingelt, G. Conducting polymers: A new era in electrochemistry (Springer, Germany, 2008)


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