Chapter 4

Photovoltaic property evaluation of conjugated polymers
Chapter 4: Photovoltaic property evaluation of conjugated polymers

4.1. Introduction

Sustainability of our ecosystem depends on the development of renewable energy sources. The toxic and climate changing by-products of our current energy sources are doing serious damage to the planet. Healing effect to the mess that has been already done to the earth can be made by photo conversion of sunlight to electricity directly by means of solar cells or photovoltaic cells. This seems to be the viable long term strategy for a sustainable energy future. Utilization of solar energy as alternative to fossil fuel is a promising option and hence receiving impetus in research field.\textsuperscript{1,2} Polymer based organic photovoltaic systems hold the promise for a cost-effective, light weight solar energy conversion platform which could benefit from simple solution processing of the active layer.\textsuperscript{3-9} The function of such excitonic solar cells is based on photoinduced electron transfer from a donor to an acceptor. Significant advances in the fundamental understanding of the complex interplay between the active layer morphology and electronic properties are required if this technology is to find viable application.

Although common materials used for photovoltaic are generally inorganic, a serious attention has been made to develop conjugated polymers for polymeric solar cell during last few decades due to its easy processibility, flexibility and low cost.\textsuperscript{10-16} Extended $\pi$-conjugation along the polymer chain is the pre-requisite condition for photovoltaic applications for such polymers, yet choice of suitable side chains also influences the properties like band gap, ionic conductivity, morphology and miscibility with other substances.\textsuperscript{10-12,15} The semiconducting polymers, to be a good photovoltaic material should have effective absorption of the visible light i.e. they are preferred to be low band gap materials.\textsuperscript{11,13,17} Generally, polythiophene derivatives viz. poly(3-hexylthiophene) (P3HT), poly(3-octylthiophene)(P3OT) and polyphenylene vinylene (PPV) derivatives are commonly used for this purpose.\textsuperscript{8,13,18-21}

The first generation of organic solar cells includes a single organic layer sandwiched between two metal electrodes of different work functions.\textsuperscript{22,23} Gradually, development of new conjugated polymers with tailor made properties opened a new path for organic solar cell application. But the single layer devices based on these polymers were showing power conversion efficiency of less than 0.1% only.\textsuperscript{24,25} This shortfall of efficiency had harnessed for new device architecture which led to the development of
Chapter 4: Photovoltaic property evaluation of conjugated polymers

polymer-fullerene bilayer heterojunction and bulk heterojunction device incorporating C-60 or C-60 derivatives. C-60 and C-60 derivatives act as electron acceptor favoring ultrafast photoinduced electron transfer from optically excited conjugated polymers which provides efficient exciton splitting and improved power conversion efficiency in turn.26-31

The concept of hybrid solar cells using simultaneously organic and inorganic materials has been implemented to overcome certain drawbacks of organic semiconductors. Common conjugated polymers suffer from low charge carrier mobility and narrow absorption spectrum. Hybrid polymer-inorganic nanocomposites offer combined advantage of both the materials like solution processing of organic semiconductors and high electron mobility of inorganic semiconductors.32 Moreover, strong size dependent optical properties of inorganic semiconductor nanoparticles provide the opportunity of optical band gap tuning and sensitization of conjugated polymers. Several hybrid polymer bulk heterojunction solar cells have been reported including nanoparticles of CdSe, TiO2 and ZnO.11,32,33-37

The other useful approach for organic solar cells is the guest-host approach. The basic idea is to form a system composed of three components: donor component, acceptor component and the polymeric matrix. The embedding of the photoactive conjugated polymer-acceptor blend into a conventional polymer matrix i.e. guest-host approach is a sound and promising method to improve photoactive sample quality for the following reasons: less interchain interaction, possibility of ordering in the matrix, increase in the stability of the photoactive polymer, possibility of tuning of charge transfer by changing intermolecular distance or dielectric permittivity of the host matrix. In the guest-host approach the conjugated polymers are better encapsulated against environmental influences.38-40

In this chapter, we have demonstrated the photovoltaic performance of the synthesized polymers. Single layer, bulk heterojunction, hybrid organic-inorganic and host-guest approach of solar cells for the developed conjugated polymers have been reported. The polymers showed power conversion efficiency in the range 0.019-0.38% with respect to polymers and processing conditions.
4.2. Experimental

4.2.1. Materials

Poly(ethylene-dioxy-thiophene):poly(styrene sulphonate) (PEDOT:PSS) (Aldrich), (6,6)-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM) (Aldrich), ITO coated glass (Aldrich), TiO<sub>2</sub> nanoparticles (5 nm) (Aldrich) were used as received. All the solvents were properly purified before use by standard methods. The synthesized polymers reported in Chapter 2 were used for study of photovoltaic performance.

4.2.2. Fabrication and characterization of polymer solar cells

Solar cells were fabricated with the structure of ITO/PEDOT:PSS/Polymer:PCBM (or TiO<sub>2</sub> nanoparticles)/Al. The ITO coated glasses were pre-cleaned and a thin layer PEDOT:PSS was spin cast from a PEDOT:PSS (Aldrich) aqueous solution onto it and dried in vacuum oven at 120°C for 20 min. The thickness of PEDOT:PSS layer was ca. 60 nm. The photosensitive blend layers were composed of polymer and PCBM in tetrahydrofuran (THF) (1:2, w/w) in case of organic bulk heterojunction (BHJ) device. Polymer-inorganic hybrid solar cells involve dispersion of TiO<sub>2</sub> nanoparticles in polymer solution in THF (1:2 w/w). In both the cases, concentration of polymer is maintained at 10mg/ml for active layer film formation. The photosensitive blend layer was spin-cast on the ITO/PEDOT:PSS electrode and dried at 75°C for 30 min. The thickness of the photosensitive layer was ca. 90 nm which was spin cast at the rotating speed of 1200rpm for 60 seconds. Then the metal cathode of Al was deposited on the polymer layer by vacuum evaporation under (4X10<sup>-3</sup>Pa). The effective area of one cell is about 3 mm<sup>2</sup>. The single layer solar cell was also fabricated by the same procedure with the structure ITO/Polymer/Al. The current-voltage (I-V) measurements of the device were conducted on Keithley 2420 Source Measure Unit. A Xenon lamp with AM1.5 filter (Newport Oriel, USA) was used as the white light source, and the incident optical power at the sample was 100mW/cm<sup>2</sup>.

The photovoltaic cells with host-guest structures using two polyurethanes viz. PU<sub>1</sub> and PU<sub>2</sub> with Rhodamine B were fabricated with the structure of ITO/PEDOT:PSS/PU<sub>1</sub> (or PU<sub>2</sub>) + Rhodamine B:TiO<sub>2</sub> nanoparticles/Al. The
Chapter 4: Photovoltaic property evaluation of conjugated polymers

photosensitive blend layer comprising polyurethane and Rhodamine B as host-guest mixture as well as dispersed TiO$_2$ nanoparticles in tetrahydrofuran (THF) was spin-coated on the ITO/PEDOT:PSS electrode and dried at 75°C for 30 min. Polyurethane and Rhodamine B, the host-guest mixture were taken in 3:1 (w/w) ratio whereas TiO$_2$ nanoparticles was taken in 2:1 (w/w) ratio to the composite weight of host-guest mixture. This composition gives stable film when 2% (w/v) host-guest mixture in THF is spin coated onto anode.

4.2.3. Test system and configuration

Figure 4.1 illustrates the measurement configuration for generating the illuminated forward bias $I-V$ characteristics, using a Keithley Model 2420 and a 4-wire connection to the cell. A solar simulator provides appropriate illumination for the cell and a cooled, vacuum hold-down chuck secures the cell and provides isothermal test conditions.

![Figure 4.1: $I-V$ Measurement configuration](image-url)
4.2.4. Evaluation of photovoltaic parameters

Photovoltaic parameters and efficiency of the cells can be evaluated from the characteristic $I-V$ curve under illumination of AM 1.5 with intensity of 100 mW/cm$^2$. The typical $I-V$ curve of a sample is shown in Figure 4.2 to illustrate the calculation of different parameters.

![Figure 4.2: Typical I-V curve of a photovoltaic cell](image)

The device parameters can be calculated using the following equations:

$$\text{FF} = \frac{P_{\text{max}}}{I_{\text{SC}} \cdot V_{\text{OC}}} = \frac{I_{\text{max}} \cdot V_{\text{max}}}{I_{\text{SC}} \cdot V_{\text{OC}}}$$

(4.1)

$$\eta_e (\%) = \frac{\text{FF} \cdot I_{\text{SC}} \cdot V_{\text{OC}}}{P_{\text{in}}} \times 100$$

(4.2)

where $V_{\text{OC}}$ is the open-circuit voltage, $I_{\text{SC}}$ is the short-circuit current, FF is the fill factor, $\eta_e$ is the power conversion efficiency, $P_{\text{in}}$ is the intensity of the white light and $V_{\text{max}}$ and $I_{\text{max}}$ are the voltage and the current at the maximum power point of the $I-V$ curve.
4.3. Results and discussion

4.3.1. Single layer and bulk heterojunction photovoltaic performance of PBTD

Single layer solar cells consisting of only one semiconductor material are often referred to as Schottky type devices. In such cells, a single organic layer is sandwiched between two metal electrodes of different work functions. The structure is simple but an absorption covering the entire visible range is rare using a single type of molecules. In our case, the single layer solar cell based on PBTD with the structure ITO/Polymer/Al has power conversion efficiency ($\eta_{\text{e}}$) of 0.019% with short circuit current $I_{\text{SC}} = 0.86$ mA/cm$^2$ and open circuit voltage $V_{\text{OC}} = 0.1$ V. The fill factor (FF) of the device is calculated to be 0.23. The photoactive region is very thin and since both positive and negative photoexcited charges may travel through the same path, recombination losses are generally very high. So, Power conversion efficiency in the case of single layer polymer solar cells is low as witnessed in case of PBTD based single layer solar cell.

The increase in power conversion efficiency (PCE) to high extent is observed for the bulk heterojunction solar cell device based on the same polymer. The structure of the solar cell is ITO/PEDOT:PSS/PBTD:PCBM (1:2 w/w)/Al where the polymer is used as electron donor, PCBM is used as the electron acceptor and PEDOT:PSS layer is used as hole injecting layer. The power conversion efficiency (PCE) for this device is 0.38% with the calculated $V_{\text{OC}}$ and $I_{\text{SC}}$ values of 0.37 V and 2.51 mA/cm$^2$, respectively. $I-V$ curves of single layer and bulk heterojunction devices (BHJ) are shown in Figure 4.3 and the photovoltaic parameters are listed in Table 4.1. The PCE of bulk heterojunction structured solar cell has shown increase of PCE to 20 times compared to single layer cell which is the result of efficient exciton harvesting by creating a highly folded architecture such that all excitons are formed near a heterojunction. This favours splitting as well as collection of opposite charges by the respective electrodes. Although, the polymer possesses matching HOMO levels as shown in Figure 4.4 to inject holes to ITO through PEDOT:PSS layer, PCE of the BHJ is found to be low. This may be attributed to the comparatively high band gap of PBTD ($>2.0$ eV) and inability of harvesting higher range solar spectrum thereby limiting the photocurrent. PCE of the polymer (PBTD) based solar cell may be increased to higher level by optimization. Polymer purity, polymer to
acceptor (PCBM) ratio, use of processing additives, solvent annealing are the some of the factors which affect the efficiency ($\eta_e$) of the polymeric solar cells.\textsuperscript{6,42-45} Although by introducing PCBM as electron acceptor we are achieving higher conversion efficiency, the cost of the same is much higher than inorganic known acceptor, TiO$_2$. This encourages us to replace PCBM as acceptor for rest of our studies.

\textbf{Table 4.1:} Summary of the photovoltaic performance for the solar cells based on PBTD

<table>
<thead>
<tr>
<th>Photoactive layer</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE, $\eta_e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Layer</td>
<td>0.1</td>
<td>0.86</td>
<td>0.23</td>
<td>0.019</td>
</tr>
<tr>
<td>PBTD / PCBM</td>
<td>0.37</td>
<td>2.51</td>
<td>0.41</td>
<td>0.38</td>
</tr>
<tr>
<td>BHJ Layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textbf{Figure 4.3:} $I$-$V$ characteristics of photovoltaic devices (a) single layer structure (ITO/PBTD/Al), and (b) bulk heterojunction structure (ITO/PEDOT:PSS/PBTD:PCBM (1:2 w/w)/ Al
Chapter 4: Photovoltaic property evaluation of conjugated polymers

Figure 4.4: Schematic energy level diagram for PBTD based bulk heterojunction device, with energy levels in eV relative to vacuum.
4.3.2. Polymer-inorganic hybrid photovoltaic cells based on PPAET and PPABT

The concept of hybrid solar cells using simultaneously organic and inorganic materials has been implemented to overcome certain drawbacks of organic semiconductors. Hybrid polymer-inorganic nanocomposites offer the combined advantages of both the materials: solution processing of polymer semiconductors and high electron mobility of inorganic semiconductors. Moreover, strong size dependent optical properties of inorganic semiconductor nanoparticles provide the opportunity of optical band gap tuning and potentially sensitization of conjugated polymers by mixing them. Several hybrid polymer bulk heterojunction solar cells have been reported including nanoparticles of CdSe, TiO\textsubscript{2} and ZnO. Hybrid device based on zinc oxide (ZnO) nanoparticles (5 nm) and poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV) exhibited power conversion efficiency (PCE) of 1.1\%.\textsuperscript{37} PCE reported for hybrid solar cells based on blends of isotropic TiO\textsubscript{2} particles with poly(3-hexylthiophene) (P3HT) and elongated TiO\textsubscript{2} rods with poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) were 0.42\% and 0.49\%, respectively.\textsuperscript{46,47} G. D. Sharma et al. reported hybrid solar cell from poly(3-phenyl azomethine thiophene) (PPHT) with ZnO and dye-sensitized PPHT with ZnO thin films. The dependence of photovoltaic parameters on the weight fraction of ZnO in PPHT: ZnO was also investigated and found that the device with 45\% of ZnO in both composites exhibited the best photovoltaic performance with PCE being 0.12\% and 0.52\%, respectively.\textsuperscript{48}

The photovoltaic properties of the side chain azomethine linkage containing polythiophene derivatives i.e. PPAET and PPABT have been studied by fabricating the device with the structure of ITO/PEDOT:PSS/Polymer:TiO\textsubscript{2} nanoparticles (1:2 w/w)/ Al where the conjugated polymers are used as electron donor and TiO\textsubscript{2} nanoparticle is used as the electron acceptor. The exciton formation upon absorption of photon is the primary process which is followed by ultrafast electron transfer from LUMO of donor to acceptor. Thus electrons are collected at Al electrode through acceptor and holes are collected at ITO via hole injecting PEDOT: PSS layer thereby causing voltage difference in two electrodes. \textit{I-V} curve for the devices based on PPAET and PPABT is shown in Figure 4.5 and photovoltaic parameters are listed in Table 4.2.
Chapter 4: Photovoltaic property evaluation of conjugated polymers

Figure 4.5: *I-V* characteristics of photovoltaic devices of the structures (a) (ITO/PEDOT:PSS/PPAET:TiO$_2$ nanoparticles (1:2 w/w)/ Al) and (b) (ITO/PEDOT:PSS/PPABT: TiO$_2$ nanoparticles (1:2 w/w)/ Al)

The fabricated photovoltaic devices based on the synthesized polymers, PPAET and PPABT show power conversion efficiency (PCE) ($\eta_e$) of 0.102% and 0.125%, respectively. $I_{SC}$, $V_{OC}$ and FF exhibited by the device based on PPAET are 1.16 mA/cm$^2$, 0.24 V and 0.36 while the same parameters exhibited by the device based on PPABT are 1.29 mA/cm$^2$, 0.26 V and 0.37. PPABT based hybrid photovoltaic device shows higher PCE compared to the device based on PPAET though the devices are fabricated in similar conditions. This is attributed to higher donor ability of PPABT than that of PPAET as revealed in electrochemical study resulting easier exciton formation. Moreover, lower band gap of PPABT facilitates higher absorption of irradiated radiation thereby affecting improvement of PCE. The energy level diagram (Figure 4.6) of the devices also explain the reason of higher $I_{SC}$ and PCE exhibited by the photovoltaic device with the donor polymer, PPABT compared to the other fabricated device with PPAET. The HOMO
energy level of PPAET is lying 0.06 eV lower to that of PPABT causing less efficient hole migration to PEDOT:PSS hole injecting layer.

Table 4.2: Photovoltaic properties of PPAET and PPABT based hybrid devices

<table>
<thead>
<tr>
<th>Photoactive layer</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE, $\eta_\text{e}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAET: TiO$_2$ nanoparticles</td>
<td>0.24</td>
<td>1.16</td>
<td>0.36</td>
<td>0.102</td>
</tr>
<tr>
<td>PPABT: TiO$_2$ nanoparticles</td>
<td>0.26</td>
<td>1.29</td>
<td>0.37</td>
<td>0.125</td>
</tr>
</tbody>
</table>

Figure 4.6: Schematic energy level diagram for the PPAET and PPABT based hybrid photovoltaic devices, with energy levels in eV relative to vacuum.
Chapter 4: Photovoltaic property evaluation of conjugated polymers

4.3.3. Polymer-inorganic hybrid photovoltaic device for PDDC and PDDCT and effect of annealing

Among the different conjugated polymers, polycarbazole derivatives are of great importance owing to its various useful properties; such as easy formation of relatively stable radical cations (holes), high charge carrier mobility’s, and high thermal and photochemical stability and hence are suitable in many optoelectronic applications. A soluble and processable polycarbazole with a branched 2-decyltetradecyl substituent on nitrogen was designed and synthesized by a Ni(COD)2-mediated Yamamoto coupling polymerization by J. Li et al. The same polymer was used to fabricate photovoltaic device with perylene diimide dye as an electron acceptor and showed a short circuit current ($I_{sc}$) of 0.26 mA/cm², an open circuit voltage ($V_{oc}$) of 0.71 V, a fill factor (FF) of 37%, and a PCE value of 0.63%. Leclerc and co-workers further reported a series of poly(3,6-carbazole) derivatives using different electron-deficient moieties fabricated solar cell with the acceptor [6,6]-phenyl C$_{61}$-butyric acid methyl ester (PCBM) and found power conversion efficiency in the range of 0.8-1.1%. The power conversion efficiency of polymeric solar cells can be improved by multiparametric optimization, where annealing of active layer plays a vital role. J. H.-J. Huang et al. reported the effect of annealing on polymer photovoltaic devices with blends of poly[9,9'-dioctyl-fluorene-co-bithiophene] with PCBM. The highest PCE of 2.14% with $V_{oc}$ of 0.99 V and $I_{sc}$ of 4.24 mA/cm² was achieved by annealing of polymer films at 70 °C for 30 minutes. Although many reports regarding study of photovoltaic characteristic of polycarbazole derivatives with organic acceptors (PCBM, perylene diimide etc.) are ubiquitous, very few reports mentioned the study of photovoltaic performance of these derivatives with inorganic acceptors like TiO$_2$, ZnO, CdSe etc. Hence, in our approach we have attempted to study the photovoltaic performance of the photoactive layer containing TiO$_2$ nanoparticles blended with N-alkyl substituted polycarbazole derivatives.

The photovoltaic properties of PDDC and PDDCT have been studied by fabricating the device with the structure of ITO/PEDOT:PSS/Polymer:TiO$_2$ nanoparticles (1:2 w/w)/ Al where the polymers are used as electron donor and TiO$_2$ nanoparticle is used as the electron acceptor. The photovoltaic performances of these devices are evaluated before annealing and after annealing at 150 °C for 30 minutes. Figure 4.7 and
Chapter 4: Photovoltaic property evaluation of conjugated polymers

Figure 4.8 show the $I-V$ curves of the PDDC and PDDCT based solar cells under the illumination of AM 1.5, 100mW/cm$^2$, and photovoltaic properties obtained from the $I-V$ curves are listed in Table 4.3.

The fabricated solar cells based on PDDC and PDDCT have power conversion efficiency ($\eta_e$) of 0.11% and 0.14% for poly(9-dodecylcarbazole) (PDDC) and poly(9-dodecylcarbazole)-co-thiophene (PDDCT), respectively, before annealing. Short circuit current, $I_{SC}$ of 1.27 mA/cm$^2$ and open circuit voltage, $V_{OC}$ of 0.25 V are calculated for PDDC based device and the same for PDDCT based device are 1.39 mA/cm$^2$ and 0.28V. The fill factors of the photovoltaic cells are 0.35 and 0.36 for PDDC and PDDCT based polymer-inorganic devices before annealing. The photovoltaic device based on PDDCT shows higher power conversion efficiency compared to that based on PDDC even the devices were fabricated in similar environment and keeping the polymer to acceptor proportion same. This may be due to higher donor ability of PDDCT than PDDC as revealed in electrochemical study and lower band gap of PDDCT compared to PDDC facilitating more absorption of irradiated radiation. The energy level diagram for the fabricated solar cells is shown in Figure 4.9.

The solar cells based on same polymers have been evaluated after annealing the polymer films above their $T_g$ and near melting region where maximum chain re-organization can be achieved. The spin-coated polymer: acceptor film was thermally annealed at 150°C to enhance the film morphology characteristic. The fabricated solar cells based on PDDC and PDDCT show power conversion efficiency ($\eta_e$) of 0.18% and 0.24% for poly(9-dodecylcarbazole) (PDDC) and poly(9-dodecylcarbazole)-co-thiophene (PDDCT), respectively, with short circuit current, $I_{SC}$ = 1.34 mA/cm$^2$ and open circuit voltage, $V_{OC}$ = 0.33 V for PDDC and $I_{SC}$ = 1.74 mA/cm$^2$ and $V_{OC}$ = 0.36 V for PDDCT based devices. The fill factors of the solar Cells are 0.41 and 0.39 for PDDC and PDDCT donor polymer based polymer-inorganic heterojunction solar cells after annealing. The increase in power conversion efficiency of the cells in this case is the result of thermal annealing. The thermal annealing process enables spatial rearrangements of the polymer chains leading to tight stacking and a strong interchain interaction thereby increasing absorption ability of light. Thus a higher extraction of photocurrent can be expected due to strong absorption of light after annealing of the polymer films.
Table 4.3. Photovoltaic properties of PDDC and PDDCT based photovoltaic devices before and after annealing at 150°C for 30 minutes

<table>
<thead>
<tr>
<th>Processing condition</th>
<th>Photoactive layer</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA/cm²)</th>
<th>Fill factor (FF)</th>
<th>PCE, $\eta_e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before annealing</td>
<td>PDDC: TiO₂</td>
<td>0.25</td>
<td>1.27</td>
<td>0.35</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>PDDCT: TiO₂</td>
<td>0.28</td>
<td>1.39</td>
<td>0.36</td>
<td>0.14</td>
</tr>
<tr>
<td>After annealing at 150°C for 30 minutes</td>
<td>PDDC: TiO₂</td>
<td>0.33</td>
<td>1.34</td>
<td>0.41</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>PDDCT: TiO₂</td>
<td>0.36</td>
<td>1.74</td>
<td>0.39</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Figure 4.7: I-V characteristics before annealing of photovoltaic devices with the structures (a) (ITO/PEDOT:PSS/PDDC:TiO₂ nanoparticles (1:2 w/w)/ Al) and (b) (ITO/PEDOT:PSS/PDDCT: TiO₂ nanoparticles (1:2 w/w)/ Al)
Figure 4.8: $I$-$V$ characteristics after annealing to 150°C of photovoltaic devices with the structures (a) (ITO/PEDOT:PSS/PDDC:TiO$_2$ nanoparticles (1:2 w/w)/ Al) and (b) (ITO/PEDOT:PSS/PDDCT: TiO$_2$ nanoparticles (1:2 w/w)/ Al
Figure 4.9: Schematic energy level diagram for PDDC and PDDCT based devices, with energy levels in eV relative to vacuum.
4.3.4. Host-guest system based photovoltaic cells comprising optically active polyurethanes and Rhodamine B dye

The guest-host approach has been used with success for various applications for the following reasons: less interchain interaction, possibility of ordering in the matrix, increase in stability of the photoactive polymer, possibility of tuning of charge transfer by changing intermolecular distance or dielectric permittivity of the host matrix.\textsuperscript{38-40} A set of systems based on conjugated polymer–methanofullerene networks in polystyrene matrix may serve as an example. Solar cell based on a soluble derivative of \textit{p-phenylene vinylene} (MDMO-PPV), and a highly soluble methanofullerene, \[6,6\]-phenyl C\textsubscript{61}-butyric acid methyl ester (PCBM), embedded into a conventional polymer, polystyrene showed the power conversion efficiency (PCE) of 1.5\%.\textsuperscript{38} W. A. Luhman et al. reported a composite electron donor layer with host-guest approach consisting of a \textit{N,N’-bis(naphthalene-1-yl)-N,N’-bis(phenyl)-benzidine} (NPD) host doped with the phosphorescent guest \textit{fac}-tris(2-phenylpyridine)iridium [\textit{Ir(ppy)\textsubscript{3}}] where the presence of phosphor allows increase in exciton diffusion length. This led to ~80\% improvement in power conversion efficiency relative to devices containing an undoped donor layer.\textsuperscript{60} The use of small molecules like dyes in organic solar cell is also growing rapidly although there possesses stability issue and dye molecules are one of the widely studied organic compounds in solar cells.\textsuperscript{61} P. Ruankham et al. studied performance of ZnO dye sensitized solar cells (DSSC) with Eosin-Y, Rhodamine B and Crystal Violet dyes as sensitizer and showed the energy conversion efficiency of 0.42\%.\textsuperscript{62} Whereas Rhodamine B and Crystal Violet based DSSCs exhibited an energy conversion efficiency of 0.18\% and 0.08\%, respectively. But guest-host approach with optically active host materials and small molecule i.e. dye as guests are not properly addressed for solar cell applications yet. In our approach, we have demonstrated the use photoluminescent polyurethane as host material and Rhodamine B dye as guest for efficient solar cells performance so that combination of both would offer easy way of fabricating solar cell by solution processing.

The photovoltaic properties of the guest-host system have been studied by fabricating the device with the bulk heterojunction structure using polyurethane and Rhodamine B dye composite as active material and TiO\textsubscript{2} as acceptor. Figure 4.10 shows
Chapter 4: Photovoltaic property evaluation of conjugated polymers

the $I-V$ Characteristic curve of the fabricated solar cells under the illumination of AM 1.5, 100mW/cm$^2$, and photovoltaic properties obtained from the curve are listed in Table 4.4.

The hybrid polymer-inorganic solar cell based on the guest-host system with the structure ITO/PEDOT:PSS/PU+$+$Rhodamine B:TiO$_2$ nanoparticles/Al exhibits power conversion efficiency ($\eta_b$) of 0.043% with short circuit current $I_{SC} = 0.81$ mA/cm$^2$ and open circuit voltage $V_{OC} = 0.19$ V. The fill factor (FF) of the device is calculated to be 0.28. Whereas PCE for the device structure ITO/PEDOT:PSS/PU$_2$+Rhodamine B:TiO$_2$ nanoparticles/Al is 0.029%, with $I_{SC}, V_{OC}$ and FF being 0.56 mA/cm$^2$, 0.17 V and 0.30, respectively.

The photovoltaic devices based on polyurethanes viz. PU$_1$ and PU$_2$ as host and Rhodamine B dye as guest are fabricated so that the host molecules get well dispersed in polymer matrix to give uniform films. Generally, small organic molecules bear stability issue compared to polymers as their low thermal stability may cause recrystallization or diffusion into one another, owing to repeated heating and cooling condition. The Rhodamine B dye thus will receive better thermal stability when embedded into polyurethane matrix. Moreover, the combination of optically active photoluminescent host polymer with dye molecule (guest) ensures wide range of absorption ability by the active host-guest material over the solar spectrum thereby providing good option to choose photoluminescent host material to fabricate a solar cell device. Thus efficient photon absorption as well as increase in power conversion efficiency in such devices is desired. But power conversion efficiencies shown by both the guest-host system devices are very low. The reason can be explained with the help of energy level diagram shown in the Figure 4.11. The collection of holes at the anode is limited due to high energy barrier (> 0.82 eV) between low lying HOMO level of polyurethanes and hole injecting PEDOT: PSS level. This will restrict the charge separation and migration to the two opposite electrodes and results in decrease of $V_{OC}$ and PCE as well. Moreover, it is apparent that the PCE of the device based on PU$_1$ matrix showed improvement in PCE compared to that of PU$_2$. This can also be explained from energy level diagram as HOMO of PU$_2$ is lying 0.1 eV lower to that of PU$_1$ thereby causing relatively hindered hole migration to hole injecting layer. This shortfall of inefficient charge collection at the anode could be solved by incorporating a layer with intermediate energy level between
Chapter 4: Photovoltaic property evaluation of conjugated polymers

the polymer and PEDOT:PSS layer in multilayer solar cell devices. PU₁ or PU₂ with large band gaps does not show any photovoltaic characteristic when used as donor but they viability for thin film preparation by spin casting with Rhodamine B dye as guest material to use in photovoltaic cells.

Table 4.4: Photovoltaic parameters of devices based on PU₁ and PU₂ with Rhodamine B

<table>
<thead>
<tr>
<th>Photoactive layer</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>PCE, $\eta_e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU₁ + Rhodamine B</td>
<td>0.19</td>
<td>0.81</td>
<td>0.28</td>
<td>0.043</td>
</tr>
<tr>
<td>PU₂ + Rhodamine B</td>
<td>0.17</td>
<td>0.56</td>
<td>0.30</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Figure 4.10: $I$-$V$ Characteristics of (a) PU₁ + Rhodamine B (b) PU₂ + Rhodamine B based photovoltaic devices
Chapter 4: Photovoltaic property evaluation of conjugated polymers

Figure 4.11: Schematic energy level diagram for the host-guest system based hybrid heterojunction device, with energy levels in eV relative to vacuum.
4.4. Comparison of power conversion efficiency of devices based on the synthesized polymers

Table 4.5: Power conversion efficiency of polymers for different device structures

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Photovoltaic Device Structure</th>
<th>Power Conversion Efficiency ($\eta_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTD</td>
<td>Single layer</td>
<td>0.019%</td>
</tr>
<tr>
<td></td>
<td>Bulk heterojunction</td>
<td>0.38%</td>
</tr>
<tr>
<td>PPAET</td>
<td>Polymer-TiO$_2$ hybrid</td>
<td>0.102%</td>
</tr>
<tr>
<td>PPABT</td>
<td>Polymer-TiO$_2$ hybrid</td>
<td>0.125%</td>
</tr>
<tr>
<td>PDDC</td>
<td>Polymer-TiO$_2$ hybrid (Before annealing)</td>
<td>0.11%</td>
</tr>
<tr>
<td></td>
<td>Polymer-TiO$_2$ hybrid (After annealing)</td>
<td>0.18%</td>
</tr>
<tr>
<td>PDDCT</td>
<td>Polymer-TiO$_2$ hybrid (Before annealing)</td>
<td>0.14%</td>
</tr>
<tr>
<td></td>
<td>Polymer-TiO$_2$ hybrid (After annealing)</td>
<td>0.24%</td>
</tr>
<tr>
<td>PU$_1$</td>
<td>Guest-host</td>
<td>0.043%</td>
</tr>
<tr>
<td>PU$_2$</td>
<td>Guest-host</td>
<td>0.029%</td>
</tr>
</tbody>
</table>

Comparison of photovoltaic device performance of all the polymers with respect to different device architectures is shown in the Table 4.5. The bulk heterojunction solar cell based on PBTD using PCBM as acceptor has shown the highest efficiency of 0.38% among all other devices. This is due to low turn-on potential for p-doping and good absorption ability for PBTD. PPAET and PPABT also hold a promise to be good photovoltaic materials as polymer-inorganic hybrid devices based on these polymers exhibit PCE of 0.102% and 0.125%, respectively. The effect of annealing on improvement of PCE is also witnessed for hybrid devices based on PDDC and PDDCT. The annexed thiophene unit with carbazole derivative in case of PDDCT has immense effect to lower the band gap favoring the quinoid structure of polymer and thus reduces
4. Conclusion

The synthesized polymers were tested for photovoltaic applications and found that they possess all the concomitant properties to be the photovoltaic materials. The polymers were used as active material in the devices and their performance was calculated with respect to different structures and processing conditions.

- PBTD polymer shows the highest power conversion efficiency of 0.38% for BHJ structure based on organic acceptor PCBM while single layer structure manifested PCE equal to 0.019% only. Efficient charge splitting to respective electrodes due to ultrafast photoinduced electron transfer from polymer to PCBM acceptor is the key factor of increase in PCE in the case of bulk heterojunction solar cell compared to single layer device.

- PPAET and PPABT based polymer-inorganic hybrid solar cells with TiO$_2$ as acceptor show power conversion efficiency of 0.102% and 0.125%. Use of TiO$_2$ nanoparticles offers easy and low cost devices apart from other certain advantages.

- PDDC and PDDCT polymer based hybrid solar cells show improvement in PCE on annealing due to better morphological arrangements. The power conversion efficiency for hybrid cell based on PDDC is improved to 0.18% from 0.11% and that of hybrid cell based on PDDCT is found to increase to 0.24% from 0.14% upon annealing at 150°C for 30 minutes.
• PU₁ and PU₂ polymers are used as host material for photovoltaic performance using Rhodamine B dye as guest and showed 0.043% for PU₁ whereas 0.029% for PU₂. PU₁ or PU₂ with large band gaps does not show any significant photovoltaic characteristic when used as donor but they viability for thin film preparation by spin casting with Rhodamine B dye as guest material to use in photovoltaic cells.
Chapter 4: Photovoltaic property evaluation of conjugated polymers

References


Chapter 4: Photovoltaic property evaluation of conjugated polymers


Chapter 4: Photovoltaic property evaluation of conjugated polymers


Chapter 4: Photovoltaic property evaluation of conjugated polymers


