In this chapter, we have investigated the effect of introduction of two chalcogenadiazoles 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole in to the poly(ProDOT) chain. On introduction of chalcogenadiazole unit, the HOMO and LUMO of the poly(ProDOT) was decreased by about 1eV and we get polymers with almost the same band gap as that of the homopolymer poly(ProDOT). So we have achieved tuning the energy level of homopolymer by introducing acceptors, without affecting the band gap. Both the polymers are synthesized through direct arylation reaction. Polymers are characterized using optical and electrochemical methods. Experimental results support the theoretical prediction. Polymers PPRO-BTZ and PPRO-BSE possess theoretical band gap of 1.8 eV and 1.79 eV and optical band gap of 1.52 eV and 1.51 eV. The photovoltaic activity of the polymer was also tested using the ITO/In_{2}S_{3}/polymer/Ag heterojunction. The heterojunctions of PPRO-BTZ and PPRO-BSE showed efficiency of 0.014% and 0.006% respectively.
5.1. Introduction

The 3,4-propylenedioxythiophene (ProDOT), is one of the symmetrical members of 3,4-alkylenedioxythiophene family like 3,4-ethylenedioxythiophene (EDOT). The main advantage of ProDOT over EDOT is that, we can graft solubilizing side chains to the polymer without disrupting the regiosymmetry of the polymers\textsuperscript{1-5}. The application of 3,4-propylenedioxythiophene in electrochromic devices\textsuperscript{6-10}, photovoltaic devices\textsuperscript{11-13}, light emitting diodes\textsuperscript{14} and non linear optical devices\textsuperscript{15} are well reviewed in the literature.

In this chapter, we describe the electronic structure calculation, synthesis by direct arylation reaction, characterization and photovoltaic properties of two alternating copolymers of 3,4-propylenedioxythiophene with 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole. The aim was to tune the energy levels of the poly(ProDOT), make them suitable for photovoltaic application and increase the air stability of the poly(ProDOT). This was prompted by the encouraging result that incorporation of the acceptor, cyanovinylene to Poly(ProDOT) decreased both the HOMO and LUMO levels of poly(ProDOT) and polymers with the same band gap as that of the homopolymer was obtained\textsuperscript{12}. The photovoltaic properties of the 3,4-propylenedioxythiophene/cyanovinylene copolymers with PCBM acceptor was studied in detail\textsuperscript{12}. Similarly, 3,4-propylenedioxythiophene and 2,1,3-benzothiadiazole copolymer was synthesized through Stille reaction\textsuperscript{16}. The main problem associated with this method is that the synthesis of tributyltin compound of 3,4-propylenedioxythiophene was very difficult. They used stannane compound without purification. This might have led to the formation of side products and resulted in low molecular weight polymers. One way to overcome this problem is to avoid the use of stannane derivatives. So direct
arylation reaction is the right choice for the cost effective method for polymerizing 3,4-propylenedioxythiophene and 2,1,3-benzothiadiazole. 3,4-propylenedioxythiophene/2,1,3-benzoselenadiazole was also synthesized, keeping in mind the higher acceptor strength of the 2,1,3-benzoselenadiazole unit than the 2,1,3-benzothiadiazole.

5.2. Results and discussion

5.2.1. Band structure calculation

The ground state geometries of oligomers were optimized by means of the hybrid density functional theory (DFT)\(^{17}\) at the B3LYP \(^{18,19}\) (Becke, three-parameter, Lee-Yang-Parr) level of theory using double zeta basis set LANL2DZ (Los Alamos ECP plus DZ)\(^{20}\). LANL2DZ basis set describes core electrons of the heavier elements by means of an effective core potential. This permits the study of Se containing compounds with less computational time. The harmonic vibrational frequencies obtained with B3LYP/LANL2DZ were used to characterize the stationary points as local minima. All the calculations described here were carried out using Gaussian 03 suite of codes\(^{21}\).

The optimized unit cell for the periodic boundary calculation on poly(ProDOT), PPRO-BTZ and PPRO-BSE are shown in figure 1. The length of the translational vector of poly(ProDOT) is 7.9\(\text{Å}\)\(^{0}\) and for PPRO-BTZ and PPRO-BSE, it is 16.6\(\text{Å}\)\(^{0}\). The calculated band structures and density of states are depicted in figure 2 and figure 3. It could be seen from the band structure that all the polymers are direct band gap polymers.
Figure 1: Unit cell for the PBC/B3LYP/LANL2DZ calculation of poly(ProDOT), PPRO-BTZ and PPRO-BSE

Figure 2: Band structure and density of states of poly(ProDOT)
On comparing the band structure of copolymers with homopolymer poly(ProDOT), we can see that HOCO was decreased by 1.21 eV and 1.09 eV for PPRO-BTZ and PPRO-BSE respectively. Similarly LUCO was decreased by 1.17 eV and 1.06 eV respectively. The band gap of PPRO-BTZ and PPRO-BSE are calculated to be 1.8 eV and 1.79 eV. There is no considerable decrease in the band gap on the introduction of 2,1,3-benzoselenadiazole unit instead of 2,1,3-benzothiadiazole. This may be due to the slight increase in the dihedral angle between the adjacent ProDOT and BSE than the BTZ unit. Also we can observe that, on introduction of 2,1,3-benzoselenadiazole and 2,1,3-benzothiadiazole, band gap of the homopolymer poly(ProDOT) is not affected much. We have tuned the energy levels of the homopolymer by introducing acceptors and have made them suitable for photovoltaic application by matching the levels with acceptor In$_2$S$_3$.

**Table 1:** Band structure$^{\#}$ data of poly (ProDOT), PPRO-BTZ and PPRO-BSE

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOCO (eV)</th>
<th>LUCO (eV)</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ProDOT)</td>
<td>-3.79</td>
<td>-2.03</td>
<td>1.76</td>
</tr>
<tr>
<td>PPRO-BTZ</td>
<td>-5.0</td>
<td>-3.2</td>
<td>1.8</td>
</tr>
<tr>
<td>PPRO-BSE</td>
<td>-4.88</td>
<td>-3.09</td>
<td>1.79</td>
</tr>
</tbody>
</table>

$^{\#}$Method: PBC/B3LYP/LANL2DZ
5.2.2. Synthesis of monomers and polymers

The synthetic routes towards the key monomers are depicted in chapter II and chapter IV. The polymers are synthesized through direct arylation reaction between ProDOT and 4,7-dibromo-2,1,3-benzothiadiazole or 4,7-dibromo-2,1,3-benzoselenadiazole using palladium acetate as catalyst (Scheme 1). As benefitted from the side chain of ProDOT, both the polymers are readily soluble in THF, chlorobenzene, toluene, chloroform and can be easily processed as thin film. The polymers are characterized using UV-Visible spectroscopy, Cyclic voltammetry, $^1$H NMR etc. The $^1$H NMR spectra of the polymers are shown in figure 4. The polymers show only one broad peak in the aromatic region due to protons in the BTZ and BSE and one broad peak in the $\delta$ 4-4.1 region due to -OCH$_2$- proton of ProDOT. The isolated yield and molecular weight of both the polymers are summarized in table 2.

Scheme 1: Synthesis of 3,4-propylenedioxythiophene/2,1,3-chalcogenadiazole copolymer
5.2.3. Optical and photoluminescence properties

Absorption spectrum of the polymers are measured both in chloroform solution (figure 5a) and as thin film on glass slides (figure 5b). PPRO-BTZ shows absorption maximum at 604 nm while PPRO-BSE shows maximum at 607 nm. Absorption maximum of PPRO-BTZ and PPRO-BSE in chloroform solution is red shifted by 68 nm and 37 nm in solid state and absorption maximum occurs at 672 nm and 644 nm respectively. This may be due to the inter chain interaction leading to the increase in coplanarity of the polymer chain in thin films. The onset of absorption is used to calculate the optical band gap of the polymers. For PPRO-BTZ and PPRO-BSE the onset of absorption occurs at 814 nm and 818 nm, corresponding to the band gap of 1.52 eV and 1.51 eV. Both the polymers possess almost the same band gap, as predicted by theoretical
calculation. The lowest energy transition is assigned as charge transfer band. This fact is supported theoretically by analyzing the HOCO and LUCO energy levels of the polymers. The HOCO and LUCO are localized on ProDOT and 2,1,3-chalcogenadiazoles respectively.

**Figure 5:** UV-Visible spectra of the polymers a. in chloroform solution and b. in thin film form. The polymer films were spun coated from 5mg/mL chlorobenzene solution on to glass substrate

The photoluminescence spectra of PPRO-BTZ and PPRO-BSE in chloroform solution are presented in figure 6. The wavelengths corresponding to the absorption maxima of the polymers are used as the excitation wavelength. The PPRO-BTZ shows emission maximum at 694 nm and PPRO-BSE and exhibited peak emission at about 745 nm.

**Figure 6:** PL of PRO-BSE and PRO-BTZ in chloroform solution
Table: Optical properties of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption $\lambda_{\text{max}}$ (nm)</th>
<th>Emission $\lambda_{\text{max}}$ (nm)</th>
<th>Absorption onset (film) $\lambda_{\text{onset}}$</th>
<th>$E_{\text{gopt}}$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution</td>
<td>Film</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPRO-BTZ</td>
<td>604</td>
<td>672</td>
<td>694</td>
<td>814</td>
</tr>
<tr>
<td>PPRO-BSE</td>
<td>607</td>
<td>644</td>
<td>745</td>
<td>818</td>
</tr>
</tbody>
</table>

*Calculated from the onset of absorption

5.2.4. Electrochemical properties

Investigations on the electrochemical properties of the polymers are done using polymer film on platinum electrode in 0.1 M Bu$_4$NPF$_6$/acetonitrile electrolyte solution. Both the polymers possess one reduction peak and one oxidation peak. The HOMO and LUMO values are calculated from the onset of oxidation and reduction. The band gap of the PPRO-BTZ and PPRO-BSE are calculated to be 1.85 eV and 1.94 eV respectively. This band gap values do not correlate with the theoretical and optical band gap. A possible explanation for these differences can be found in the fact that, in the optical experiment the electrons and holes formed are bound, forming an exciton, whereas in the electrochemical experiment, ions are created. Apart from the exciton binding energy (which lowers the energy of the exciton, relative to that of the free charges), the solvation energy of the ions created in the electrochemical experiment has also an influence on the observed electrochemical band gap.$^{22, 23}$
Figure 7: Cyclic voltamgrams (scan rate of 100 mV/s) of polymer drop-cast onto a platinum electrode (0.02 cm$^2$) in 0.1M Bu$_4$NPF$_6$/Acetonitrile electrolyte solution

Table 4: Electrochemical properties of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{ox}}$ (V)</th>
<th>$E_{\text{red}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPRO-BTZ</td>
<td>0.629</td>
<td>-1.22</td>
<td>-5.03</td>
<td>-3.18</td>
<td>1.85</td>
</tr>
<tr>
<td>PPRO-BSE</td>
<td>0.511</td>
<td>-1.43</td>
<td>-4.91</td>
<td>-2.97</td>
<td>1.94</td>
</tr>
</tbody>
</table>

5.2.5. Photovoltaic device

The applicability of polymers for photovoltaic device was verified by fabricating a bilayer heterojunction device with the structure ITO/In$_2$S$_3$/Polymer/Ag. Figure 8 shows the current density-voltage characteristics of the heterojunctions under illumination and dark. Under white light illumination (50mW/cm$^2$), the device exhibits a short circuit current density ($J_{sc}$) of 51.4 µA/cm$^2$ and an open circuit voltage ($V_{oc}$) of 547.47 mV for PPRO-BTZ and 31.4 µA/cm$^2$ and 340.86 mV respectively for PPRO-BSE. The fill factor (FF) and efficiency were calculated to be 24.0 % and 26.2% and 0.014% and 0.006% respectively for PPRO-BTZ and PPRO-BSE. Photovoltaic characteristics of bilayer heterojunction devices of PPRO-BTZ and PPRO-BSE are summarized in table 5.
Figure 8: J-V Characteristics of ITO/ In\textsubscript{2}S\textsubscript{3}/Polymer/Ag heterojunctions of PPRO-BTZ and PPRO-BSE

Table 5: Photovoltaic characteristics of bilayer heterojunction devices of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ ($\mu$A/cm\textsuperscript{2})</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPRO-BTZ</td>
<td>547.47</td>
<td>51.4</td>
<td>24.0</td>
<td>0.014</td>
</tr>
<tr>
<td>PPRO-BSE</td>
<td>340.86</td>
<td>31.4</td>
<td>26.2</td>
<td>0.006</td>
</tr>
</tbody>
</table>

5.3. Conclusion and Perspectives

Electronic properties of two low band gap polymers based on 3,4-propylenedioxythiophene and 2,1,3-chalcogenadiazole was calculated using density functional theory in periodic boundary condition formalism. According to theoretical calculation the energy levels are changed by introducing 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole unit to ProDOT chain without affecting the band gap. The polymers are synthesized through cost effective palladium acetate catalysed direct arylation reaction in good yield. The band gap and energy levels of the polymers are determined using both optical and electrochemical methods, and showed agreement with the theoretical results. Both the polymers showed photo activity in the linear heterojunction ITO/In\textsubscript{2}S\textsubscript{3}/polymer/Ag. The device performance can be
improved by designing a bulk heterojunction using an acceptor, which have matching energy levels with the In$_2$S$_3$ and polymer.

**5.4. Experimental section**

The synthetic path towards the ProDOT, 4,7-Dibromo-2,1,3-benzothiadiazole and 4,7-Dibromo-2,1,3-benzoselenadiazole are depicted in chapter II and chapter IV.

**5.4.1. Synthesis of PPRO-BTZ**

To a solution of ProDOT (0.132 g, 0.347 mmol) in 20 ml of DMF, tetrabutylammonium bromide (0.112 g, 0.347 mmol), and sodium acetate (0.188 g, 1.38 mmol) were added. The solution was stirred at room temperature for 15 min followed by addition of 4,7-dibromo-2,1,3-benzothiadiazole (0.102 g, 0.347 mmol) and palladium acetate (10 mol%). The reaction mixture was stirred for 3 days at 90°C and cooled to room temperature. It was precipitated into methanol (200 mL). The precipitate was filtered and purified via Soxhlet extraction with methanol and acetone successively to remove oligomers and catalyst residues. The polymer was dissolved in toluene and filtered. The filtrate was concentrated by evaporation, precipitated in methanol (200 mL), and collected as a dark blue solid.

Yield : 61% (0.11 g)

GPC : $M_n=4795$, PDI=2.54

$T_d (^0C)$ : 285

UV-Visible $\lambda_{max}$(nm) : 604
5.4.2. Synthesis of PPRO-BSE

To a solution of ProDOT (0.132 g, 0.347 mmol) in 20 ml of DMF, tetrabutylammonium bromide (0.112 g, 0.347 mmol), and sodium acetate (0.188 g, 1.38 mmol) was added. The solution was stirred at room temperature for 15 min followed by addition of 4,7-dibromo-2,1,3-benzoselenadiazole (0.118 g, 0.347 mmol) and palladium acetate (10 mol%). The reaction mixture was stirred for 3 days at 90°C and cooled to room temperature. It was precipitated into methanol (200 mL). The precipitate was filtered and purified via Soxhlet extraction with methanol and acetone successively to remove oligomers and catalyst residues. The polymer was dissolved in toluene and filtered. The filtrate was concentrated by evaporation, precipitated in methanol (200 mL), and collected as a dark blue solid.

Yield : 46% (89.2 mg)

GPC : M_n=3805, PDI=2.86

T_d(°C) : 354

UV-Visible λ_max (nm) : 607

1H NMR (400 MHz, CDCl3) : δ 8.34 (b, Ar-H of benzoselenadiazole), 4.05-4.16 (b, ~4H of ProDOT), 1.55-1.29 (m, ~28H, aliphatic-H), 0.88 (m, ~6H, -CH₃)
5.5. References


