3.1. Introduction

Quinoxaline is an n-type building block in semiconducting polymers and this N-heterocycle has been utilized to construct large number of donor-acceptor polymers in photovoltaic devices, with typical donor-acceptor structure. The π-conjugated heterocyclic polymers of
poly(quinoxaline) derivatives has been explored as electron transporting or electron accepting materials because of their high electron affinity due to the two symmetric unsaturated nitrogen atoms in quinoxaline\textsuperscript{1-5}. Quinoxaline-containing segments were shown to be promising acceptors when combined with fluorene or thiophene forming D-A polymers\textsuperscript{6-8}. The impressive performance of quinoxaline-based polymers has shown its obvious potential for achieving high performance in PSCs\textsuperscript{9-11}.

In this chapter, we discuss the effect of structural change in the quinoxaline unit on the band gap and energy levels of alternating copolymer of phenothiazine with acenaphthylene, phenyl and phenanthrene substituted quinoxalines. The electronic properties are calculated using density functional theory to get more insight into the structure-property correlation. Synthesis, optical and electrochemical properties of the copolymers were also studied. Suitability of the polymers for photovoltaic application was explored by fabricating a linear heterojunction device using In\textsubscript{2}S\textsubscript{3} as n-type material.

3.2. Results and Discussion

3.2.1. Theoretical Calculation

3.2.1.1. Theoretical Methodology

The ground state geometries of oligomers were optimized by means of the hybrid density functional theory (DFT)\textsuperscript{12} at the HSEh1PBE referred to as HSE06 in the literature (full Heyd-Scuseria-Ernzerhof functional)\textsuperscript{13,14}, level of theory using 6-31G basis set. The harmonic vibrational frequencies obtained with HSE06/6-31G were used to characterize the stationary points as local minima. The band structure was calculated using HSE06/6-31G theory using the unit cell taken from the central portion of the optimized
tetramer. The calculation described in this chapter was done using G09 suite of codes\textsuperscript{15} on IBM power servers.

\subsection*{3.2.1.2. Model compounds}

In order to investigate the effect of structural change of the quinoxaline derivatives on the band gap of phenothiazine/quinoxaline copolymers, we start the calculation from model compounds (figure 1). The HOMO and LUMO levels are calculated using HSE06/6-31G method. From the energy level diagram, it is noted that the LUMO level of DDACE, DDQ and DBDP occurs at -2.26 eV, -2.36 eV and -2.56 eV. Thus, the acceptor strength is in the order DDACE< DDQ< DBDP. As expected, the energy gap of the model compounds PT-DDACE, PT-DDQ and PT-DBDP are in the order, PT-DDACE> PT-DDQ> PT-DBDP, as a function of acceptor strength (figure 2). The reduction in the energy gap of the D-A monomer is due to the charge transfer from donor phenothiazine unit to the acceptor quinoxaline. This can be visualized from the frontier orbital distribution of the model compounds (figure 3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Structure of model compounds}
\end{figure}
3.2.1.3. Band structure of polymers

Optimized unit cells for the periodic boundary calculation are shown in figure 4. The length of the translational vector is 25 Å. The band structure of the polymers PPHENO-DADCE, PPHENO-DDQ and PPHENO-DBDP is shown in figure 5. It can be noted from the band structure that all the polymers are direct band gap polymers, because the lowest band gap occurs at k=0. It could be seen from the band structure that LUMO level of the
poly(phenothiazine) is reduced by 0.84 eV, 0.97 eV and 1.32 eV respectively by introducing DDACE, DDQ and DBDP units to the phenothiazine chain. The band gaps of PPHENO-DDACE, PPHENO-DDQ and PPHENO-DBDP are 2.38 eV, 2.3 eV and 2.0 eV respectively. The band structure data of the polymers are summarized in table 1.

Figure 4: Unit cell for the band structure calculation of PPHENO-DDACE, PPHENO-DDQ, and PPHENO-DBDP
3.2.2. Synthesis and characterization of monomers and polymers

3.2.2.1. Monomer synthesis

The scheme for the synthesis of diboronate ester of phenothiazine has been depicted in chapter II. The synthetic route for the preparation of acenaphthylene, phenyl and phenanthrene substituted quinoxalines are shown in scheme 1. 5,8-Dibromo-acenaphthyl quinoxaline (DDACE), 5,8-
dibromo-2,3-diphenylquinoxaline (DDQ), 10,13-dibromodibenzo[a,c]phenazine (DBDP) were synthesized through condensation reaction\textsuperscript{16} of 1,2-dibromo-3,4-phenylenediamine with 1,2-acenaphthaquinone, benzil and 9,10-phenanthrenequinone in ethanol/acetic acid, in 79%, 70% and 80% yields. The compounds were characterized using $^1$H NMR, and $^{13}$C NMR spectroscopy and melting point measurement.

\textbf{Scheme 1:} Synthesis of monomers DDACE, DDQ and DBDP

### 3.2.2.2. Polymer synthesis

The polymers were synthesized through typical Suzuki polycondensation reaction between diboronate ester of phenothiazine and DDACE, DDQ and DBDP, which gave PPHENO-DDACE, PPHENO-DDQ and PPHENO-DBDP in 37%, 51% and 46% yields (scheme 2). The polymers are endcapped with phenyl group by quenching the reaction with phenyl boronic acid and bromobenzene. All the polymers are soluble in THF, chloroform, chlorobenzene, toluene etc. The polymerization results and molecular weight data of the polymers are summarized in table 2. All
the polymers were characterized using UV-Visible spectroscopy, $^1$H NMR, cyclic voltammetry etc. The thermal properties of the polymers were investigated by thermogravimetric analysis. All the polymers showed thermal decomposition under nitrogen in the range of 250-295°C (table 2). The $^1$H NMR spectra of the polymers are shown in figure 6. It could be seen that aromatic region is highly populated and all the polymers showed triplet in the region $\delta$ 3.8-3.9 due to –NCH$_2$- protons. PPHENO-DDACE and PPHENO-DBDP show peaks in the region $\delta$ 2-2.2, which may be due incomplete capping of the polymers using phenyl boronic acid and bromobenzene.
Scheme 2: Synthesis of polymers PPHENO-DDACE, PPHENO-DDQ and PPHENO-DBDP

Table 2: Results of polymerization and thermal stability of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ a</th>
<th>$M_w$ a</th>
<th>PDI</th>
<th>Yield (%)</th>
<th>$T_d$ (°C)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPHENO-DDACE</td>
<td>4248</td>
<td>7541</td>
<td>1.77</td>
<td>37</td>
<td>257</td>
</tr>
<tr>
<td>PPHENO-DDQ</td>
<td>9578</td>
<td>18427</td>
<td>1.92</td>
<td>51</td>
<td>270</td>
</tr>
<tr>
<td>PPHENO-DBDP</td>
<td>5905</td>
<td>7078</td>
<td>1.19</td>
<td>46</td>
<td>295</td>
</tr>
</tbody>
</table>

a. Determined using GPC in toluene based on polystyrene standard. b. Onset of decomposition measured by TGA under nitrogen.
3.2.3. Optical properties

Figure 7a shows the absorption spectrum of polymers in chloroform as the solvent along with the photograph of polymer solution. It can be seen that with polymers based on the strong acceptor, ie DBDP, brown colour is achieved due to the red shifted absorbance in solution. The absorption maximum of PPHENO-DDACE, PPHENO-DDQ and PPHENO-DBDP occur at 439 nm, 450 nm and 477 nm. To optically evaluate the magnitude of the band gap, the thin film absorbance is measured as shown in figure 7b for spin cast film from chlorobenzene solution on to glass substrates. The absorption maximum in thin film is slightly red shifted than in solution. This may be due to the slight increase in the coplanarity of the polymer chain in the solid state. It is observed that the band gap ranges from 1.92-2.24 eV. The band gap is less than the band gap of the homopolymer poly(phenothiazine). This is due to the orbital mixing of phenothiazine donor unit and quinoxaline acceptor unit. The variation in the band gap is in the order PPHENO-DDACE> PPHENO-DDQ> PPHENO-DBDP. As expected, the optical band gap varies as the function of the electron withdrawing property of the comonomers. It is assumed that greater the acceptor strength of the quinoxaline, greater will be the donor –
acceptor interaction, which leads to greater reduction in the band gap. The reduction in the band gap is induced by the charge transfer from phenothiazine unit to the quinoxaline unit. This is visualized by analyzing the wave functions of the HOCO and LUCO of the polymers. The wave functions of HOCO and LUCO are localized on the phenothiazine and quinoxaline unit respectively.

Figure 7: UV-Visible absorption spectrum of polymers in (a). chloroform (b) thin film on glass substrate cast from chlorobenzene solution

The photoluminescence spectrum of the polymers is shown in figure 8. The wavelength corresponding to the absorption maximum of each polymer is used as excitation wavelength. The emission maximum of the PPHENO-DDACE, PPHENO-DDQ and PPHENO-DBDP occur at 657 nm, 652 nm and 687 nm respectively.

Figure 8: PL spectra of polymers in chloroform solution
Table 3: Optical properties of the polymers in solution and in thin film on glass substrate

<table>
<thead>
<tr>
<th>Polymer</th>
<th>UV-Visible Absorption λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Emission λ&lt;sub&gt;max&lt;/sub&gt; (nm) (solution)</th>
<th>UV-Visible Absorption Onset (film)</th>
<th>E&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;opt&lt;/sup&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHENO-DDACE</td>
<td>439</td>
<td>657</td>
<td>555</td>
<td>2.24</td>
</tr>
<tr>
<td>PHENO-DDQ</td>
<td>450</td>
<td>652</td>
<td>590</td>
<td>2.11</td>
</tr>
<tr>
<td>PHENO-DBDP</td>
<td>477</td>
<td>687</td>
<td>646</td>
<td>1.92</td>
</tr>
</tbody>
</table>

3.2.4. Electrochemical properties

To determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level of the three polymers, cyclic voltammetry was carried out for the three polymer films on Pt electrode in 0.1M Bu₄NPF₆ solution in acetonitrile. The cyclic voltammograms of the polymers are shown in figure 9. All the three polymers showed a couple of irreversible oxidation peaks in the positive potential region and a reversible reduction peak in the negative potential. The HOMO and LUMO were estimated from the onset of oxidation and reduction potential according to the equation proposed by Bredas.""
3.2.5. Photovoltaic device

The suitability of the polymers for photovoltaic applications was verified by fabricating a heterojunction device using the polymers as active layer and the semiconductor In$_2$S$_3$ as n-type material. Figure 10 shows the current density-voltage (J-V) characteristics of the heterojunction under illumination and in the dark. As could be seen, the device clearly exhibits rectifying behaviour in the dark which may be due to the barrier formed at the In$_2$S$_3$/ polymer interface. Under white light illumination (50 mW/cm$^2$), the device of PPHENO-DDACE, PPHENO-DDQ, and PPHNEO-DBDP
exhibits a short circuit current density ($J_{sc}$) of 54.1 $\mu$A/cm$^2$, 80.4 $\mu$A/cm$^2$, 61.7 $\mu$A/cm$^2$ and open circuit voltage ($V_{oc}$) of 477.42 mV, 169.93 mV, and 610.51 mV respectively. The fill factor (FF) /efficiency were calculated to be 19.95%/0.02%, 28.19%/0.01and 28.27%/0.02% respectively for PPHENO-DDACE, PPHENO-DDQ, and PPHNEO-DBDP. Photovoltaic characteristics of bilayer heterojunction devices of the polymers are summarized in table 5.

![Figure 10: J-V characteristics of ITO/In$_2$S$_3$/polymer/Ag heterojunctions of PPHENO-DDACE, b. PPHENO-DDQ, and c. PPHENO-DBDP](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ ($\mu$A/cm$^2$)</th>
<th>Efficiency (%)</th>
<th>Fill factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPHENO-DDACE</td>
<td>477.42</td>
<td>54.1</td>
<td>0.02</td>
<td>19.95</td>
</tr>
<tr>
<td>PPHENO-DDQ</td>
<td>169.93</td>
<td>80.4</td>
<td>0.01</td>
<td>28.19</td>
</tr>
<tr>
<td>PPHENO-DBDP</td>
<td>610.51</td>
<td>61.7</td>
<td>0.02</td>
<td>28.27</td>
</tr>
</tbody>
</table>
3.3. Conclusion and perspectives

Theoretical calculation predicted that structural modification of quinoxaline unit allowed successful tuning of the band gap and energy level of the phenothiazine copolymer over a broad range from 2.38 eV to 1.93 eV. The reduction in the energy level is the function of the acceptor strength of the quinoxaline unit. The lower band gap of phenothiazine/quinoxaline copolymers compared to homopolymer poly(phenothiazine) may be due to the charge transfer from donor phenothiazine unit to the acceptor quinoxaline unit. The designed polymers are synthesized through Suzuki polycondensation reaction. Theoretically predicted values are in good agreement with the optically and electrochemically determined band gap. We have explored the photoactivity of all the polymers by fabricating a heterojunction with a device structure of ITO/In_{2}S_{3}/polymer/Ag. A further improvement in the device can be achieved by optimizing the device parameters.

3.4. Experimental methods

3.4.1. Synthesis of 5,8-dibromoacenaphthyl quinoxaline (DDACE):

A solution of 3,6-dibromo-1, 2-phenylenediamine (0.15 g, 0.56 mmol) and acenaphthenequinone (0.10 g, 0.55 mmol) in ethanol (20 mL) and few drops of glacial acetic acid was heated to reflux for 1h, and cooled to 0°C. The precipitate formed was separated by filtration and washed with ethanol to afford 5,8-dibromoacenaphthyl quinoxaline as light yellow solid.

Yield : 79% (0.183 g)

\[ ^1 \text{H NMR (400MHz, CDCl}_3) \text{ : } \delta \text{ 8.54 (d, J=7.2 Hz, 2H), 8.15 (d, J=8.4 Hz, 2H), 7.92 (s, 2H), 7.89-7.86 (m, 2H) } \]

3.4.2. Synthesis of 5,8-Dibromo-2,3-diphenyl quinoxaline (DDQ):

A solution of 3,6-dibromo-1, 2-phenylenediamine (1.0 g, 3.8 mmol) and benzil (0.80 g, 3.8 mmol) in ethanol (40 mL) and few drops of glacial acetic acid was heated to reflux for 1h, and cooled to 0°C. The
precipitate formed was isolated by filtration and washed with ethanol to afford 5,8-dibromo-2,3-diphenyl quinoxaline as light yellow solid.

Yield : 1.16 g (70%)  
M. P. : 221°C.

$^1$H NMR (400MHz, CDCl$_3$) : $\delta$ 7.92 (s, 2H), 7.64 (m, 4H), 7.37 (m, 6 H).

$^{13}$C NMR (100MHz, CDCl$_3$) : $\delta$ 123.7, 128.4, 129.6, 130.2, 133.1, 137.9, 139.4, 154.14

GC-MS : m/z=439.9

3.4.3. Synthesis of 10,13-dibromodibenzo[a,c]phenazine (DBDP):

A solution of 3,6-dibromo-1,2-phenylenediamine (1.03 g, 3.9 mmol) and phenanthrene-9,10-dione (0.81 g, 3.9 mmol) in 42 mL ethanol/acetic acid (20:1) was heated to reflux for 2 h, and cooled to 0°C. The precipitate formed was isolated by filtration and washed with ethanol to afford 10,13-dibromodibenzo[a,c]phenazine as yellow solid.

Yield : 1.37 g (80%).  
M.P. (°C) : 317

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 9.48 (dd, $J_1$=8 Hz, $J_2$=1.2 Hz, 2 H), 8.57 (dd, $J_1$=8 Hz, $J_2$=0.8 Hz, 2 H), 8.04 (s, 2H), 7.87-7.83 (dt, $J_1$=15.2 Hz, $J_2$=1.6 Hz, 2 H), 7.81-7.77 (dt, $J_1$=13.2 Hz, $J_2$=1.2 Hz, 2 H).

$^{13}$C NMR (100MHz, CDCl$_3$) : $\delta$ 123.1, 124.2, 127.3, 128.4, 129.6, 131.3, 132.7, 132.9, 143.5.

GC-MS : m/z=437.9
3.4.4. General Procedure for Polymerization through Suzuki Coupling

Under nitrogen atmosphere, dibromo monomers (0.18 mmol), 10-octyl-3,7-bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-10H-phenothiazine (0.18 mmol) were mixed together with 10 mol\% of Pd(PPh\(_3\))\(_4\) (0.018 mmol) in a small R. B. flask. Degassed aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) (1:2, volume ratio) were added to the flask. The mixture was stirred vigorously at 80-90°C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into stirring methanol to precipitate the polymer. The fibrous solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

3.4.4.1. Synthesis of PPHENO-DDACE

10-octyl-3,7-bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-10H phenothiazine (0.1 g, 0.18 mmol), 5,8-dibromoacenaphthyl quinoxaline (0.078 g, 0.18 mmol), Pd(PPh\(_3\))\(_4\) (0.02 g, 0.018 mmol) were used. Red coloured solid.

Yield : 37\% (36.8 mg)

UV/Vis (CHCl\(_3\)) \(\lambda_{\text{max}}\) : 439 nm

\(T_d(0°C)\) : 257

\(^1\)H NMR (400 MHz, CDCl\(_3\)) : 8.4-7.55 (m, ~8H of quinoxaline part), 7.38-7.3 (m, 2H of phenothiazine), 7.13-7.08 (m, 2H of phenothiazine), 6.96-6.8 (m, 2H of phenothiazine), 3.89 (t, ~2H, -NCH\(_2\)-), 1.8-1.1 (m, ~12H, aliphatic-H), 1.6-0.9 (m, ~3H, -CH\(_3\))
3.4.4.2. Synthesis of PPHENO-DDQ

10-octyl-3,7-bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-10H-phenothiazine (0.1 g, 0.18 mmol), 5,8-Dibromo-2,3-diphenyl quinoxaline (0.079 g, 0.18 mmol), Pd(PPh₃)₄ (0.02 g, 0.018 mmol) were used. Red coloured solid.

Yield : 51% (53.5 mg)

UV/Vis (CHCl₃) \( \lambda_{\text{max}} \) : 450 nm

\( T_d (^{\circ} \text{C}) \) : 270

\(^1\text{H} \text{NMR} (400 \text{ MHz}, \text{CDCl}_3) \) : \( \delta \) 8.03-7.52 (m, ~10H of quinoxaline part), 7.31-6.71 (m, ~6H of phenothiazine), 3.84 (t, 2H, -NCH₂-), 1.9-1.1 (m, ~12H, aliphatic-H), 0.86-0.8 (t, ~3H, -CH₃).

\(^{13}\text{C} \text{NMR} (100\text{MHz}, \text{CDCl}_3) \) : \( \delta \) 137.49, 132.07, 131.98, 129.19, 129.1, 128.26, 127.34, 30.75, 28.21, 26.07, 25.94, 21.61, 13.08.

GPC : \( M_n=9578, \text{PDI}=1.92 \)

3.4.4.3. Synthesis of PPHENO-DBDP:

10-octyl-3,7-bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-10H-phenothiazine (0.1 g, 0.18 mmol), 10,13-Dibromodibenzo[a,c]phenazine (0.078 g, 0.18 mmol), Pd(PPh₃)₄ (0.02 g, 0.018 mmol) were used. Red coloured solid.

Yield : 46% (47.8 mg)

UV/Vis (CHCl₃) \( \lambda_{\text{max}} \) : 477 nm

\( T_d (^{\circ} \text{C}) \) : 295
$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 9.46-7.76 (m, ~10H of quinoxaline part), 7.4-6.77 (m, ~6H of phenothiazine), 3.9 (t, 2H, -NCH$_2$-), 1.18-2.1 (m, ~12 H, aliphatic-H), 0.86-0.79 (m, ~3H, -CH$_3$).

GPC : $M_n$=5905, PDI=1.19

3.5. References