Chapter 6

Electrochemical STUDIES
6.1 Introduction
6.2 Electrochemical properties
6.1. Introduction

This chapter deals with the electrochemical studies carried out and the discussions there upon. Cyclic Voltammetry (CV) was used as the main tool for the studies. Oxidation and reduction potential values of the spiro CTMs were investigated. HOMO-LUMO values, band gap, electron affinity and ionization potential of the same are determined and also discussed in detail.

6.2. Electrochemical properties

One of the most accurate methods to characterize the organic materials and estimation about energy band diagram is cyclic voltammetry (CV) [304]. The oxidation and reduction potentials can be measured by cyclic voltammetry and then the HOMO and LUMO values are calculable [305]. For estimation of oxidation potential, cyclic voltammetry (CV) experiments were carried out in a three-electrode cell consisting of a platinum working electrode, a platinum counter electrode and a SCE reference electrode using a scan rate of 50 mV/s (Solartron 1286). The supporting electrolyte was 0.1 M TEABF4 in acetonitrile. In addition the Eox which was obtained from cyclic voltammetry and $E_{HOMO}$ where the complete band diagram was calculated. Ferrocence is used in this experiment as a known reference to calculate the Eox or Ered [304]. The estimations can be done with the empirical relation $E_{LUMO}= [(E_{red}-E_{1/2}(ferrocene)) +4.8] \text{ eV}$ including the ferrocene value of -4.8 eV [306]. Cyclic voltametry was employed as an accurate method to measuring the HOMO/LUMO of donor and acceptor.

HOMO and LUMO of organic compounds are basic parameters for the design and fabrication of an organic solar cell. The charge injection from the LUMO of the dye and the TiO$_2$ conduction band as
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well as dye regeneration are crucial points in dye sensitized solar cells. Thus, energy-level matching is crucial in designing sensitizer. The energy level of active organic materials can be investigated by cyclic voltammetry. From this point, the values can be extrapolated to the glass phase by choosing an appropriate reference and neglecting the influence of the polarity of the solvent in which the measurement are taken. The ionisation energy of ferrocene is assumed to be +4.8 eV, thus linking the electrochemical potential to the work function scale of the electrode [304]. Therefore, the energy of the molecular orbital is the negative value, that is,

\[ EMO = - (4.8 + E_{1/2}) \tag{1} \]

\( E_{1/2} \) being the reversible half-wave potential of the electron-transfer reaction with respect to ferrocene. All potentials were obtained vs Fc/Fc+ and were recalculated with respect to NHE. The measured potentials are recorded with respect to the Ag/AgCl reference electrode against ferrocene/ferrocenium (Fc/Fc+, 0.577 V vs NHE). From this investigation the energy levels of materials match perfectly the conduction band edge of TiO\( _2 \) and the redox potential of HTM. For a compound to be used in an optoelectronic device its HOMO and LUMO values should be in accordance with that of the semiconductor. The HOMO and LUMO values of these compounds are calculated from the anodic oxidation potential using HOMO of ferrocene (4.8eV) with respect to zero vacuum level as described by Daub et al [307].

Oxidation potential and reduction potential of organic materials are obtained from cyclic voltammetry curve. HOMO-LUMO values, band gap (Eg), electron affinity (EA) and ionization potential (PI) of spiro CTM’s are calculated from these values. Cyclic voltametry curve of 3,3'-((1,4-phenylene bis (phenyl azanediyl)) bis (7-alkoxy-4-methyl-2H-
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Chromen-2-one) (series I) compounds are represented in figure 6.1 and table 6.1 gives the details of the electrochemical properties of the compounds.
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![Graph showing current (A) vs. potential (V)]
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![Graph of Current vs. Potential](image)

PPPE
Figure 6.1: Cyclic voltametry curves of 3,3’-(1,4-phenylene bis (phenyl azanediyl)) bis (7-alkoxy-4-methyl-2H-chromen-2-one) (series I) compounds

Table 6.1: C V data and HOMO-LUMO values of the compounds 3,3’-(1,4-phenylene bis (phenylazanediyl)) bis (7-alkoxy-4-methyl-2H-chromen-2-one) (series I).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Eox vs Fc (V)</th>
<th>HOMO (eV)</th>
<th>Ered vs Fc (V)</th>
<th>LUMO (eV)</th>
<th>Eg (eV)</th>
<th>PI (eV)</th>
<th>EA (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPEC</td>
<td>0.726</td>
<td>-5.526</td>
<td>-1.228</td>
<td>-3.572</td>
<td>1.958</td>
<td>5.526</td>
<td>3.572</td>
</tr>
<tr>
<td>PPPC</td>
<td>0.733</td>
<td>-5.533</td>
<td>-1.400</td>
<td>-3.400</td>
<td>2.133</td>
<td>5.533</td>
<td>3.400</td>
</tr>
<tr>
<td>PPBC</td>
<td>0.814</td>
<td>-5.568</td>
<td>-1.462</td>
<td>-3.338</td>
<td>2.230</td>
<td>5.568</td>
<td>3.338</td>
</tr>
<tr>
<td>PPPEC</td>
<td>0.730</td>
<td>-5.530</td>
<td>-1.389</td>
<td>-3.411</td>
<td>2.119</td>
<td>5.530</td>
<td>3.411</td>
</tr>
</tbody>
</table>

The lowest value of HOMO is observed for PPBC and the lowest LUMO value for PPEC. All the compounds vary nearly 0.04 eV for HOMO values and 0.1 eV for LUMO values. The band gap is nearly 2.0 eV, which is required for optoelectronic studies.

Cyclic Voltametry curve of N,N’-bis-(2-alkoxy naphthalen-1-yl)-N,N’-diphenyl benzene-1,4-diamine (Series II) compounds are
Electrochemical Studies represented in figure 6.2 and table 6.2 gives the details of the electrochemical properties of the compounds.
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PENDB

potential(V)
current(A)
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Figure 6.2: Cyclic voltametry curve of \(N,N'\)-bis-(2-alkoxy-naphthalen-1-yl)-\(N,N'\)-diphenyl benzene-1,4-diamine(SeriesII) compounds

Table 6.2: C V data and HOMO-LUMO values of the \(N,N'\)-bis-(2-alkoxy-naphthalen-1-yl)-\(N,N'\)-diphenyl benzene-1,4-diamine (Series II) compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>\text{E}_{\text{ox}} \text{ vs Fc (v)}</th>
<th>HOMO (eV)</th>
<th>\text{E}_{\text{red}} \text{ vs Fc (v)}</th>
<th>LUMO (eV)</th>
<th>\text{E}_g (eV)</th>
<th>PI (eV)</th>
<th>EA (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENDB</td>
<td>-1.400</td>
<td>-6.200</td>
<td>-1.300</td>
<td>-3.500</td>
<td>2.700</td>
<td>6.20</td>
<td>3.500</td>
</tr>
<tr>
<td>BNDB</td>
<td>-1.300</td>
<td>-6.100</td>
<td>-1.100</td>
<td>-3.700</td>
<td>2.400</td>
<td>6.10</td>
<td>3.700</td>
</tr>
<tr>
<td>PNDB</td>
<td>-1.153</td>
<td>-5.953</td>
<td>-1.046</td>
<td>-3.756</td>
<td>2.197</td>
<td>5.93</td>
<td>3.756</td>
</tr>
</tbody>
</table>

Among series II compounds, PENDB shows lowest HOMO value of -6.38 eV and PNDB has the lowest LUMO value of -3.756 eV. The band gap values are higher by 0.4 eV when compared to series I compounds.
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Cyclic voltametry curve of N,N,N',N'-tetrakis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (series III) are represented in figure 6.3 and table 6.3 gives the details of the electrochemical properties of the compounds.
Electrochemical Studies

![Graph showing current (A) vs. potential (V)]
Electrochemical Studies

![Graph showing current versus potential](image)
Electrochemical Studies
Electrochemical Studies

![Cyclic voltametry curve of N,N,N',N'-tetrakis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (series III) compounds](image)

**Figure 6.3:** Cyclic voltametry curve of $N,N,N',N'$-tetrakis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (series III) compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$E_{\text{ox}}$ vs Fc (v)</th>
<th>HOMO (eV)</th>
<th>$E_{\text{red}}$ vs Fc (v)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>PI (eV)</th>
<th>EA (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TENBD</td>
<td>1.4</td>
<td>-6.2</td>
<td>-1.618</td>
<td>-3.172</td>
<td>3.028</td>
<td>6.2</td>
<td>3.172</td>
</tr>
<tr>
<td>TPNBD</td>
<td>1.067</td>
<td>-5.867</td>
<td>-1.3</td>
<td>-3.5</td>
<td>2.367</td>
<td>5.867</td>
<td>3.5</td>
</tr>
<tr>
<td>TBNBD</td>
<td>1.169</td>
<td>-5.969</td>
<td>-1.350</td>
<td>-3.450</td>
<td>2.519</td>
<td>5.969</td>
<td>3.450</td>
</tr>
<tr>
<td>TPENBD</td>
<td>1.2</td>
<td>-6.0</td>
<td>-1.312</td>
<td>-3.488</td>
<td>2.512</td>
<td>6.0</td>
<td>3.488</td>
</tr>
</tbody>
</table>

**Table 6.3:** CV data and HOMO-LUMO values of $N,N,N',N'$-tetrakis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (series III).

The band gap is found to be higher for the compounds of this series compared with other series and is ranging from 2.3 to 3.0 eV. Comparatively there is a change in HOMO values also. The lowest HOMO value is found at -6.2 eV for TENBD and that of LUMO is -3.488 eV for TPENBD.
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Cyclic voltametry curve of N,N'-bis-(2-alkoxy-naphthalen-1-yl)-N,N'-bis-(4-methoxy phenyl)-benzene-1,4-diamine (Series IV) are shown in figure 6.4 and table 6.4 gives the details of the electrochemical properties of the compounds.
Figure 6.4: Cyclic voltametry curve of \(N,N'-\text{bis-(2-alkoxy-naphthalen-1-yl)}\)-\(N,N'-\text{bis-(4-methoxy-phenyl)}\) benzene-1,4-diamine (Series IV) compounds

Table 6.4: CV data and HOMO-LUMO values of the compounds \(N,N'\)-\text{bis-(2-alkoxy-naphthalen-1-yl)}-\(N,N'\)-\text{bis-(4-methoxy-phenyl)} benzene-1,4-diamine (Series IV) compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(E_{\text{ox}} ) vs Fc (v)</th>
<th>(E_{\text{HOMO}}) (eV)</th>
<th>(E_{\text{red}} ) vs Fc (v)</th>
<th>(E_{\text{LUMO}}) (eV)</th>
<th>(E_{\text{g}}) (eV)</th>
<th>(\text{PI}) (eV)</th>
<th>(\text{EA}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENMBD</td>
<td>1.4</td>
<td>-6.2</td>
<td>-1.3</td>
<td>-3.5</td>
<td>2.7</td>
<td>6.2</td>
<td>3.5</td>
</tr>
<tr>
<td>PNMBD</td>
<td>1.1</td>
<td>-5.9</td>
<td>-0.97</td>
<td>-3.83</td>
<td>2.07</td>
<td>5.9</td>
<td>3.83</td>
</tr>
<tr>
<td>BMNBD</td>
<td>1.12</td>
<td>-5.92</td>
<td>-1.04</td>
<td>-3.76</td>
<td>2.16</td>
<td>5.92</td>
<td>3.76</td>
</tr>
</tbody>
</table>

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In this series, HOMO, LUMO values are also different. The lowest HOMO value is observed for ENMBD and that of LUMO for PENMBD. The band gap of ENMBD is found to be higher.

The electrochemical studies of the four series of compound are listed in tables 6.1 to 6.4. The CV curves of these compounds are placed in figures 6.1 to 6.4. The substituents at the outer naphthalene ring could significantly affect the HOMO and LUMO values. An electron withdrawing groups in the compounds reduced the capability of the arylamine nitrogen to hold a positive charge. As a result, the arylamine nitrogen become more difficult to oxidize which in turn yielded higher HOMO value. In the case of series I compounds, due to the presence of an electron releasing carbonyl group the HOMO values are comparatively higher than other series. The band gap of these compounds are also comparatively lesser. This property makes these compounds acquire both hole transporting and electron transporting property.
Figure 6.5: Variation of HOMO, LUMO and Band gap of the compounds for all the four series

Figure 6.5 shows the variation of HOMO, LUMO and Band gap of all the synthesized compounds for the four series. The compounds of series II exhibited the lowest HOMO values. HOMO values are higher for series I compounds. There is no common trend observed for all these compounds in the case of LUMO values. The band gap is highest for series III compounds and is lowest for series I compounds.

The electrochemical properties of all the four series of compounds are in good agreement with the reported hole transporting material [296].
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This indicated that these compounds show good hole transporting property. Also the compounds of series I show both hole and electron transporting property.