6.1 INTRODUCTION

Heterocyclic styryl colorants have been in demand in high value-added products such as sensitizers in optical recording materials, photography, laser dyes and fluorescent probes (Kasada et al. 2002; Haidekker et al. 2001; Pommeret et al. 1995). Their wide scope of structural modifications allows desirable changes in properties including physical properties, chemical stability and solubility (Lehmann et al. 1995). Such colorants are also suitably used for application in non-linear optics (NLO).

Nonlinear optics is the branch of optics, which deals with the phenomena that occurs as a consequence of modification of the optical properties of material with the incident light wave. In the last few years, the interest in the design and synthesis of novel materials organic materials with nonlinear optical (NLO) properties has grown considerably because of their potential applications in photonic technologies. The basic structure of these molecules consists of a donor (D) and an acceptor (A) linked via a conjugation bridge or linker (Zernike and Midwinter 1973; Prasad and Williams 1990). Some limitations of such systems include extended visible absorption and reduction in thermal as well as photo stability with increase in conjugation. This limitation proves to be every serious since molecules for NLO application have to typically endure extremely high temperatures during fabrication processes (Burland et al. 1994). Hence this field remains quite challenging and suitable design is very important to obtain higher NLO activity.

Among electron donor groups, we have discussed the significance of heterocyclic systems such as carbazole, indole, phenothiazine and julolidene in chapter no. 5. In
this chapter, we aim to modify the linker from phenyl ring to heterocyclic compounds such as furan and thiophene. Aromatic rings as linkers are known to enhance thermal stability but it sometimes leads to decrease in molecular hyperpolarizability (Singer et al. 1989; Cheng et al. 1991). However, replacing simple aromatic rings with more easily delocalizable 5-membered heteroaromatic rings such as thiophene and furan results in an enhanced molecular hyperpolarizability (Song et al. 1999; Jen et al. 1997). This could possibly be due to more easily delocalizable \( \pi \)-orbitals in 5-membered rings than in benzene that results in decrease of aromatic character in the ground state thereby leading to higher value of hyperpolarizability \( \beta \) (Rao et al. 1993; Rao et al. 1996; Jen et al. 1993). In addition, other factors including steric effects also contribute to these high values of hyperpolarizability (Breitung et al. 2000).

Park and co-workers have accounted a systematic study that proposes effect of the nature of the heteroaromatic rings and the substitution pattern at the conjugated bridges on molecular hyperpolarizability (Park et al. 2004). Moreover, the presence of furan and nitro group is known to introduce strong charge-transfer (CT) character in molecules (Carlotti et al. 2011; Ciorba et al. 2011; Baraldi 2009). Recently, Kikas et al. have described a more efficient intramolecular charge-transfer transfer by using heteroaromatic central rings and stronger donor-acceptor groups at the end of the molecule (Kikas et al. 2012).

Quinones are another group of molecules that possess exceptional ability to attract electrons. The various anionic radicals forms of quinones leads to intense absorption in the visible or near-infrared (NIR) region. This feature has made them suitable for several hi-technological applications such as materials in communication devices,
optical storage and organic nonlinear optical (NLO) (Koroteev et al. 1997; Kawai et al. 1995; Marder et al. 1995). With this in mind, we have synthesized dyes having naphthoquinone ring fused with oxazole as the acceptor end connected by styryl linkage to various strong donor groups.

In this chapter, we have synthesized dyes suitable for non-linear optical application by using furan or thiophene as the linker group connected with various heterocyclic donors. We have also synthesized dyes containing naphthoquinone based acceptor group. All these dyes were purified by column chromatography and characterized by mass, $^1$H-NMR and $^{13}$C-NMR spectroscopic methods.
6.2 RESULTS AND DISCUSSION

6.2.1 Synthesis of heterocyclic bridged styryl dyes

A variety of heterocyclic bridged novel chromophores (Figure 6.1 and 6.2) were synthesized by condensation of different donor aldehydes with furan or thiophene acetonitrile based acceptor moieties by refluxing in ethanol using catalytic amount of piperidine (Scheme 6.2 and 6.4). These derivatives possess a Donor-π bridge-Acceptor system (D-π-A) system. The donor groups contain varied groups with strong donating ability such as indole, carbazole, phenothiazine and substituted aniline derivatives. The heterocyclic bridges either contain thiophene or furan rings. The molecular weights and yields of all these derivatives are summarized in Table 6.1. These colorants were studied for their photo-physical properties. All the synthesized chromophores were purified by column chromatography and characterized using $^1$H-NMR, $^{13}$C-NMR and Mass spectra.

The alkylation of nitrogen atom in indole, carbazole and phenothiazine was performed by phase transfer catalysis reaction using quaternary ammonium salt as catalyst. The preparation of mono formyl derivatives of N-butyl indole [4c], N-butyl carbazole [4d], and N-butyl phenothiazine [4e] was done by classical Vilsmeier Haack formylation as described in the experimental section. The acceptor heterocyclic bridged moiety [3] and [7] were synthesized by condensation of 5-methylthiophene-2-carbaldehyde [1] and 5-methylfuran-2-carbaldehyde [6] with 4-nitrophenylacetonitrile [2] in ethanolic media using piperidine as a base (Scheme 6.1 and 6.3). The intermediates were characterized by $^1$H-NMR spectroscopy.
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Scheme 6.1: Synthesis of heterocyclic acceptor unit [3]

Scheme 6.2: Synthesis of thiophene bridged styryl colorants [5a-5e]

<table>
<thead>
<tr>
<th>Dye no.</th>
<th>5a</th>
<th>5b</th>
<th>5c</th>
<th>5d</th>
<th>5e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td><img src="image1.png" alt="image" /></td>
<td><img src="image2.png" alt="image" /></td>
<td><img src="image3.png" alt="image" /></td>
<td><img src="image4.png" alt="image" /></td>
<td><img src="image5.png" alt="image" /></td>
</tr>
</tbody>
</table>
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis

Figure 6.1: Structures of thiophene bridged styryl dyes
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis
Scheme 6.3: Synthesis of furan based acceptor unit [7]

![Scheme 6.3: Synthesis of furan based acceptor unit](image)

Scheme 6.4: Synthesis of furan bridged styryl colorants [8a-8e]

![Scheme 6.4: Synthesis of furan bridged styryl colorants](image)

<table>
<thead>
<tr>
<th>Dye no.</th>
<th>8a</th>
<th>8b</th>
<th>8c</th>
<th>8d</th>
<th>8e</th>
</tr>
</thead>
<tbody>
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<td>Ar</td>
<td>4a</td>
<td>4b</td>
<td>4c</td>
<td>4d</td>
<td>4e</td>
</tr>
<tr>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
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<tr>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
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<td>H</td>
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</tr>
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</tr>
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<td>Ar</td>
<td>Ar</td>
<td>Ar</td>
<td>Ar</td>
<td>Ar</td>
<td>Ar</td>
</tr>
<tr>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
<td>H₃C</td>
</tr>
<tr>
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<tr>
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<td>H</td>
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<td>H</td>
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</tr>
</tbody>
</table>
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis

Figure 6.2: Structures of furan bridged styryl dyes

Dye – 8a

Dye – 8b

Dye – 8c
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis

Dye – 8d

Dye – 8e
6.2.2 Synthesis of naphthoquinone based colorants with heterocyclic acceptor units

Various naphthoquinone based colorants (12a-12d as shown in figure 6.3) were synthesized by condensation of different donor groups [4a-4d] and naphthoquinone based active methyl derivative [11] by heating at 80 °C with stirring in dioxane using catalytic amount of piperidine (Scheme 6.6). These derivatives possess a Donor-π bridge-Acceptor system (D-π-A) system. The naphthoquinone intermediate [11] was synthesized by heating 2,3-dichloronaphthoquinone [9] with acetamide [10] in dioxane medium using triethylamine as catalyst (Scheme 6.5). This results in a fused oxazole ring structure attached to naphthoquinone ring. The donor groups contain varied groups with strong donating ability such as indole, carbazole and substituted aniline derivatives. The molecular weights and yields of all these derivatives are summarized in Table 6.1.

Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Scheme 6.6: Synthesis of napthoquinone based styryl dyes [12a-12d]

![Diagram of synthesis process]

<table>
<thead>
<tr>
<th>Dye no.</th>
<th>12a</th>
<th>12b</th>
<th>12c</th>
<th>12d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>4a</td>
<td>4b</td>
<td>4c</td>
<td>4d</td>
</tr>
<tr>
<td>![Structure of 12a]</td>
<td>![Structure of 12b]</td>
<td>![Structure of 12c]</td>
<td>![Structure of 12d]</td>
<td></td>
</tr>
</tbody>
</table>

Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis

Figure 6.3: Structures of naphthoquinone based styryl dyes

Dye – 12a

Dye – 12b

Dye – 12c

Dye – 12d
Table 6.1: Physical properties of dyes (5a-5e, 8a-8e and 12a-12d)

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Yield in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>C_{23}H_{19}N_{3}O_{2}S</td>
<td>401</td>
<td>72</td>
</tr>
<tr>
<td>5b</td>
<td>C_{25}H_{23}N_{3}O_{3}S</td>
<td>445</td>
<td>65</td>
</tr>
<tr>
<td>5c</td>
<td>C_{27}H_{23}N_{3}O_{2}S</td>
<td>453</td>
<td>59</td>
</tr>
<tr>
<td>5d</td>
<td>C_{31}H_{25}N_{3}O_{2}S</td>
<td>503</td>
<td>54</td>
</tr>
<tr>
<td>5e</td>
<td>C_{31}H_{25}N_{3}O_{2}S</td>
<td>535</td>
<td>62</td>
</tr>
<tr>
<td>8a</td>
<td>C_{23}H_{19}N_{3}O_{3}</td>
<td>385</td>
<td>68</td>
</tr>
<tr>
<td>8b</td>
<td>C_{25}H_{23}N_{3}O_{4}</td>
<td>429</td>
<td>72</td>
</tr>
<tr>
<td>8c</td>
<td>C_{27}H_{23}N_{3}O_{3}</td>
<td>437</td>
<td>59</td>
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<tr>
<td>8d</td>
<td>C_{31}H_{25}N_{3}O_{3}</td>
<td>487</td>
<td>54</td>
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<tr>
<td>8e</td>
<td>C_{31}H_{25}N_{3}O_{3}S</td>
<td>519</td>
<td>60</td>
</tr>
<tr>
<td>12a</td>
<td>C_{21}H_{16}N_{2}O_{3}</td>
<td>344</td>
<td>54</td>
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<tr>
<td>12b</td>
<td>C_{23}H_{20}N_{2}O_{4}</td>
<td>388</td>
<td>48</td>
</tr>
<tr>
<td>12c</td>
<td>C_{25}H_{20}N_{2}O_{3}</td>
<td>396</td>
<td>40</td>
</tr>
<tr>
<td>12d</td>
<td>C_{29}H_{22}N_{2}O_{3}</td>
<td>446</td>
<td>45</td>
</tr>
</tbody>
</table>
6.2.3 Spectral characteristics of heterocyclic bridged styryl colorants

In order to investigate the photo-physical properties, the absorption and photoluminescence spectra of final dyes were measured for known concentrations (1x $10^{-4}$M) in solvents such as toluene, chloroform, acetonitrile, dimethyl sulphoxide and dimethyl formamide. The path length of the cell was 1 cm whereby the influences of the quartz cuvette and the solvent have been substracted. The basic spectral characteristics of the dyes such as the absorption maxima ($\lambda_{\text{max}}$), emission maxima ($\lambda_{\text{em}}$) and stokes shifts ($\Delta \lambda$) measured in different organic solvents are presented in Table 6.2 for thiophene bridged colorants, Table 6.3 for furan bridged colorants and Table 6.4 for napthoquinone bridged dyes.

The UV-visible absorption spectra of thiophene bridged styryl dyes 5a-5e showed greater bathochromic shift in comparison to furan bridged dyes. The absorption of these dyes ranged from 340 to 458 nm whereas the fluorescence emission maxima of these dyes were in the range of 458 to 617 nm and stokes shift varied from 67-215nm. The dyes with substituted aniline donor groups, showed good stokes shifts in chloroform whereas the heterocyclic donor containing dyes showed better stokes shift in more polar solvents such as acetonitrile and dimethylformamide.

The UV-visible absorption spectra of furan styryl dyes 8a-8e showed bathochromic shift with increase in solvent polarity with maximum absorption in the range of 353 to 479 nm. The fluorescence emission maxima of styryl dyes were in the range of 501 to 616 nm, with stokes shift varies from 62-207 nm. These colorants showed good stokes shifts in DMSO as compared to other organic solvents as summarized in Table 6.3.
## Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Table 6.2: UV-Visible absorption data of dyes (5a-5e)

<table>
<thead>
<tr>
<th>Dyes</th>
<th>5a</th>
<th>5b</th>
<th>5c</th>
<th>5d</th>
<th>5e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>$\lambda_{\text{max}}$</td>
<td>416</td>
<td>425</td>
<td>419</td>
<td>416</td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{em}}$</td>
<td>528</td>
<td>504</td>
<td>502</td>
<td>498</td>
</tr>
<tr>
<td></td>
<td>$\Delta \lambda$</td>
<td>112</td>
<td>79</td>
<td>83</td>
<td>82</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>$\lambda_{\text{max}}$</td>
<td>428</td>
<td>420</td>
<td>419</td>
<td>422</td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{em}}$</td>
<td>617</td>
<td>603</td>
<td>568</td>
<td>576</td>
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<tr>
<td></td>
<td>$\Delta \lambda$</td>
<td>189</td>
<td>183</td>
<td>149</td>
<td>154</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>$\lambda_{\text{max}}$</td>
<td>395</td>
<td>428</td>
<td>416</td>
<td>410</td>
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<tr>
<td></td>
<td>$\lambda_{\text{em}}$</td>
<td>538</td>
<td>495</td>
<td>608</td>
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<td></td>
<td>$\Delta \lambda$</td>
<td>143</td>
<td>67</td>
<td>192</td>
<td>215</td>
</tr>
<tr>
<td>DMF</td>
<td>$\lambda_{\text{max}}$</td>
<td>419</td>
<td>434</td>
<td>416</td>
<td>416</td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{em}}$</td>
<td>524</td>
<td>505</td>
<td>613</td>
<td>616</td>
</tr>
<tr>
<td></td>
<td>$\Delta \lambda$</td>
<td>105</td>
<td>71</td>
<td>197</td>
<td>200</td>
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<tr>
<td>DMSO</td>
<td>$\lambda_{\text{max}}$</td>
<td>458</td>
<td>446</td>
<td>425</td>
<td>422</td>
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<td></td>
<td>$\lambda_{\text{em}}$</td>
<td>525</td>
<td>558</td>
<td>612</td>
<td>602</td>
</tr>
<tr>
<td></td>
<td>$\Delta \lambda$</td>
<td>67</td>
<td>112</td>
<td>187</td>
<td>180</td>
</tr>
</tbody>
</table>
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Table 6.3: UV-Visible Absorption of the Dyes (8a-8e)

<table>
<thead>
<tr>
<th>Dyes</th>
<th>8a</th>
<th>8b</th>
<th>8c</th>
<th>8d</th>
<th>8e</th>
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<tbody>
<tr>
<td><strong>Toluene</strong></td>
<td></td>
<td></td>
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<tr>
<td>$\lambda_{\text{max}}$</td>
<td>428</td>
<td>350</td>
<td>392</td>
<td>407</td>
<td>390</td>
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<tr>
<td>$\lambda_{\text{em}}$</td>
<td>531</td>
<td>521</td>
<td>584</td>
<td>501</td>
<td>525</td>
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<tr>
<td>$\Delta\lambda$</td>
<td>103</td>
<td>171</td>
<td>192</td>
<td>91</td>
<td>135</td>
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<tr>
<td><strong>CHCl$_3$</strong></td>
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</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>446</td>
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<td>395</td>
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<td>$\lambda_{\text{em}}$</td>
<td>616</td>
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<td>498</td>
<td>583</td>
<td>510</td>
</tr>
<tr>
<td>$\Delta\lambda$</td>
<td>170</td>
<td>151</td>
<td>103</td>
<td>179</td>
<td>148</td>
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<tr>
<td><strong>CH$_3$CN</strong></td>
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</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>437</td>
<td>361</td>
<td>386</td>
<td>392</td>
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<tr>
<td>$\lambda_{\text{em}}$</td>
<td>600</td>
<td>558</td>
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<td>530</td>
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<tr>
<td>$\Delta\lambda$</td>
<td>163</td>
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<td>180</td>
<td>170</td>
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<tr>
<td>$\lambda_{\text{max}}$</td>
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<td>372</td>
<td>479</td>
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<td>392</td>
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<tr>
<td>$\lambda_{\text{em}}$</td>
<td>505</td>
<td>560</td>
<td>556</td>
<td>567</td>
<td>597</td>
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<tr>
<td>$\Delta\lambda$</td>
<td>62</td>
<td>188</td>
<td>88</td>
<td>163</td>
<td>205</td>
</tr>
<tr>
<td><strong>DMSO</strong></td>
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<td></td>
</tr>
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<td>583</td>
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<td>111</td>
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</table>
6.2.4 Spectral characteristics of styryl colorants containing heterocyclic acceptor units

The absorption and photoluminescence spectra of naphthoquinone based dyes 12a-12d were measured for known concentrations (1x 10^-4 M) in chloroform. The values are summarized in Table 6.4. The absorption lies in the visible region with absorption maxima ranging from 450-510 nm. The fluorescence emission maxima of these dyes were in the range of 486 to 604 nm, with stokes shift varying from 36 to 94 nm. The dyes with substituted aniline donor group showed good stokes shifts than that containing heterocyclic donor groups. Although these dyes did not show high value of stokes shift than the colorants with heterocyclic bridges, however, they show extremely good bathochromic shift than the latter.

Table 6.4: Photo-physical data of the dyes

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Absorption $\lambda_{\text{max}}$ in nm(CHCl$_3$)</th>
<th>Emission in nm (CHCl$_3$)</th>
<th>Stokes shift in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>510</td>
<td>604</td>
<td>94</td>
</tr>
<tr>
<td>12b</td>
<td>450</td>
<td>486</td>
<td>36</td>
</tr>
<tr>
<td>12c</td>
<td>506</td>
<td>566</td>
<td>60</td>
</tr>
<tr>
<td>12d</td>
<td>509</td>
<td>570</td>
<td>61</td>
</tr>
</tbody>
</table>
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

6.2.5 Thermal properties of the dyes

We also tested the thermal stability of dyes by thermo gravimetric analysis (TGA) carried out in the temperature range 25-600 °C under nitrogen gas at a heating rate of 10 °C min⁻¹. The TGA curves revealed that most of the dyes hold extremely good thermal stability with majority of dyes showing stability above 250 °C as revealed in Table 6.5.

Colorants with simple dimethylamino group 5a gave low stability amongst all. However, colorants containing heterocyclic donors gave better thermal stability. Among mono-substituted derivatives, best stability was obtained for phenothiazine substituted molecule 5e and 8e with thiophene and furan bridges respectively. In addition, it can be observed that the furan bridge series gave relatively lower stability than the thiophene series for most of the dyes. The higher value of thermal stability makes these molecules suitable for high-technological application such as non-linear optics.
Chapter 6: Synthesis of styryl colorants containing heterocyclic linker or acceptor units

Table 6.5: Thermal stability of Colorants

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Temperature of stability (°C) (at 3% product decomposition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>188</td>
</tr>
<tr>
<td>5b</td>
<td>222</td>
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<tr>
<td>5c</td>
<td>204</td>
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<tr>
<td>5d</td>
<td>225</td>
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<td>5e</td>
<td>287</td>
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<tr>
<td>8a</td>
<td>126</td>
</tr>
<tr>
<td>8b</td>
<td>212</td>
</tr>
<tr>
<td>8c</td>
<td>228</td>
</tr>
<tr>
<td>8d</td>
<td>243</td>
</tr>
<tr>
<td>8e</td>
<td>262</td>
</tr>
</tbody>
</table>
6.3 EXPERIMENTAL

6.3.1 Materials and equipment

All the solvents and chemicals were procured from S. D. fine chemicals (India) and were used without further purification. Reactions were monitored by using 0.25 mm E-Merck silica gel 60 F254 precoated TLC plates, which were visualized with UV light. UV–Visible absorption spectra were recorded on spectronic genesis 2 spectrophotometer instruments from dye solutions (~10^{-4} M) in different solvents. The $^1$H NMR and $^{13}$C NMR spectra were recorded on 300 MHz on Varian mercury plus spectrometer. Chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectral data were obtained with micromass Q–Tof (YA105) spectrometer.

6.3.2 Synthesis of carbaldehyde derivatives

6.3.2.1 Synthesis of 1-butyl-1H-indole-3-carbaldehyde [4c]; 9-hexyl-9H-carbazole-3-carbaldehyde [4d]; was discussed in chapter 4, section 4.3.2.1 to 4.3.2.4

6.3.2.3 Synthesis of 10-butyl-10H-phenothiazine-3-carbaldehyde (4d) was discussed in chapter 5, section 5.3.2.3 and 5.3.2.4

6.3.3 Synthesis of intermediate and dyes based on thiophene bridge

6.3.3.1 Synthesis of (Z)-3-(5-methylthiophen-2-yl)-2-(4-nitrophenyl) acrylonitrile [3]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of 2-(4-nitrophenyl)acetonitrile [2] (6.4 g, 39.5 mmol) and 5-methylthiophene-2-carbaldehyde [1] (5.0g, 39.5 mmol) were heated together in
ethanol (50mL, 10 vol) at reflux in presence of catalytic amount of piperidine for 5 hrs. The completion of the reaction was monitored by thin layer chromatography. After cooling the reaction mass, the mixture was poured into ice cold water. The solid is filtered through suction pump to obtain the final product [3] and used for further reaction without purification. Yield = 9.10 g (85%); M.P. = 136° C.

^1H NMR (CDCl₃, 300 MHz): δ (ppm) 8.26-8.20 (m, 2H, aromatic CH); 7.78-7.69 (m, 3H, 2 aromatic CH and 1 vinylic CH); 7.54-7.50 (d, 1H, aromatic CH); 6.84-6.82 (d, 1H, aromatic CH); 2.56 (s, 3H, aliphatic CH₃).

^13C NMR (CDCl₃, 300 MHz): δ (ppm) 148.6, 140.5, 137.7, 135.7, 135.5, 129.0, 126.9, 126.0, 124.4, 117.7, 16.0

6.3.3.2 Synthesis of 3-(5-(-4-(dimethylamino)styryl) thiophen-2-yl)-2-(4-nitrophenyl) acrylonitrile [5a]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of (Z)-3-(5-methylthiophen-2-yl)-2-(4-nitrophenyl) acrylonitrile 3 (1.81 g, 6.7mmoles) and 4-(dimethylamino) benzaldehyde 4a (1.0g, 6.7mmoles), were heated together in ethanol (15 mL, 15 vol) at reflux in presence of catalytic amount of piperidine for 6 hrs. The completion of the reaction was monitored by thin layer chromatography. After cooling the reaction mass, the mixture was poured into ice cold water and the solid compound so obtained was filtered through vacuum pump and dried. The product was purified by column chromatography (toluene, 60 – 120 mesh silica gel) to obtain final product 5a.

Yield =1.93 g (72%); M.P. = 146° C.
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Analysis of dye [5a]:

A. Mass spectra of the compound showed ion peak at m/z = 279, 149 which corresponds to molecular weight of [5a] after removal of phenylnitro group or both cyano and phenylnitro groups.

B. The compound was further confirmed by which showed following signals [5a]

\[ ^1H\text{ NMR (CDCl}_3, 300\text{ MHz):}\ \delta (\text{ppm}) 8.30-8.24 \text{ (m, 2H, aromatic CH);} \ 7.95-7.90 \text{ (d, 1H, aromatic CH);} \ 7.80-7.72 \text{ (m, 2H, aromatic CH);} \ 7.68-7.62 \text{ (m, 2H, aromatic CH);} \ 7.56 \text{ (s, 1H, vinylic CH);} \ 7.54-7.50 \text{ (d, 1H, aromatic CH);} \ 7.08-7.02 \text{ (d, 1H, vinylic CH);} \ 6.90-6.86 \text{ (d, 1H, vinylic CH);} \ 6.75-6.72 \text{ (m, 2H, aromatic CH);} \ 3.10 \text{ (s, 6H, aliphatic CH}_3)\. \\

C. \[ ^{13}\text{C NMR (CDCl}_3, 300\text{ MHz):}\ \delta (\text{ppm}) 152.6, 146.9, 142.3, 137.8, 135.8, 132.4, 132.2, 130.9, 127.0, 126.1, 125.8, 124.8, 124.5, 120.9, 111.4, 40.2 \]

6.3.3.3 Synthesis of (Z)-3-(5-((E)-4-(diethylamino)-3-hydroxystyryl)thiophen-2-yl)-2-(4-nitrophenyl)acrylonitrile \[5b\] was done by the same procedure as that for compound [5a] except that 4-(diethylamino)-3-hydroxybenzaldehyde(1g, 5.1 mmol) \[4b\] was taken in place of 4-(dimethylamino) benzaldehyde \[4a\].

Yield = 1.49 g (65%); M.P. = 162° C.

6.3.3.4 Synthesis of (Z)-3-(5-((E)-2-(1-butyl-1H-indol-3-yl) vinyl) thiophen-2-yl)-2-(4-nitrophenyl) acrylonitrile \[5c\] was done by the same procedure as that for compound [5a] except that 1-butyl-1H-indole-3-carbaldehyde (1g, 4.9 mmol) \[4c\] was taken in place of 4-(dimethylamino) benzaldehyde \[4a\].

Yield = 1.33 g (59%); M.P. = 158° C.
6.3.3.5 Synthesis of (Z)-3-(5-((E)-2-(9-buty 1-9H-carbazol-3-yl)vinyl)thiophen-2-yl)-2-(4-nitrophenyl)acrylonitrile [5d] was done by the same procedure as that for compound [5a] except that 9-buty 1-9H-carbazole-3-carbaldehyde (1g, 3.9 mmol) [4e] was taken in place of 4-(dimethylamino)benzaldehyde [4a]. Yield = 1.08 g (54%); M.P. = 210° C.

6.3.3.6 Synthesis of (Z)-3-(5-((E)-2-(10-butyl-10H-phenothiazin-3-yl)vinyl)thiophen-2-yl)-2-(4-nitrophenyl)acrylonitrile [5e] was done by the same procedure as that for compound [5a] except that 10-butyl-10H-phenothiazine-3-carbaldehyde (1g, 3.5 mmol) [4e] was taken in place of 4-(dimethylamino) benzaldehyde [4a]. Yield = 1.17 g (62%); M.P. = 236° C.

6.3.4 Synthesis of intermediate and dyes based on furan bridge

6.3.4.1 Synthesis of (Z)-3-(5-methylfuran-2-yl)-2-(4-nitrophenyl) acrylonitrile [7]
In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of 2-(4-nitrophenyl)acetonitrile [2] (7.36 g, 8.3mmol) and 5-methylfuran-2-carbaldehyde [6] (5g, 45 mmol) were heated together in ethanol (50mL, 10 vol) at reflux in presence of catalytic amount of piperidine for 5 hrs. The completion of the reaction was monitored by thin layer chromatography. After cooling the reaction mass, the mixture was poured into ice cold water. The solid is filtered through suction pump to obtain the final product [7] and used for further reaction without purification. Yield = 9.46 g (82%); M.P. = 126° C.
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$^1$H NMR (CDCl$_3$, 300 MHz): δ (ppm) 8.27-8.25 (m, 2H, aromatic CH); 7.78-7.76 (m, 2H, aromatic CH); 7.44 (s, 1H, vinylic CH); 7.26-7.21 (d, 1H, aromatic CH); 6.35-6.24 (d, 1H, aromatic CH); δ 2.44 (s, 3H, aliphatic CH$_3$).

$^{13}$C NMR (CDCl$_3$, 300 MHz): δ (ppm) 157.5, 148.1, 146.6, 140.1, 130.9, 126.0, 124.1, 121.2, 117.1, 110.4, 101.4, 13.7

6.3.4.2 Synthesis of (Z)-3-(5-((E)-4-(dimethylamino) styryl) furan-2-yl)-2-(4-nitrophenyl) acrylonitrile [8a]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of (Z)-3-(5-methylfuran-2-yl)-2-(4-nitrophenyl)acrylonitrile [7] (1.70 g, 6.7 mmol) and 4-(dimethylamino) benzaldehyde [4a] (1.0g, 6.7 mmol), were heated together in ethanol (15 mL, 15 vol) at reflux in presence of catalytic amount of piperidine for 6 hrs. The completion of the reaction was monitored by thin layer chromatography. After cooling the reaction mass, the mixture was poured into ice cold water and the solid compound so obtained was filtered through vacuum pump and dried. The product was purified by column chromatography (toluene, 60 – 120 mesh silica gel) to obtain final product 8a.

Yield = 1.75 g (68%); M.P. = 138° C.

6.3.4.3 Synthesis of (Z)-3-(5-((E)-4-(diethylamino)-3-hydroxystyryl)furan-2-yl)-2-(4-nitrophenyl)acrylonitrile [8b] was done by the same procedure as that for compound [8a] except that 4-(diethylamino)-3-hydroxybenzaldehyde (1g, 5.1 mmol) [4b] was taken in place of 4-(dimethylamino) benzaldehyde [4a].

Yield = 1.60 g (72%); M.P. = 164° C.
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Analysis of dye [8b]:

A. Mass spectra of the compound showed ion peak at m/z = 228, 194 which corresponds to molecular weight of [8b] after removal of ethyl, hydroxy and 4-nitrophenylacetonitrile groups.

B. The compound was further confirmed by which showed following signals [8b]

\[ ^1H \text{NMR (CDCl}_3, 300 \text{ MHz)}: \delta \text{ (ppm) 8.35-8.20 (m, 3H, 2 aromatic CH and 1 vinylic CH); 7.90-7.70 (m, 2H, aromatic CH); 7.46-7.40 (m, 2H, aromatic CH); 7.25-7.14 (m, 2H, vinylic CH); 7.52-7.48 (bs, 1H, OH); 7.34-7.24 (m, 2H, aromatic CH); 6.10-6.00 (m, 1H, aromatic CH); 3.45-3.34 (m, 4H, aliphatic CH2); 1.70-1.54 (m, 6H, aliphatic CH3). \]

6.3.4.4 Synthesis of (Z)-3-((E)-2-(1-butyl-1H-indol-3-yl)vinyl)furan-2-yl)-2-(4-nitrophenyl)acrylonitrile [8c] was done by the same procedure as that for compound [8a] except that 1-butyl-1H-indole-3-carbaldehyde (1g, 5.3 mmol) [4c] was taken in place of 4-(dimethylamino) benzaldehyde [4a].

Yield = 1.28 g (59%); M.P. = 192° C.

6.3.4.5 Synthesis of (Z)-3-((E)-2-(9-butyl-9H-carbazol-3-yl)vinyl)furan-2-yl)-2-(4-nitrophenyl)acrylonitrile [8d] was done by the same procedure as that for compound [8a] except that 9-butyl-9H-carbazole-3-carbaldehyde (1g, 3.9 mmol) [4d] was taken in place of 4-(dimethylamino)benzaldehyde [4a].

Yield = 1.0 g (54%); M.P. = 214° C.
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6.3.4.6 Synthesis of (Z)-3-(5-((E)-2-(10-butyl-10H-phenothiazin-3-yl)vinyl)furan-2-yl)-2-(4-nitrophenyl)acrylonitrile [8e] was done by the same procedure as that for compound [8a] except that 10-butyl-10H-phenothiazine-3-carbaldehyde (1g, 3.5 mmol) [4e] was taken in place of 4-(dimethylamino) benzaldehyde [4a].

Yield = 1.10 g (60%); M.P. = 232° C.

6.3.5 Synthesis of intermediate and dyes based on napthoquinone bridged

6.3.5.1 Synthesis of 2-methylnaphtho [2, 3-d] oxazole-4, 9-dione [11]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of 2,3-dichloronaphthalene-1,4-dione [9] (10g, 44 mmol) and acetamide [10] (2.5g, 44 mmol) were heated together in dioxane (80 mL, 8 vol) at 80 °C in presence of catalytic amount of triethylamine for 10 hrs. The completion of the reaction was monitored by thin layer chromatography. After cooling the reaction mass, the mixture was poured into ice cold water. The solid is filtered through suction pump to obtain the final product [11] and used for further reaction without purification. Yield = 5.25 g (56%); M.P. = 132° C. Mass spectra of the compound showed molecular ion peak at m/z = 217 which corresponds to molecular weight of [11] = 216; $^{13}$C NMR (CDCl3, 300 MHz): $\delta$ (ppm) 189.8, 179.2, 175.1, 134.8, 132.6, 129.7, 126.2, 125.8, 111.0, 12.6
6.3.5.2 Synthesis of (E)-2-(4-(dimethylamino) styryl)naphtho[2,3-d]oxazole-4,9-dione [12a]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of 2-methylnaphtho [2, 3-d] oxazole-4, 9-dione [11] (1.43 g, 6.7mmol) and 4-(dimethylamino) benzaldehyde [4a] (1.0g, 6.7mmol), were heated together in dioxane (15 mL, 15 vol) at reflux in presence of catalytic amount of piperidine for 6 hrs. The completion of the reaction was monitored by thin layer chromatography. After cooling the reaction mass, the mixture was poured into ice cold water and extract with ethyl acetate. The product was purified by column chromatography (toluene, 60 – 120 mesh silica gel) to obtain final product 12a.

Yield = 1.2 g (54%); M.P. = 154° C.

Analysis of dye [12a]:

A. IR spectra of [12a]
   - Presence of band at 3000-3100cm⁻¹ (s) indicating aromatic C-H
   - Presence of band at 1725 cm⁻¹ (m) indicating C=O stretching
   - Presence of band at 1069 cm⁻¹ (s) indicating C-N stretching

B. The compound was further confirmed by ¹H NMR and ¹³C NMR which showed following signals [12a]

   ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.27-8.23 (m, 2H, aromatic CH); 7.91-7.78 (m, 2H, aromatic CH); 7.54-7.26 (d, 2H, vinylic CH); 7.05-6.52 (m, 2H, aromatic CH); 3.10 (s, 6H, aliphatic CH₃).

C. ¹³C NMR (CDCl₃, 300 MHz): δ (ppm) 160.0, 150.4, 134.1, 131.2, 116.6, 116.2, 110.7, 51.5
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6.3.5.3 Synthesis of (E)-2-(4-(diethylamino)-2-hydroxystyryl)naphtho[2,3-d]oxazole-4,9-dione [12b] was done by the same procedure as that for compound [12a] except that 4-(diethylamino)-3-hydroxybenzaldehyde (1g, 5.1 mmol) [4b] was taken in place of 4-(dimethylamino) benzaldehyde [4a].

Yield = 0.9 g (48%); M.P. = 182° C.

6.3.5.4 Synthesis of (E)-2-(2-(1-butyl-1H-indol-3-yl)vinyl)naphtho[2,3-d]oxazole-4,9-dione [12c] was done by the same procedure as that for compound [12a] except that 1-butyl-1H-indole-3-carbaldehyde (1g, 4.9 mmol) [4c] was taken in place of 4-(dimethylamino) benzaldehyde [4a].

Yield = 0.79 g (40%); M.P. = 163° C.

6.3.5.5 Synthesis of (E)-2-(2-(9-butyl-9H-carbazol-3-yl)vinyl)naphtho[2,3-d]oxazole-4,9-dione [12c] was done by the same procedure as that for compound [12a] except that 9-butyl-9H-carbazole-3-carbaldehyde (1g, 3.9 mmol) [4d] was taken in place of 4-(dimethylamino) benzaldehyde [4a].

Yield = 0.79 g (45%); M.P. = 214° C.
6.4 CONCLUSION

In this chapter, we aimed at synthesizing novel colorants containing heterocyclic rings as linker or acceptor units. We successfully incorporated furan and thiophene moieties as $\pi$-bridges and these novel derivatives possess a Donor- $\pi$ bridge-Acceptor system ($D-\pi-A$) system. On subjecting these molecules for study of photophysical properties, we observed that the incorporation of thiophene rings gave absorption of higher wavelength than those with furan rings. However, these dyes absorbed at relatively lower wavelengths in comparison to benzene bridged dyes synthesized in chapter 5. All these dyes have absorption below 500 nm thereby exhibiting better transparency in the visible region. These features are quite desirable in non-linear optical applications. We have also synthesized heterocyclic styryl colorants containing quinone ring. The incorporation of these rings as acceptor units extended the absorption in the visible region. Although this affected the transparency in the visible region, however such quinone moieties could be useful for two-photon applications.
Mass spectra
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\( ^1 \)H NMR spectra
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$^{13}$C NMR spectra
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**FT – IR Spectra**

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