5.1 INTRODUCTION

Organic colorants possessing heterocyclic core and linked by styryl bond have gained much attention in terms of application in high value-added products such as sensitizers in optical recording materials, photography, laser dyes and fluorescent probes (Park et al. 2001; Kasada et al. 2002; Lim et al. 1998; Pommeret et al. 1995; Haidekker et al. 2001). The properties of these colorants such as solubility and physical properties can be easily modified by tailoring the dye structure. (Lehmann et al. 1995; Horiguchi et al. 2002) Such tunability assists in improving chemical stability of these molecules and also allows suitable design of dye for its respective applications.

Such colorants are also suitably used for application in non-linear optics (NLO). Nonlinear optics deals with the interactions of applied electromagnetic fields in various materials, to generate new electromagnetic fields altered in phase, frequency, amplitude and various other physical properties. Although, this application uses both organic and inorganic dyes as materials, but the organic colorants possess several advantages over inorganic and organometallic compounds for non-linear optics. Some of them include easier synthesis, ultra fast response time, photo-stability and large first hyperpolarizability (β) values.

The design of colorants for nonlinear optics has become a focus of current research owing to their significance in several 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 Williams1990). Some
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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.

The magnitude of the nonlinear behaviour depends greatly on the strengths of the donor-acceptor groups (Cheng et al. 1991). Keeping in mind the requirement of higher thermal stability, it is important to choose a rigid heterocyclic system containing electron donating groups. Heterocyclic systems such as carbazole and phenothiazine hold good charge transporting ability and hence are usually employed as donors in non-linear optically active molecules as shown in the figure below (Kim et al. 1997; Cho et al. 2005; Lee et al. 2004).

Indole is another significant heterocycle that has been employed as efficient donor system in NLO molecules (Moon et al. 2000; Hwang et al. 2001). One such example has been reported by Gong et al. wherein indole based moieties (as shown in figure below) exhibited superior non-linearity, greater thermal stability and good
transparency in comparison to aniline based analogues (Gong et al. 2006). Heterocycles including indole or julolidene attached to squaraine moiety with extended absorption in the near IR region has also been studied (Scherer et al. 2002; Keil and Hartmann 2001).

![Chemical structure](image)

The nature of conjugation is another important factor that affects the optical non-linear characteristics of the molecules (Cheng et al. 1991). It is observed that increased $\pi$-conjugation between donor and acceptor system helps to improve the hyperpolarizability value although at the cost of loss in optical transparency which is undesirable (Garito et al. 1994). The presence of longer conjugation chains also lowers the thermal stability and photo stability. Hence, in this chapter we have incorporated phenyl ring as conjugation bridge instead of repeated longer double bond units. Apart from donor and linker, the incorporation of electron-withdrawing substituents such as nitro (-NO$_2$) and cyano (-CN) are known to improve the properties of molecules for non-linear optical applications (Abe et al. 1997).

In this chapter, we explore different heterocyclic ring systems as donors bridged by phenyl ring to 4-nitrophenyl acetonitrile acceptor unit. Some heterocycles such as carbazole were both mono-substituted and di-substituted to form a Donor-$\pi$ bridge-
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Acceptor system (D-π-A) and Acceptor-π bridge-Donor- π bridge-Acceptor system (A-π-D-π-A). The aromatic analogues with amino substitution as donor groups were also synthesized for comparison of properties with heterocyclic units. The synthesized derivatives were also subjected for photo-physical and thermal stability studies. In addition, one styryl derivative was also subjected to three photon absorption studies as discussed further.
5.2 RESULTS AND DISCUSSION

5.2.1 Synthesis of benzene bridged styryl colorants

A variety of benzene bridged novel chromophores were synthesized by condensation of various donor aldehydes with p-nitro phenyl acetonitrile based acceptor moieties by refluxing in ethanol using catalytic amount of piperidine (Scheme 5.2). The acceptor benzene bridged moiety [3] was synthesized by condensation of tolualdehyde [1] with 4-nitrophenylacetonitrile [2] in ethanolic media using piperidine as a base (Scheme 5.1). The intermediate was characterized by \(^{1}\text{H-NMR}\) spectroscopy.

The preparation of mono and di formyl derivatives of N-butyl carbazole [4e] and [6] as well as mono formyl derivatives of other heterocyclic moieties such as indole [4c], julolidene [4d] and phenothiazine [4f] was done by classical Vilsmeier Haack formylation as described in the experimental section. The condensation of dicarbaldehyde of carbazole [6] with 2 equivalents of 2-(4-nitrophenyl)-3-(p-tolyl)acrylonitrile [3] by refluxing in ethanol using catalytic amount of piperidine gave di-substituted carbazole derivative compound [8] as depicted in Scheme 5.3. This derivative has an Acceptor-\(\pi\) bridge-Donor- \(\pi\) bridge-Acceptor (A-\(\pi\)-D-\(\pi\)-A) system in comparison to Donor- \(\pi\) bridge-Acceptor system (D-\(\pi\)-A) system as in other mono-substituted derivatives [5a-5f]. The molecular weights and yields of all these derivatives are summarized in Table 5.1. All the synthesized chromophores were purified by column chromatography and characterized using FT-IR, \(^{1}\text{H-NMR}, \(^{13}\text{C-NMR}\) and Mass spectra.
Scheme 5.1: Synthesis of 1-methyl-4-[2-(4-nitrophenyl) prop-1-en-1-yl] benzene [3]

Scheme 5.2: Condensation of aldehydes with 1-methyl-4-[2-(4-nitrophenyl) prop-1-en-1-yl] benzene [5a-5f]
Figure 5.1: Structure of mono-substituted final colorants [5a-5f]
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Scheme 5.3: Synthesis of disubstituted carbazole chromophore [6]

Ethanol, piperidine

Reflux

[6] [3]

[7]
Chapter 5: Synthesis, photo-physical data and study of multi-photon absorption properties of benzene bridged styryl colorants

Table 5.1: Physical data of the Dyes 5a-5f and Dye 7

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Yield in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye – 5a</td>
<td>C_{25}H_{21}N_{3}O_{2}</td>
<td>395</td>
<td>78</td>
</tr>
<tr>
<td>Dye – 5b</td>
<td>C_{27}H_{25}N_{3}O_{3}</td>
<td>439</td>
<td>82</td>
</tr>
<tr>
<td>Dye – 5c</td>
<td>C_{29}H_{25}N_{3}O_{2}</td>
<td>447</td>
<td>75</td>
</tr>
<tr>
<td>Dye – 5d</td>
<td>C_{29}H_{25}N_{3}O_{3}</td>
<td>463</td>
<td>62</td>
</tr>
<tr>
<td>Dye – 5e</td>
<td>C_{33}H_{27}N_{3}O_{2}</td>
<td>497</td>
<td>71</td>
</tr>
<tr>
<td>Dye – 5f</td>
<td>C_{33}H_{27}N_{3}O_{2}S</td>
<td>529</td>
<td>74</td>
</tr>
<tr>
<td>Dye – 7</td>
<td>C_{58}H_{37}N_{5}O_{4}</td>
<td>771</td>
<td>56</td>
</tr>
</tbody>
</table>
5.2.2 Photo-physical properties and solvatochromism of benzene bridged colorants

In order to investigate photo-physical properties, the absorption and photoluminescence spectra of dyes 5a-5f and 7 were measured for concentrations of \(1 \times 10^{-4}\) M in solvents such as hexane, methanol, acetonitrile and dimethylformamide (DMF). The path length of the cell was 1 cm whereby the influences of the quartz cuvette and the solvent have been subtracted. 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 solvent are presented in Table 5.2, 5.3, 5.4.

The absorption maxima for these colorants were in the range of 410-482 nm. It was observed that all colorants gave bathochromic shift with increase in solvent polarity. The emission wavelength ranged from 411-621 nm whereas stokes shift was in the range of 67-193 nm. The data given in Table 5.4 indicates that the highest stokes shift for compounds 5a, 5e, 5f and 7 are observed in acetonitrile whereas compound 5c shows best stokes shift in dimethylformamide. The di-substituted derivative 7 shows a bathochromic shift compared to its mono-substituted counterpart 5e.
Chapter 5: Synthesis, photo-physical data and study of multi-photon absorption properties of benzene bridged styryl colorants

Table 5.2: UV-Visible absorption data in different organic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption maxima ($\lambda_{\text{max}}$ in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5a</td>
</tr>
<tr>
<td>n-hexane</td>
<td>412</td>
</tr>
<tr>
<td>Methanol</td>
<td>410</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>416</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>449</td>
</tr>
</tbody>
</table>

Table 5.3: Emission data in different organic solvents

<table>
<thead>
<tr>
<th>Medium</th>
<th>Emission wavelength (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5a</td>
</tr>
<tr>
<td>n-hexane</td>
<td>460</td>
</tr>
<tr>
<td>Methanol</td>
<td>583</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>592</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>518</td>
</tr>
</tbody>
</table>
Table 5.4: Stokes shift of colorants in different organic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>5a</th>
<th>5b</th>
<th>5c</th>
<th>5d</th>
<th>5e</th>
<th>5f</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>74</td>
<td>75</td>
<td>64</td>
<td>76</td>
<td>60</td>
<td>80</td>
<td>62</td>
</tr>
<tr>
<td>Methanol</td>
<td>173</td>
<td>80</td>
<td>120</td>
<td>116</td>
<td>121</td>
<td>110</td>
<td>126</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>176</td>
<td>77</td>
<td>71</td>
<td>70</td>
<td>190</td>
<td>162</td>
<td>160</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>69</td>
<td>67</td>
<td>193</td>
<td>86</td>
<td>120</td>
<td>112</td>
<td>126</td>
</tr>
</tbody>
</table>
5.2.3 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 5.5.

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. In addition, the di-substituted chromophore 7 showed best thermal stability up to 305 °C which might be owing to the rigid nature of the di-substituted carbazole moiety. The higher value of thermal stability makes these molecules suitable for high-technological application such as non-linear optics. In this regards, we will discuss, in the next sub-section, the study of one of these synthesized dye for three-photon absorption.
Table 5.5: Thermal stability of Colorants

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Temperature of stability (°C) (at 4-6% product decomposition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>145</td>
</tr>
<tr>
<td>5b</td>
<td>205</td>
</tr>
<tr>
<td>5c</td>
<td>220</td>
</tr>
<tr>
<td>5d</td>
<td>205</td>
</tr>
<tr>
<td>5e</td>
<td>269</td>
</tr>
<tr>
<td>5f</td>
<td>280</td>
</tr>
<tr>
<td>7</td>
<td>308</td>
</tr>
</tbody>
</table>
5.2.4 Three-photon absorption study of benzene bridged styryl dyes

5.2.4.1 Experimental set up

Figure 5.2: Experimental set up for Z-scan experiments

Figure 5.2 illustrates the schematic of experimental set up used. The sample was translated using a high resolution stage (Newport, ILS250PP) and the transmitted light was collected using a lens and a photodiode (Thorlabs, SM1PD2A) combination. An aperture was placed in front of the lens for closed aperture scans and total light was collected during open aperture scans. The photodiode output was fed to a lock-in amplifier (7265, Signal Recovery). Several neutral density filters were used to cut down the input intensity before the sample and also the intensity reaching photodiode. The translation stage and the photodiode/lock-in were controlled by a personal computer using a Labview program. Fresnel losses from the optics were considered during these calculations. The pulse duration was
measured using an external Autocorrelator (SHG) in the non-collinear geometry using a 2-mm thick BBO crystal. Figure 2 shows a typical autocorrelation curve depicting the pulse duration to be 2.08 ps (FW1/e2M).

**Theory**

Assuming a spatial and temporal Gaussian profile for laser pulses the equation for 2PA open aperture (OA) normalized power transmittance given by

\[
T_{OA}(2PA) = \frac{1}{\pi^{1/2} q_0(z,0)} \int_{-\infty}^{\infty} \ln\left[1 + q_0(z,0) \exp(\tau^2)\right] d\tau
\]

Three-photon absorption (3PA) equation is

\[
T_{OA}(3PA) = \frac{1}{\pi^{1/2} p_0} \int_{-\infty}^{\infty} \ln\left[1 + p_0^2 \exp(-2\tau^2)\right]^{1/2} + p_0 \exp(-\tau^2) d\tau
\]

For \(|p_0|<1\), and ignoring the higher order terms, we obtain,

\[
T_{OA}(3PA) = 1 - 2\gamma I_{00}^2 L_{eff}' \frac{2\gamma I_{00}^2 L_{eff}'}{\left(1 + (z/z_0)^2\right)^{3/2}}
\]

where,

\[
q_0(z,0) = \frac{\beta I_{00} L_{eff}'}{1 + (z/z_0)^2},
\]

\[
p_0(z,0) = \frac{2\gamma I_{00}^2 L_{eff}'}{\left(1 + (z/z_0)^2\right)^{3/2}}.
\]

\(I_{00}\) is the peak intensity, \(z\) is the sample position, \(z_0 = \pi \omega_0^2 / \lambda\) is the Rayleigh range: \(\omega_0\) is the beam waist at the focal point \((z=0)\), \(\lambda\) is the laser wavelength; effective path length in the sample of length \(L\) for 2PA, 3PA is given as

\[
L_{eff} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}, L_{eff}' = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0}.
\]

We have evaluated the three photon cross-section \((\sigma_3)\) using the relation

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\[
\sigma_3 = \left( \frac{\hbar \omega}{N} \right)^2 \gamma
\]

where \( \omega \) is the frequency of the laser radiation, and \( N \) is the number density.

The closed aperture data were fitted using the equation,\(^1\)

\[
T_{ca} = 1 + \frac{4\Delta \phi \left( \frac{z}{z_0} \right)}{\left( \frac{z}{z_0} \right)^2 + 9 \left( \frac{z}{z_0} \right)^2 + 1}
\]

\( T \) is the normalized transmittance, \( \Delta \phi \) is the nonlinear phase shift, \( x = Z/Z_r \) is the normalized position with respect to the Rayleigh range.

\[
I_0 = \frac{I_{00}}{1 + \left( \frac{z^2}{z_0^2} \right)}
\]

where \( I_{00} \) is the peak intensity at focus calculated using the relation

\[
I_{00} = \frac{2E}{\pi^{3/2} w_0^2 \left( HW \frac{1}{e^2} M \right) \tau_p \left( HW \frac{1}{e} M \right)}
\]

\( E \) is the input pulse energy, \( \tau \) is the pulse duration, \( 2w_0 \) is the beam diameter at focus.

Since such molecules are suited for hi-tech applications like non-linear optics, one suitable chromophore was tested for its non-linear optical properties where it exhibited three-photon absorption phenomenon with good values of three photon absorption co-efficient and non-linear refractive index.
5.2.4.2 Open and closed aperture curves derived from Z-scan technique

Figures 5.3 show typical open aperture and closed aperture (inset) Z-scan data for the compounds 5c with concentrations of 2 mM. Solvent contribution, obtained by recording the open aperture data with pure solvents, was negligible (at least 25 times lower) in the present studies.

Open aperture data was recorded with a peak intensity of 83 GW/cm² while the closed aperture data was recorded at 28 GW/cm² in order to avoid any contribution from higher order nonlinearities. Closed aperture of the solvent provided a value of 2.8×10⁻¹⁶ cm²/W but, most importantly, the sign was opposite to that of the solution suggesting that the actual value of solutes could be higher than values estimated and presented here.

The magnitudes of three photon absorption cross sections obtained were 4.83×10⁻⁷⁷ cm⁶s²/photon² for dye 5c. These values are comparable/higher than some of the recently reported molecules. Moreover, this is the first study of three photon absorption in case of benzene bridged styryl dyes. There is further scope for tailoring these molecules to achieve superior cross-sections.

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>I₀₀ (GW/cm²)</th>
<th>3PA Cross section (σ³(cm⁶s²/photon²))</th>
<th>3PA coefficient (γ (cm³/W²) × 10⁻²²)</th>
<th>Refractive Index (n² (cm²/W) × 10⁻¹⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5c</td>
<td>83</td>
<td>4.83×10⁻⁷⁷</td>
<td>4.3</td>
<td>6</td>
</tr>
</tbody>
</table>
Chapter 5: Synthesis, photo-physical data and study of multi-photon absorption properties of benzene bridged styryl colorants

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

Figure 5.3: Open and closed aperture curves
5.3 EXPERIMENTAL

5.3.1 Materials and equipments

All the solvents and chemicals were procured from S D fine chemicals (India) and were used without further purification. The reactions were monitored by TLC using 0.25 mm E-Merck silica gel 60 F254 precoated 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.

The linear absorption spectra of the newly synthesized push pull chromophores were measured for concentrations of $1 \times 10^{-3}$ M in chloroform in a cell of 1 cm path length whereby the influences of the quartz cuvette and the solvent have been subtracted. We had also tested the thermal stability of dyes by thermal gravimetric analysis (DSC-TGA) carried out in the temperature range 25-600 °C under nitrogen gas at a heating rate of 10 °C min$^{-1}$.

Nonlinear absorption (NLA) of 5c were measured by the open aperture Z-scan technique at room temperature with laser pulses from a chirped pulse amplified Ti:sapphire laser system operating at a wavelength 800 nm delivering nearly transform-limited (~2 ps, 1 kHz repetition rate) pulses (Sarma et al. 2011; Venugopal Rao et al. 2011; Swain et al. 2012; Podagatlapalli et al. 2012; Hamad et
al. 2012; Saravanan et al. 2010; Anusha et al 2012; Anusha et al. 2010a). The measurements were performed with solutions (chloroform) at a concentration of 2-5 mM. A quartz cuvette (1-mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length. The beam waist ($\omega_0$) at focal plane was estimated to be ~70 $\mu$m (FW1/e^2M) with a corresponding Rayleigh range ($Z_r$) of ~4.5 mm ensuring the validity of thin sample approximation. Typically <3 $\mu$J energy pulses were used for the experiments. The nonlinear absorption coefficients [3PA coefficients ($\gamma$) in this case] were obtained from the open aperture data analysis whereas the intensity dependent nonlinear refractive indices ($n_2$) of the samples were obtained from the closed aperture data.

5.3.2 Synthesis of intermediates and final colorants molecules

5.3.2.1 Synthesis of 1-butyl-1H-indole-3-carbaldehyde [4c]; 9-hexyl-9H-carbazole-3-carbaldehyde [4e]; 9-hexyl-9H-carbazole-3,6-dicarbaldehyde [6] was discussed in chapter 4, section 4.3.4

5.3.2.2 Synthesis of 8-hydroxy-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline-9-carbaldehyde [4d] was discussed in chapter 2, section 2.3.2.9

5.3.2.3 Synthesis of N-butyl-phenothiazine
In a 500 ml round bottomed flask fitted with a mercury sealed stirrer, 1-bromobutane (3.84g, 28 mmol) was added dropwise to a mixture of phenothiazine (5.00g, 25 mmol), sodium hydroxide (20.0 g, 500 mmol), and dimethylsulfoxide (DMSO) (150 mL). This reaction mixture was stirred for 1 day at room temperature. The resulting mixture was extracted with EA/brine solution and the organic layer was
dried with NaSO₄. The ethyl acetate layer was further subjected to evaporation under vacuum using rotary evaporator. The resulting crude product was purified by silica-gel column chromatography using toluene as the mobile phase. A yellow viscous product was obtained after drying with a yield of 81% (5.19 g). M.P. = 145 °C

5.3.2.4 Synthesis of N-butyl-3-formyl-phenothiazine [4f]

In a three necked 500ml round bottom flask fitted with a mercury sealed stirrer, addition dropping funnel topped by calcium chloride guard tube and reflux condenser also topped by calcium chloride guard tube. N, N-dimethyl formamide (d=0.944, 4.58g, 4.85ml, 62.7 mmol) was taken and cooled to 0-5°C with stirring. To the above solution phosphorous oxychloride (d=1.645, 7.2g, 4.3 ml, 47 mmol) was added drop wise maintaining the temperature of the reaction mass at 0-5°C. The Vilsmeier complex so formed was stirred for further 15 minutes and compound 3 (4g, 15.6 mmol) was added in lots (15-25 minutes) to the complex. The reaction mixture was stirred at 0-5°C for 3 hrs and then allowed to attain room temperature. The mixture was then vigorously stirred under vigorously stirring and heated to 75°C for 8 h. This solution was then cooled to room temperature, poured in to ice water, and neutralized to pH 6-7 by drop wise addition of saturated aqueous sodium hydroxide solution. The mixture was extracted with dichloromethane. The organic layer was dried with anhydrous NaSO₄ and then concentrated on rotary evaporator. The crude product on purification by column chromatography (mobile phase-toluene and silica gel 60-120 mesh) afforded yellow oil. Yield = 3.2 g (72%); ¹H NMR (CDCl₃, TMS): δ 9.79 (s, 1H), 6.87–7.65 (m, 7H), 3.90 (t, 2H), 1.79 (m, 2H),
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1.48 (m, 2H), 0.95 (t, 3H). $^{13}$C NMR (CDCl$_3$, ppm) $\delta$ 198.95, 150.66, 143.34, 130.94, 128.24, 124.9, 123.68, 115.93, 114.73, 77.52, 47.61, 28.75, 20.02, 13.74.

5.3.2.5 Synthesis of 1-methyl-4-[2-(4-nitrophenyl) prop-1-en-1-yl] benzene [3]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of 2-(4-nitrophenyl)acetonitrile [2] (1.35g, 8.3mmoles) and 4-methylbenzaldehyde [1] (1.0g, 8.3mmoles) were heated together in ethanol (15mL, 15 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 = 1.87 g (85%); M.P. = 146 °C; $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ (ppm) 8.28-8.27 (m, 2H, aromatic CH); 7.95-7.80 (m, 4H, aromatic CH); 7.62 (s, 1H, vinylic CH); 7.29-7.24 (m, 2H, aromatic CH); 2.41 (s, 3H, aliphatic CH$_3$).

5.3.2.6 Synthesis of 3-(4-(4-(dimethylamino)styryl)phenyl)-2-(4-nitrophenyl) acrylonitrile [5a]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of 1-methyl-4-[2-(4-nitrophenyl) prop-1-en-1-yl] benzene [3] (1.77 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 = 2.0 g (78%); M.P. = 118 °C;

**Analysis of dye \([5a]\):**

A. Mass spectra of the compound showed molecular ion peak at m/z = 398 which corresponds to molecular weight of \([5a]\) = 396; Other molecular ion peaks were found at m/z = 354 which corresponds to mass of fragment obtained after removal of CH\(_3\) and CN groups; m/z = 335 is obtained by removal of NO\(_2\) and CH\(_3\) group.

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

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) (ppm) 8.25 (m, 3H, aromatic CH and vinylic CH); 7.91-7.78 (m, 6H, aromatic CH); 7.54 (m, 2H, vinylic CH); 7.26 (m, 1H, aromatic CH); 6.73-6.50 (m, 3H, aromatic CH); 3.10 (s, 6H, aliphatic CH\(_3\))

C. \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) (ppm) 152.6, 147.1, 146.9, 145.6, 142.2, 132.4, 132.2, 130.2, 125.8, 124.4, 120.8, 118.9, 111.7, 111.4, 101.6, 40.2.

**5.3.2.7 Synthesis of 3-(4-(4-(diethylamino)-3-hydroxystyryl)phenyl)-2-(4-nitrophenyl)acrylonitrile \([5b]\)** was done by the same procedure as that for compound \([5a]\) except that 4-(diethylamino)-3-hydroxybenzaldehyde \([4b]\) was taken in place of 4-(dimethylamino) benzaldehyde \([4a]\). Yield = 1.86 g (82%); M.P. = 154 °C.
Analysis of dye [5b]:

A. Mass spectra of the compound showed molecular ion peak at m/z = 440 which corresponds to molecular weight of [5b] = 439; Other molecular ion peaks were found at m/z = 422 which corresponds to mass of fragment obtained after removal of OH group; m/z = 353 is by removal of NO₂ and CN group.

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

\[ \delta \text{ (ppm)}: 8.27 \text{ (m, 2H, aromatic CH)}; 7.92-7.83 \text{ (m, 2H, aromatic CH)}; 7.27 \text{ (m, 3H, aromatic CH)}; 6.64-6.54 \text{ (m, 2H, aromatic CH)}; 3.46 \text{ (m, 4H, aliphatic CH₂)}; 1.58-1.25 \text{ (m, 6H, aliphatic CH₃)}. \]

5.3.2.8 **Synthesis of** 3-((E)-2-(1-butyl-1H-indol-3-yl)vinyl)phenyl)-2-(4-nitrophosphophenyl) acrylonitrile [5c] **was done by the same procedure as that for** compound [5a] **except that 1-butyl-1H-indole-3-carbaldehyde [4c] was taken in place of 4-(dimethylamino) benzaldehyde [4a]**

Yield = 1.66 g (75%); M.P. = 172 °C.

Analysis of dye [5c]:

A. Mass spectra of the compound showed molecular ion peak at m/z = 446 which corresponds to molecular weight of [5c] = 447.

B. The compound was further confirmed by which showed following signals [5c]
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1H NMR (CDCl3, 300 MHz): δ (ppm) 8.47-8.26 (m, 4H, aromatic CH); 8.04 (m, 2H, aromatic CH); 7.83-7.64 (m, 5H, 4 aromatic CH and 1 vinylic CH); 7.43-7.32 (m, 5H, 3 aromatic CH and 3 vinylic CH); 2.44-2.35 (m, 2H, aliphatic CH2); 1.91 (m, 2H, aliphatic CH2); 1.58-1.41 (m, 2H, aliphatic CH2); 0.99 (s, 3H, aliphatic CH3);

C. 13C NMR (CDCl3, 300 MHz): δ (ppm) 147.7, 146.6, 145.6, 141.5, 140.8, 136.1, 131.2, 130.2, 130.0, 129.9, 128.3, 126.6, 125.4, 125.3, 124.4, 124.3, 123.6, 121.9, 119.6, 110.7, 108.1, 100.8, 47.3, 32.0, 20.2, 13.7.

5.3.2.9 Synthesis of 3-((E)-2-(8-hydroxy-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)vinyl)phenyl)-2-(4-nitrophenyl) acrylonitrile [5d] was done by the same procedure as that for compound [5a] except that 8-hydroxy-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline-9-carbaldehyde [4d] was taken in place of 4-(dimethylamino)benzaldehyde [4a]. Yield = 1.32 g (62%); M.P. = 164 ⁰C.

Analysis of dye [5d]:

A. Mass spectra of the compound showed ion peak at m/z = 375 which corresponds to molecular weight of [5d] after removal of OH, NO2 and CN groups.

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

1H NMR (CDCl3, 300 MHz): δ (ppm) 8.27-8.23 (m, 4H, aromatic CH); 8.03-8.02 (m, 2H, aromatic CH); 7.95-7.94 (m, 2H, aromatic CH); 7.78-7.74 (m, 2H, aromatic CH); 7.50-7.40 (m, 2H, aromatic CH); 7.30-7.20 (m, 2H, aromatic CH); 7.10-7.00 (m, 2H, aromatic CH); 6.90-6.80 (m, 2H, aromatic CH); 6.70-6.60 (m, 2H, aromatic CH); 6.50-6.40 (m, 2H, aromatic CH); 6.30-6.20 (m, 2H, aromatic CH); 6.10-6.00 (m, 2H, aromatic CH); 5.90-5.80 (m, 2H, aromatic CH); 5.80-5.70 (m, 2H, aromatic CH); 5.70-5.60 (m, 2H, aromatic CH); 5.60-5.50 (m, 2H, aromatic CH); 5.50-5.40 (m, 2H, aromatic CH); 5.40-5.30 (m, 2H, aromatic CH); 5.30-5.20 (m, 2H, aromatic CH); 5.20-5.10 (m, 2H, aromatic CH); 5.10-5.00 (m, 2H, aromatic CH); 5.00-4.90 (m, 2H, aromatic CH); 4.90-4.80 (m, 2H, aromatic CH); 4.80-4.70 (m, 2H, aromatic CH); 4.70-4.60 (m, 2H, aromatic CH); 4.60-4.50 (m, 2H, aromatic CH); 4.50-4.40 (m, 2H, aromatic CH); 4.40-4.30 (m, 2H, aromatic CH); 4.30-4.20 (m, 2H, aromatic CH); 4.20-4.10 (m, 2H, aromatic CH); 4.10-4.00 (m, 2H, aromatic CH); 4.00-3.90 (m, 2H, aromatic CH); 3.90-3.80 (m, 2H, aromatic CH); 3.80-3.70 (m, 2H, aromatic CH); 3.70-3.60 (m, 2H, aromatic CH); 3.60-3.50 (m, 2H, aromatic CH); 3.50-3.40 (m, 2H, aromatic CH); 3.40-3.30 (m, 2H, aromatic CH); 3.30-3.20 (m, 2H, aromatic CH); 3.20-3.10 (m, 2H, aromatic CH); 3.10-3.00 (m, 2H, aromatic CH); 3.00-2.90 (m, 2H, aromatic CH); 2.90-2.80 (m, 2H, aromatic CH); 2.80-2.70 (m, 2H, aromatic CH); 2.70-2.60 (m, 2H, aromatic CH); 2.60-2.50 (m, 2H, aromatic CH); 2.50-2.40 (m, 2H, aromatic CH); 2.40-2.30 (m, 2H, aromatic CH); 2.30-2.20 (m, 2H, aromatic CH); 2.20-2.10 (m, 2H, aromatic CH); 2.10-2.00 (m, 2H, aromatic CH); 2.00-1.90 (m, 2H, aromatic CH); 1.90-1.80 (m, 2H, aromatic CH); 1.80-1.70 (m, 2H, aromatic CH); 1.70-1.60 (m, 2H, aromatic CH); 1.60-1.50 (m, 2H, aromatic CH); 1.50-1.40 (m, 2H, aromatic CH); 1.40-1.30 (m, 2H, aromatic CH); 1.30-1.20 (m, 2H, aromatic CH); 1.20-1.10 (m, 2H, aromatic CH); 1.10-1.00 (m, 2H, aromatic CH); 1.00-0.90 (m, 2H, aromatic CH); 0.90-0.80 (m, 2H, aromatic CH); 0.80-0.70 (m, 2H, aromatic CH); 0.70-0.60 (m, 2H, aromatic CH); 0.60-0.50 (m, 2H, aromatic CH); 0.50-0.40 (m, 2H, aromatic CH); 0.40-0.30 (m, 2H, aromatic CH); 0.30-0.20 (m, 2H, aromatic CH); 0.20-0.10 (m, 2H, aromatic CH); 0.10-0.00 (m, 2H, aromatic CH).
2H, aromatic CH); 7.25 (s, 2H, aromatic CH); 3.32-3.28 (m, 4H, alicyclic CH₂); 2.8-2.74 (m, 4H, alicyclic CH₂); 2.01-1.92 (m, 4H, alicyclic CH₂).

C. $^{13}$C NMR (CDCl₃, 300 MHz): δ (ppm) 157.9, 147.5, 146.5, 143.0, 139.5, 126.3, 125.5, 124.4, 119.4, 117.8, 113.18, 113.10, 99.9, 62.3, 50.2, 49.8, 27.7, 21.6, 21.4, 21.0

5.3.2.10 Synthesis of 3-(4-((E)-2-(9-butyl-9H-carbazol-3-yl)vinyl)phenyl)-2-(4-nitrophenyl)acrylonitrile [5e] was done by the same procedure as that for compound [5a] except that 9-butyl-9H-carbazole-3-carbaldehyde [4e] was taken in place of 4-(dimethylamino)benzaldehyde [4a]. Yield = 1.40 g (71%); M.P. = 206 °C.

5.3.2.11 Synthesis of 3-(4-((E)-2-(10-butyl-10H-phenothiazin-3-yl)vinyl)phenyl)-2-(4-nitrophenyl)acrylonitrile [5f] was done by the same procedure as that for compound [5a] except that 10-butyl-10H-phenothiazine-3-carbaldehyde [4f] was taken in place of 4-(dimethylamino)benzaldehyde [4a]. Yield = 1.38 g (74%); M.P. = 214 °C.

Analysis of dye [5f]:

A. Mass spectra of the compound showed molecular ion peak at m/z = 428 which corresponds to molecular weight of [5f] after removal of butyl group and nitro group.

B. IR spectra of [5f]

- Presence of band at 3000-3100cm⁻¹(s) indicating aromatic C-H
- Presence of band at 2211 cm⁻¹(s) indicating C≡N stretching
- Presence of band at 1516 and 1337 cm⁻¹(m) indicating NO₂ stretching
- Presence of band at 1108 cm⁻¹(s) indicating C-N stretching
C. The compound was further confirmed by which showed following signals [5f]

\[1^H \text{NMR (CDCl}_3, 300 \text{ MHz): } \delta \text{ (ppm) 8.30-8.20 (m, 3H, 2 aromatic CH and 1 vinylic CH); 7.90-7.70 (m, 5H, aromatic CH); 7.65-7.55 (m, 2H, aromatic CH); 7.50 (s, 1H, aromatic CH); 7.30-7.05 (m, 4H, aromatic CH); 6.95-6.80 (m, 3H, 1 aromatic CH and 2 vinylic CH); 3.95-3.80 (t, 2H, aliphatic CH\_2); 1.85-1.75 (m, 2H, aliphatic CH\_2); 1.50-1.40 (m, 2H, aliphatic CH\_2); 1.00-0.90 (t, 3H, aliphatic CH\_3)\]

D. \[^{13}C \text{NMR (CDCl}_3, 300 \text{ MHz): } \delta \text{ (ppm) 148.3, 147.4, 145.6, 143.9, 143.5, 142.7, 141.1, 140.8, 130.2, 130.0, 1299, 129.5, 128.9, 127.6, 127.5, 125.0, 126.6, 126.3, 124.9, 124.3, 123.4, 117.7, 115.7, 115.1, 108.1, 105.5, 8, 47.6, 28.8, 20.1, 13.8.\]

5.3.2.12 Synthesis of \[3,3\'-(((9-butyl-9H-carbazole-3,6-diyl)bis(ethene-2,1-diyl))bis(4,1-phenylene))bis(2-(4-nitrophenyl)acrylonitrile) [7]\]

In a three necked 100ml round bottom flask fitted with a mercury sealed stirrer, a suspension of 1-methyl-4-[2-(4-nitrophenyl) prop-1-en-1-yl] benzene [3] (1.89 g, 7.1mmoles) and 9-butyl-9H-carbazole-3,6-dicarbaldehyde [6] (1.0g, 3.5mmoles), were heated together in ethanol (15mL, 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 obtained product was purified by column chromatography (toluene, 60 – 120 mesh silica gel) to obtain final product [7].

Yield = 1.54 g (56%); M.P. = 232 °C.
5.4 CONCLUSION

In this chapter, we aimed at synthesizing novel colorants suitable for application in non-linear optics. The solvatochromism studies revealed that all colorants gave bathochromic shift with increase in solvent polarity. In addition, all the dyes absorbed below 490 nm thereby exhibiting better transparency in the visible region. These dyes also possess good thermal stability. These features are quite desirable in non-linear optical applications.

One of the synthesized colorant molecules [5c] was subjected to three-photon absorption studies. The studies revealed good values of nonlinear refractive index ($n_2$) that is useful for optical switching applications. Importantly, these values were obtained at a non-resonant wavelength of 800 nm. The magnitudes of three photon absorption cross sections obtained were $4.83 \times 10^{-77} \text{ cm}^6 \text{s}^2/\text{photon}^2$ for dye 5c. These values are comparable/higher than some of the recently reported molecules. Moreover, this is the first study of three photon absorption in case of styryl dyes based on benzene bridged. There is further scope for tailoring these molecules to achieve superior cross-sections.
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Mass spectra

![Mass spectra graph]

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$^{13}\text{C} – \text{NMR Spectra}$
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FT – IR spectra

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