CHAPTER 5

SPECTRAL CHARACTERISTICS OF NONLINEAR DYES IN LIQUID MEDIUM

5.1 INTRODUCTION

The new nonlinear optical (NLO) materials with high optical nonlinearities are gaining interest both in research as well as industrial point of view. The essential requirements of good photonic materials are its laser and fast acting non linearity, synthetic flexibility and ease of processing. The potential use in optical information processing devices has been the driving force behind most of the research into characterization of nonlinear optical properties of materials. For this purpose, considerable attention has been paid in particular to the third order nonlinearities of organic dyes. Azobenzene type organic non-linear dyes represent one promising class of organic nonlinear materials (Tomov et al 1991).

With the rapid developments of the optical communication, people have the higher demand for the photoelectron device and light storage medium. Not only the rapid response but also the large third-order nonlinear susceptibility for materials as needed. Zhang et al (1989) reported that there exists laser optical nonlinearities in common liquid medium such as Chinese tea and so on which are easy to obtain. Third-order nonlinear optical susceptibility, $\chi^{(3)}$, is responsible for phenomena such as third harmonic generation or optical phase conjugation (Nalda et al 2002). Nonlinear optical phase conjugation is an important technique with application in many fields
of Science and Engineering such as spectroscopy, adaptive optics, real-time image processing or phase-conjugate mirrors (Costela et al 1995).

The selection of organic dyes that show nonlinearity is accomplished by trial and error. Thousands of organic dyes have been synthesized over the last hundred years and are commercially available, but only a few of them exhibit efficient nonlinear action. In order to find the suitability of a material for such applications one needs to find its optical characteristics such as type of nonlinearity, its magnitude, spectrum, response time etc. Fluorescence spectroscopy has been proven to be a versatile tool for a variety of applications. It has been used for various environmental, industrial and biotechnological applications (Bright 1988). It is a valuable analytical tool for both qualitative and quantitative analysis (Sharma and Schulam 1999). It is highly sensitive, selective and simple and is rich in information. It is a zero background technique. The point of safety in fluorimetry refers to the fact that the samples are not affected or destroyed in the process, and no hazardous by-products are generated. Its high sensitivity is due to the fact that the emitted radiation is measured directly. Sensitivity can also be increased by increasing the incident intensity.

Absorption measurements can reliably determine concentrations only as low as several tenths of a micro molar. Fluorescence techniques can accurately measure concentrations in pico or even in femto molar range. Fluorimetry is more selective than UV-Visible absorption spectrometry for two reasons. Firstly many molecules absorb strongly in the UV or visible region but do not exhibit detectable fluorescence. Secondly, two wavelengths (excitation and emission) are available in fluorimetry while only one is available in absorptimetry. Fluorimetry has a number of measurable characteristics which making it inherently information rich (Bright 1988, Wolfbeis 1993). Several parameters can be employed to characterize and
quantitatively evaluate a fluorescent analyte and this can be either steady-state parameter or time-dependent parameter. Emission maxima, Fluorescence intensity etc. are steady-state parameters while intensity decay life time is a time-dependent parameter.

Time-resolved measurements are widely used in fluorescence spectroscopy because they contain more information than the steady-state data. Information on the number of fluorescence entities and number of different sites of binding a single fluorophore is available through time-resolved measurements. Lifetime $\tau$, is measured as the average time the molecule spends in the excited state prior to the return to the ground state. Generally, fluorescence lifetimes are in the range of nano to pico seconds. The fluorescence lifetime can function as a molecular stopwatch to observe a variety of molecular events which occur in the above timescale.

Therefore, to evaluate azo dyes with respect to nonlinear optical processes, their lasing behavior must be elucidated. Its of much use if we can observe a link between the lasing characteristics of the organic dyes and their molecular structures to their nonlinearity, making the tiresome process of producing new nonlinear materials more systematic. The spectral characteristics of these dyes give an insight about their lasing characteristics. In this chapter a study of the absorption and fluorescence spectra, fluorescence quantum yield and lifetimes of the dyes in liquid environment are studied. The molecular structures of dyes chosen are shown in Figure 2.1(a-h). In general, there is a lack of corroborated data elaborating the spectral and optical properties of azo dyes over different spectral regions of scientific and application oriented interest. To the best of our knowledge there are very few literatures which deal with the spectral characteristics of the azo dyes. No comprehensive data is available for reference or comparison. Therefore, thorough investigation of these dyes in liquid media are necessary
to understand the lasing characteristics dyes in solvent. The solvent medium can force the solute particle to get solute-solvent interactions.

The dyes chosen for our study, Sudan III, Brilliant Crocein, Azophloxine, Ponceau S, Evan’s blue and Amido black 10B. Work was also done on two laser grade chromophores, [2-[4-[4-(dimethylamino) phenyl]-1, 3-butadienyl]-1-ethylpyridinium monoperchlorate; Pyridine 1 and 4-[4-[4-(dimethylamino) phenyl]-1, 3-butadienyl]-1-ethyl-pyridinium perchlorate; Pyridine 2.

5.2 SPECTRAL CHARACTERISTICS OF AZO DYES

5.2.1 Synthesis of Azo Dye Solutions

The azo dyes are obtained from SD Fine Chem, India. Thin layer chromatography (TLC) test confirms the absence of any impurities. The dye solutions for each respective dye is made for 0.01mM concentration in distilled water.

5.2.2 Absorption and Fluorescence Spectra of Azo Dyes

The absorption spectra is obtained using a PERKIN ELMER LAMBDA 35 UV–Vis spectrophotometer with a resolution of ± 1nm. The spectra of the solution is obtained using 1cm path length cuvettes. The absorption spectra of the azo dyes in distilled water are recorded and the spectra are shown in Figure 5.1a-f.
Figure 5.1 (Continued) Absorption spectra of the azo dyes
Figure 5.1 (Continued)  Absorption spectra of the azo dyes
Figure 5.1 Absorption spectra of the azo dyes
The peak wavelengths of the absorption spectra are measured and the spectral parameters such as molecular absorption coefficient \((\varepsilon)\), Oscillator strength \((f)\), absorption bandwidth \((\Delta \nu_{1/2})\) are calculated and given in Table 5.1.

The emission spectra was recorded using a F-4500 FL Spectrophotometer (90° geometry) using a xenon arc lamp as the excitation source. For solution measurements a fluorimetric quartz cuvette was used. The resolution of the spectrofluorometer is ± 0.5nm. Fluorescence spectra were background- subtracted and corrected for detector and monochromater background nonlinearities. The emission spectra of the azo dyes for 0.01mM concentration are recorded and shown in Figure 5.2a-e. The fluorescence bandwidth (FWHM) and Stoke’s shift are calculated from the spectra’s of these dyes for 0.01mM and given in Table 5.1.

### Table 5.1 Spectral characteristics of the azo dyes in distilled water

<table>
<thead>
<tr>
<th>Dye</th>
<th>Absorption spectra</th>
<th>Fluorescence spectra</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Peak wavelength</td>
<td>(\varepsilon)</td>
</tr>
<tr>
<td></td>
<td>nm</td>
<td>(10^4) L mol(^{-1}) cm(^{-1})</td>
</tr>
<tr>
<td>Brilliant Crocein</td>
<td>510</td>
<td>2.537</td>
</tr>
<tr>
<td>Azophloxine</td>
<td>531</td>
<td>2.492</td>
</tr>
<tr>
<td>Ponceau S</td>
<td>520</td>
<td>3.790</td>
</tr>
<tr>
<td>Evan’s Blue</td>
<td>607</td>
<td>4.903</td>
</tr>
<tr>
<td>Amido Black 10B</td>
<td>619</td>
<td>2.278</td>
</tr>
</tbody>
</table>
Figure 5.2 (Continued) Fluorescence spectra of the azo dyes
Figure 5.2 (Continued)  Fluorescence spectra of the azo dyes
Figure 5.2 Fluorescence spectra of the azo dyes

Fluorescence quantum yield of dyes are experimentally determined by comparison of dye emission with that of a dye of known quantum yield (Demas and Crosby 1971). Rhodamine B (Rh B) in ethanol is taken as the fluorescence standard to measure the quantum yield for the dyes Sudan III, Brilliant Crocein, Azophloxine, Ponceau S, Pyridine 1 and Pyridine 2 while Cresyl violet in methanol is taken as the fluorescence standard for the dyes Evan’s blue and Amido black 10B. $\phi'$ is the quantum yield of Rh B is taken to be 0.50 ((Kartstens et al 1980 and Casey et al 1988) and that of Cresyl violet is taken to be 0.54 (Douglous Madge et al 1979). The fluorescence spectra are corrected using quinine sulphate is 0.1N H$_2$SO$_4$ (Govindanunny et al 1980). Care is taken to record all the spectra under identical conditions. Very optically dilute solution of the reference and sample are taken so as to avoid re-absorption (Kubin and Flecher 1982). The refractive index values of the solvents are taken from the literature (CRC Handbook 2000).
The absorption and emission spectra are shown in the graphs 5.1, 5.2 and the spectral characteristics calculated are presented in table 5.1 and the following analysis are made:

All the azo dye molecules studied displayed two absorption bands in the range 300nm to 650nm, being transparent in the near infrared region as observed from the Figures 5.1. The fluorescence profile shows a red shift, which can be attributed to intermolecular charge transfer (ICT), which occur when these molecules are excited. The analysis of the fluorescence spectra of these dyes in distilled water (solvent) show a very weak fluorescence intensity revealing that the dyes used in the present study are very weakly fluorescent. The fluorescence lifetimes of these dyes were less than 52ps which was the response time of the system used. Internal conversion is a mechanism that is mostly responsible for the low fluorescence efficiency in organic dyes. It is a direct nonradiative decay of the lower excited state singlet state $S_1$, to the ground state $S_0$. As this mechanism results in heat transfer, we try to observe if there is a slight raise in the thermal nonlinearity of these dyes due to this process.

5.3 SPECTRAL CHARACTERISTICS OF PYRIDINE DYSES

5.3.1 Preparation of Pyridine Dye Solutions

The investigated laser grade chromophore are pyridine 1 (LDS 698) and pyridine 2 (LDS 722) from Exciton, USA whose structure is shown in Figure 2.1(g, h). TLC tests confirmed the absence of impurities. Methanol, from Fisher Chemicals is chosen as the solvent for this study, which is of spectroscopic grade. Dilute dye solutions ($1 \times 10^{-5}$ mM to avoid aggregation and self-absorption effects) are prepared in methanol for absorption / emission
measurements and fluorescence lifetime measurements, in order to study the
effect of the dye structure on fluorescence quantum yield and decay rates.

5.3.2 Absorption and Fluorescence Spectra of Pyridine Dyes

The absorption spectra is obtained using a PERKIN ELMER LAMBDA 35 UV–Vis spectrophotometer with a resolution of ± 1nm. The spectra of the solution is obtained using 1cm path length cuvettes. The absorption spectra of the pyridine dyes in methanol are recorded and the spectra are shown in Figure 5.3. The peak wavelengths of the absorption spectra are measured and the spectral parameters such as molecular absorption coefficient (ε), Oscillator strength (f), absorption bandwidth (Δυ/2) are calculated.

The emission spectra is recorded using a F-4500 FL Spectrophotometer (90° geometry) using a xenon arc lamp as the excitation source. For solution measurements a fluorimetric quartz cuvette is used. The resolution of the spectrofluorometer is ± 0.5 nm. Fluorescence spectra were background- subtracted and corrected for detector and monochromater background nonlinearities and are shown in Figure 5.4. Fluorescence quantum yields are obtained by the comparative method with Rhodamine B with φ_i = 0.50 being used as the fluorescence standard. The fluorescence bandwidth (FWHM) and Stoke’s shift are calculated from the spectra’s of these dyes for 0.01mM and is presented in Table 5.2.
Figure 5.3 Absorption spectra of the Pyridine dyes
Figure 5.4  Fluorescence spectra of the Pyridine dyes
Table 5.2 Spectroscopic parameters of the Pyridine dyes in methanol

<table>
<thead>
<tr>
<th>Dye</th>
<th>Absorption Spectra</th>
<th>Fluorescence Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_a ) (nm)</td>
<td>( \varepsilon \times 10^4 ) L mol(^{-1}) cm(^{-1})</td>
</tr>
<tr>
<td>Pyridine 1 (LDS 698)</td>
<td>483</td>
<td>4.89</td>
</tr>
<tr>
<td>Pyridine 2 (LDS 722)</td>
<td>497</td>
<td>6.61</td>
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5.2.3 Fluorescence Lifetime Measurements

The fluorescence lifetime measurements are performed using a light emitting diode (LED) and single photon counting set-up. The LED (Spectra Physics) emitting light at 450nm with pulse width of 1.4 ns is used to excite the sample. The emission is collected at magic angle polarization (54.7\(^\circ\)) to avoid bias due to polarization effects for all viewing angles and is dispersed in a monochromator (f/3) aperture counted by an MCP-PMT (Hamamatsu R 3809) and proceeded through CFD-TAC and MCA. The instrument response function for this system is 52ps. The fluorescence decay is analyzed by using the software provided by IBH (DASS-6) analysis software, which includes an iterative shift of the fitted function as part of chi-squared goodness of the fit criterion.

From the UV-Vis and fluorescence spectrum of the two LDS dyes as shown in Figures 5.3 and 5.4. It is observed that the dyes have a single band absorption and that their fluorescence intensity profiles though sharp are weak in intensity. The spectral parameters such as absorption peak wavelength, molar extinction coefficient (\( \varepsilon \)), Band width \( (\Delta \nu) \_ {1/2} \), oscillator
strength (f), fluorescence peak wavelength, full width at half maximum (FWHM), Stoke’s shift of the dyes are shown in Table 5.2. Fluorescence quantum yield of dyes in liquid media is experimentally determined by comparison of dye emission with that of a dye of known quantum yield.

The quantum yields are calculated using the expression,

\[
\phi_\text{f} = \left( \frac{A_{\text{sam}}}{A_{\text{ref}}} \right) \times \left( \frac{a_{\text{ref}}}{a_{\text{sam}}} \right) \times \left( \frac{n_{\text{sam}}}{n_{\text{ref}}} \right)^2 \phi_1',
\]

(5.1)

where, \( A_{\text{sam}} \) and \( A_{\text{ref}} \) are the areas under the corrected fluorescence spectrum, \( a_{\text{sam}} \) and \( a_{\text{ref}} \) are the absorbance at the exciting wavelength, \( n_{\text{sam}} \) and \( n_{\text{ref}} \) are the refractive indices of the respective solvent and reference, respectively. The fluorescence profile shows a red shift which can be attributed to intermolecular charge transfer (ICT) which occur when these molecules are excited.

The fluorescence decay is analyzed by using the software provided by IBH (DASS-6), which includes an iterative shift of the fitted function as part of chi-squared goodness of the fit criterion (Figure 5.5). The single exponential decay function is fitted according to the relation, \( I(t) = A \exp(-t/\tau) \). The fluorescence lifetime of LDS 698 and 722 are 195 and 305 ps in methanol, respectively. The residuals shown along with the decay are well within the error limits.
Figure 5.5  Fluorescence decay profiles of the dyes a. LDS 698 and b. LDS 722

5.4 CONCLUSION

The spectral parameters such as absorption peak wavelength, molar extinction coefficient (ε), bandwidth (Δν)_{1/2}, oscillator strength (f), fluorescence peak wavelength, full width at half maximum (FWHM), Stoke’s shift of the dyes are calculated. All the azo dye molecules studied displayed two absorption bands in the range 300nm to 650nm, being transparent in the near infrared region. The fluorescence profile shows a red shift, which can be attributed to intermolecular charge transfer (ICT), which occur when these molecules are excited. The analysis of the fluorescence spectra of these dyes in distilled water (solvent) show a very weak fluorescence intensity revealing that the dyes used in the present study are very weakly fluorescent. The
fluorescence lifetimes of these dyes were less than 52ps which was the response time of the system used. Internal conversion is a mechanism that is mostly responsible for the low fluorescence efficiency in organic dyes. It is a direct nonradiative decay of the lower excited state singlet state $S_1$, to the ground state $S_0$. As this mechanism results in heat transfer, to observe if there is a slight raise in the thermal nonlinearity of these dyes due to this process.

The spectral characteristics of the laser grade chromophores pyridine 1 (LDS 698) and pyridine 2 (LDS 722) in methanol are studied too. The dyes have a single band absorption and their fluorescence intensity profiles though sharp are weak in intensity. The fluorescence profile shows a red shift which can be attributed to intermolecular charge transfer (ICT) which occur when these molecules are excited. The fluorescence lifetime of LDS 698 and 722 are 195ps and 305ps in methanol, respectively. The residuals shown along with the decay are well within the error limits.

The quantum yields calculated for the dyes are very low while their nonlinearity is reasonably high, indicating that these dyes are promising candidates for photonic device applications than as fluorescence probes or for dye lasers.