A combined experimental and theoretical study of the molecular structure, photophysical, photostability and laser characteristics of important pyrromethene dyes.
3.1. Introduction:

Several chromophores of highly fluorescent organic compounds are now known, but the dipyrromethene BF$_2$ (PM or BODIPY) family of dyes has attracted interest over the past decade as being one of the more versatile fluorophore due to its applications as biomolecular labels$^1$, novel organic materials$^2$, fluorescent chemo-sensors$^3$, and active media in liquid$^4$ and solid-state$^5$ dye lasers, among others. The use of PMs as effective biological label has been complemented by their preference to function as an efficient laser dye. The general observation of good laser efficiency of PM dyes in solid-state, as well as, in liquid dye lasers has led to several investigations$^6$-$^8$ on its photo-physical and laser properties.

Although, photo-physical and laser characteristics of PM567 dye is widely studied, scanty reports are available for those$^6$ of PM580, and PM597 dye in liquid dye lasers and correlations of their photo-physical properties with molecular structures. Generally, a high quantum yield of fluorescence ($\Phi$) and a small non-radiative rate of decay of the dye molecule in the solvent environment are prerequisites for high laser efficiency. The non-radiative deactivation processes are normally attributed to the rigidity /flexibility of the molecular structure of the chromophore. Additional processes that may affect net laser efficiency are ground-state absorption (GSA) and excited singlet–state absorption (ESA) at laser wavelengths, and these need to be accounted while considering the effect of molecular properties of dyes on their laser efficiencies [section 1.3.1, 1.3.2] (Chapter 1). Therefore, a better understanding on correlations between molecular structures, photo-physical properties and laser efficiencies of available PM dyes is necessary to modify and design new PM dye molecules.

The present experimental and a time-dependent density functional theoretical (TDDFT) investigations on PM597 and PM580 dyes, along with commonly studied PM567 dye, were taken up to generate supplementary information on their photo-physical, laser properties and molecular parameters, as well as, the influence of the molecular structures on their properties. In this chapter of the thesis, the results of our comprehensive investigations on laser performances of alcohol solutions of these Pyrromethene dyes, along with widely used Rhodamine 6G (RH6G), Rhodamine B (RHB) and Sulforhodamine B (KRS) dyes, using a narrow-band (~0.1 cm$^{-1}$) dye laser set up, transversely pumped by the second harmonic (532 nm) of a Q-switched, pulsed (10 Hz) Nd-YAG laser has been reported. A
significant observation was efficient lasing performance of PM597 dye, comparable to PM580 and PM567 dyes and higher than RH dyes, despite poor fluorescence yield of the PM597 molecule\textsuperscript{9}.

Calculations of electronic structures of ground ($S_0$) and first excited ($S_1$) states of all three PM dyes were performed by time dependent density functional theory (TDDFT) with appropriate long-range functional to understand the effect of the molecular structures on their photo-physics and hence, laser properties. Off late, it has been shown that by adding long range correction term\textsuperscript{10-16} accounting for long-range exchange repulsions in the hybrid functional can improve excitation wavelengths significantly by eliminating overestimation of certain unphysical attraction terms. So, we have applied the formalism to calculate excitation wavelengths. The theoretical studies establish that TDDFT (B3LYP)-PCM (Polarizable Continuum Model) combination is an excellent and reliable method for predicting the longest wavelength absorption maxima and other molecular data of PM dyes. It is demonstrated that reliable prediction of excited state properties of the dyes is possible and the method may be utilized in designing new PM dyes with desirable spectral properties for specific applications.

In parallel, more fundamental studies on the chemical reactivity and photodegradation mechanism of the new PM dyes emerged. However, rapid rate of photodegradation of PM dyes in air-equilibrated liquid solutions,\textsuperscript{17,18} due to its self-sensitized photo-oxidation by reacting with generated singlet oxygen, remained a cause of primary concern for use in liquid dye lasers, especially in high-average power dye lasers. Remarkable improvement in the photo-stability of PM567 dye solutions, while deployed in low\textsuperscript{17}, as well as, in high-repetition rate dye lasers\textsuperscript{18}, was observed with addition of 1,4-diazabicyclo[2,2,2]octane (DABCO), a singlet oxygen quencher. There have also been efforts\textsuperscript{8,19-21} to synthesize various analogues of PM dyes possessing better photo-stability, as well as, higher efficiency for dye laser and other applications. The photo-stability of dyes is generally evaluated by irradiating a known volume of dye solution by the pump laser radiation of a specified power for a fixed duration and estimating the decrease in concentration of dye molecules\textsuperscript{22-25}. During pump laser excitation to the excited singlet ($S_n$) states, depending on the rates of de-excitation in the singlet manifold and intersystem crossing ($k_{ST}$) to the triplet states, a fraction of the excited dye molecules may leave the lasing cycle and populate long-lived triplet ($T_n$) states. A fraction of these dye molecules in
the excited triplet states undergo photochemical reactions with solvent, dissolved oxygen or other impurities leading to their degradation [Section 1.3.3] (Chapter 1). For example, photochemical degradation of pyrromethene (PM) dyes through triplet (T<sub>1</sub>) state, due to its self-sensitized photo-oxidation by reacting with generated singlet oxygen, in air-equilibrated liquid solutions has been extensively reported<sup>26-29</sup>. During these de-excitation processes, excited dye molecules decay primarily by spontaneous emission and residence time of dye molecules in the excited S<sub>1</sub> state is governed by fluorescence lifetime.

Thus, understanding the various photo-degradation mechanisms of PM dye molecules and reducing the degradation rate has been a vital issue for improving the performance of liquid dye lasers. In earlier works<sup>30,31</sup>, the influence of stimulated emission on the photo-stability of dye laser in a broad band configuration were reported. However, studies investigating effect of emission wavelengths of dye laser on photo-stability of dyes in liquid media are not reported. Since stimulated emission competes with photo-degradation of excited dye molecules, it is expected that the degradation rate would depend on the emission wavelength, and vary across the tuning range of the dye laser. In the present work, we report systematic investigation on photo-stability of ethanol solution of PM567 dye at different emission wavelengths, observed with a Q-Switched Nd:YAG pumped narrow band pulsed dye laser. Higher photo-stability of dye solution was noticed when dye laser was operated near peak in comparison to edge wavelengths of the dye tuning curve.

Earlier theoretical studies investigating influence of degradation of dye molecules on performance of dye lasers has been reported following a steady state approach<sup>32,33</sup>. However, in order to simulate the effect of dye degradation on dye laser efficiency at different emission wavelengths in presence of both spontaneous and stimulated emission processes in a pulsed dye laser, a time dependent analysis<sup>34</sup> describing laser pulse build up was adopted, which has been found to be in good agreement with the experimental observations.
3.2. Experimental Methods:

3.2.1 Materials:

High purity laser grade dyes were procured from Exciton and DABCO, Aldrich, and used as received. The molecular formula of all three PM dyes is shown in Figure 3.1.

\[
\begin{align*}
\text{PM 567:} & \quad R = \text{C}_2\text{H}_5 \\
\text{PM 580:} & \quad R = (\text{CH}_2)_3\text{CH}_3 \\
\text{PM 597:} & \quad R = \text{C}(\text{CH}_3)_3.
\end{align*}
\]

*Figure 3.1: Molecular structure of PM567, PM580 and PM597 dyes.*

Spectroscopy grade methanol and ethanol solvents, Merck, India, were used to prepare dye solutions for this study.

3.2.2 Absorption, Fluorescence and Lifetime Measurements:

Absorption and steady-state fluorescence spectra of alcoholic PM and RH dye solutions, were recorded with commercial UV/VIS spectrophotometer (JASCO, V-550) and spectro-fluorimeter (JASCO, FP-6500), respectively [section 2.2 & 2.3.1] (Chapter 2).

The measurement of quantum yield of fluorescence (Φ) of PM dyes were carried out using the comparative method of Williams et al\textsuperscript{35}, [Section 2.3.1] (Chapter 2) ensuring linearity of fluorescence yield across the measured concentration range (1-3 \times 10^{-6} M) of dye, which also validated the use of standard dye solution and its Φ value. PM567 was chosen as standard sample and it was cross calibrated with another dye, PM597. The time-resolved fluorescence measurements of dye solutions were carried out with a time-correlated single photon counting (TCSPC) set up from IBH [Section 2.3.2] (Chapter 2), using a 490 nm LED (~1.3 ns, 1 MHZ repetition rate) as excitation source. Fluorescence decay curves were fitted as single-exponential decay and the fluorescence lifetime (τ) was calculated from
the slope. All the measurements were performed at ambient temperature, the dye solutions being in equilibrium with the air.

3.2.3 Study of Laser properties using narrowband dye laser setup:

Comparative studies of laser performances of PM and RH dye solutions were carried out by constructing a narrow band dye laser, transversely excited by 2\textsuperscript{nd} harmonic of a Q-switched, pulsed (10 Hz) Nd-YAG laser, which have been described elsewhere [section 2.4.1] (Chapter 2). To ensure similar gain depth for all dye solutions and provide a dye laser output with high efficiency and near-circular spatial profile, the concentrations of all dye solutions were optimized to have similar optical density at the pump wavelength, 532 nm. Optimized concentration of DABCO (~100 mM) was added\textsuperscript{22} to each air equilibrated PM dye solutions to reduce the rapid rate of photo-degradation of PM dyes. The tuning curve of each dye solution was obtained by rotation of the tuning mirror, and using an optical fiber coupled wave meter and a power meter.

3.2.4 Effect of laser emission wavelength on photostability:

To study the effect of dye laser wavelength on the rate of dye photo-stability a Littrow configuration narrow band pulsed dye laser was constructed as described in section 2.4.2 (Chapter 2). A small volume (2 ml) of stirred, air-saturated ethanol solution of PM567 dye was used in a laser cuvette to accelerate the effect of dye degradation on laser efficiency. To observe the effect of dye laser wavelength on the rate of dye photo-stability, the dye laser was tuned to operate at peak (550 nm) and at two symmetrically located wavelengths (543 and 571 nm) on either side of the peak and the gradual decrease in laser efficiency was measured under lasing (L) and non-lasing conditions (NL), with similar pump energy. In this non-lasing case, the feedback in the dye laser resonator was blocked by placing a shutter, allowing only pump excitation but no buildup of dye laser action. The shutter was momentarily removed for a short period during measurement of decrease in dye laser power. However, in such non-lasing condition two walls (4\% reflectivity) of the dye cuvette served as a resonator to provide weak, broad-band window lasing (WL) action. The quantum yield of photo-stability of dye solutions, in lasing (Q_{PS}\textsuperscript{L}) and non-lasing with
window lasing ($Q_{PS}^{WL}$) conditions, was calculated $^{36}$ as number of pump photons required to decompose a dye molecule after a fixed irradiation period with similar pump energy by estimating the initial ($N_i$) and final ($N_f$) number of dye molecules. Concentration of dye in the irradiated solution (2 ml) was calculated at start and end of exposure through measurement of peak absorbance (O.D at $\lambda_{\text{abs}}^{\text{max}}$) using an UV-vis absorption spectrometer. The measurement of photo-stability ($Q_{PS}^{NL}$) of dye under entirely non-lasing (NL) condition i.e. even in absence of cuvette window lasing, was carried out by irradiating the dye solution in the cuvette with the pump of similar pulse energy while the cylindrical lens of pump beam as well as resonator cavity was removed. The cuvette window induced lasing was suppressed because of a large reduction in the pump intensity. Here, $Q_{PS} = P/(N_i-N_f)$, where $P$ is total number of pump photons absorbed in the dye solutions during the exposure period, and calculated from cumulative dose of absorbed pump energy using the power meter. A stock solution of PM567 dye with a concentration 0.77 mM was used for photo-stability measurement under different conditions such that pump beam was totally absorbed in dye solutions during laser irradiation period. The measurement on $Q_{PS}$ of dye solutions at each condition i.e. lasing (L), non-lasing with window lasing (WL) and total non-lasing (NL) was repeated thrice and average values were considered. Generally, a measurable decrease in concentration of dye solutions was noticed after pump exposure period of two to four hours, depending on various conditions. Hence, photo-stability measurements were carried out at peak (550 nm), blue-edge (543 nm) and red-edge (571 nm) wavelengths of the dye tuning curve, as a representative case of different dye laser emission wavelengths.

3.2.5 Theoretical Methods:

Search for the minimum energy structures in the ground ($S_0$) state of all the three PM dyes was carried out applying a correlated hybrid density functional, Becke’s three parameter exchange augmented by Lee, Yang, and Parr’s (B3LYP) using a Dunning-type correlation consistent atomic basis set, cc-pVDZ for all the atoms. Quasi Newton-Raphson based algorithm was applied to carry out geometry optimization for each of these dyes with various possible conformers as the initial structures. Electron correlated method, namely, time dependent density functional theory (TDDFT) with B3LYP density functional was applied to study the excited state structure of the dyes in the first excited ($S_1$) state. Of late,
different models have been proposed for long range corrections in DFT functional replacing the DFT exchange part with the HF exchange to predict accurate excitation energies within time dependent density functional formalism. Recently, density functional, PBE0 with long range correction based on a modified exchange energy density (LRC-µPBE0) due to Hirao and co-workers\textsuperscript{10-13} was also applied to find out the excited state energy parameters with the optimized geometry for the first excited state at TDDFT/B3LYP level of theory \textsuperscript{14-16}. Value of Coulomb attenuation parameter (µ) was taken as 0.33 in these excited state calculations. This DFT functional with long-range correction, LRC-µPBE0 was shown to predict accurate absorption spectra of organic dyes\textsuperscript{37}. Note that Dunning-type correlation consistent atomic basis set, cc-pVDZ was also used for all the excited state calculations. The ground (S\textsubscript{0}) state minimum energy structures of these dyes, including PCM model with B3LYP functional, was searched by testing effect of macroscopic hydration. Excited state calculations are also carried out on these solvent modified geometries to determine the effect of solvent applying TDDFT with B3LYP functional coupled with PCM solvent model. All electronic structure calculations were carried out applying the GAMESS suite of \textit{ab initio} program\textsuperscript{38}.

\textbf{3.3. Results and Discussion:}

\textbf{3.3.1 Theoretical Approach:}

Minimum energy structures of Pyrromethene dyes, PM567, PM580 and PM597 in the ground (S\textsubscript{0}) and the first excited (S\textsubscript{1}) states, applying B3LYP functional under DFT/TDDFT procedure including PCM solvent model, were computed and are displayed in Figure 3.2 (i-iii). It is observed that the geometrical parameters in the ground state (S\textsubscript{0}) are very close to that in the first excited state (S\textsubscript{1}) in case of dyes PM567 and PM580 and the rings of the chromophore are almost planar. However, in case of dye PM597, the first excited state structure is largely distorted from planarity, as evident from a large value of dihedral angle, \( \angle C_2BC_8C_6 = 14.2^\circ \).
Studies on photophysics and laser properties of important pyrromethene dyes

Figure 3.2: Optimized structures in the (ia) ground $S_0$ state and (ib) first excited $S_1$ state of the dye PM567; (iia) ground $S_0$ state and (iiib) first excited $S_1$ state of the dye PM580 and (iiia) ground $S_0$ state and (iiib) first excited $S_1$ state of the dye PM597. The ground state structures were optimized applying B3LYP/cc-pVDZ level of theory including C-PCM model. The excited state structures were optimized at TDDFT (B3LYP)/cc-pVDZ level of theory. Colour codes: yellow for F atoms, magenta for B atoms, blue for N atoms and out of rest, smaller balls are for H atoms and larger balls are for C atoms.

[Studies on photophysics and laser properties of important pyrromethene dyes]
Table 3.1: Selected geometrical parameters of PM567, PM580, and PM597 dyes in the ground ($S_0$) and the first excited ($S_1$) states, calculated applying B3LYP and TD(B3LYP) methods, respectively, taking Dunning correlated atomic basis functions, cc-PVDZ for all the atoms.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Pi-conjugation length for Long axis (Å) (Top side) #</th>
<th>Pi-conjugation length for Long axis (Å) (Bottom side) #</th>
<th>$\angle$FBF (degree)</th>
<th>$\angle$C2BC8C6 (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ground State ($S_0$)</td>
<td>First Excited State ($S_1$)</td>
<td>Ground State ($S_0$)</td>
<td>First Excited State ($S_1$)</td>
</tr>
<tr>
<td>PM567</td>
<td>8.501</td>
<td>8.598</td>
<td>8.629</td>
<td>8.619</td>
</tr>
<tr>
<td>PM580</td>
<td>8.504</td>
<td>8.585</td>
<td>8.634</td>
<td>8.617</td>
</tr>
<tr>
<td>PM597</td>
<td>8.521</td>
<td>8.627</td>
<td>8.667</td>
<td>8.674</td>
</tr>
</tbody>
</table>

#Top side refers to bond links: C2-C1-C8'-C8-C7'-C7-C6 (see Figure 3.1) and bottom side refers to bond links: C2-C3-N3'-B4-N-C5-C6

Also, a significant increase in the value of conjugation length, along the long molecular axis (C2C6), is observed for PM597 dye explaining red spectral shift of its absorption and particularly, emission spectra and low fluorescence yield in comparison to other two PM dyes. Selected geometrical parameters related to the chromophore of the three dyes in the ground and the first excited state based on DFT calculations are mentioned in Table 3.1.

A considerable modification in charge density of the atoms is observed in the first excited state compared to the ground state of PM dyes. The calculated atomic charges (in a.u.) of C(2), C(6), N(1), N(2), B, F(1) and F(2), atoms in $S_0$ state of dyes, based on B3LYP level calculation, and in the first excited state ($S_1$) at TD(B3LYP) level show significant electronic change, and these are tabulated in Table 3.2. Note that, the two terminal carbon atoms at C(2) and C(6), along long molecular axis, show positive atomic charges for the dye PM597, whereas, negative charges are shown for PM567 and PM580 molecules.
**Table 3.2:** Mulliken atomic charge density at atoms of PM chromophores.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Mulliken Atomic Charge on PM567 (a.u.)</th>
<th>Mulliken Atomic Charge on PM580 (a.u.)</th>
<th>Mulliken Atomic Charge on PM597 (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ground State (S₀)</td>
<td>First Excited State (S₁)</td>
<td>Ground State (S₀)</td>
</tr>
<tr>
<td>C2</td>
<td>-0.067</td>
<td>-0.072</td>
<td>-0.067</td>
</tr>
<tr>
<td>C6</td>
<td>-0.076</td>
<td>-0.120</td>
<td>-0.072</td>
</tr>
<tr>
<td>N1</td>
<td>-0.21</td>
<td>-0.16</td>
<td>-0.21</td>
</tr>
<tr>
<td>N2</td>
<td>-0.22</td>
<td>-0.15</td>
<td>-0.22</td>
</tr>
<tr>
<td>B</td>
<td>0.21</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>F1</td>
<td>-0.24</td>
<td>-0.13</td>
<td>-0.23</td>
</tr>
<tr>
<td>F2</td>
<td>-0.23</td>
<td>-0.14</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

Table 3.3 depicts calculated electronic transition wavelengths for the lowest transition; HOMO→LUMO at various levels of theory for all the three PM dyes and compares these values with the experimental data. It may be mentioned that the S₀-S₁ transition of PM dyes is a promotion of one electron from the HOMO to the LUMO state and it is polarized along the long molecular axis (C₂C₆), perpendicular to the molecular dipole moment. As seen from the table, vertical transitions are largely blue shifted at different level of theory incorporating different DFT functional in TDDFT calculations in case of all the three dyes.

Performance of long range corrected DFT functional, namely LRC-µPBE0 under TDDFT formalism (method 2 in Table 3.3) is also poor in the present case and largely blue shifted by ~ 90 nm, though it was shown earlier to produce accurate optical transition wavelengths with this particular DFT functional. Even application of a macroscopic model, such as conductor-like polarizable continuum model (C-PCM), does not improve the calculated transition wavelengths. However, when the structures of the dyes are fully relaxed in the first excited state, the transition wavelengths improve significantly (see Method 4 in Table 3.3) towards the experimental values and these are much better than earlier theoretical report⁸.
Surprisingly, the performance of LRC-µPBE0 functional is poor again when TDDFT calculation is repeated with this functional on relaxed structure of S1 surface calculated at TDDFT(B3LYP) level of theory. Finally, we have carried out single point excited state calculation including PCM macroscopic solvation model on relaxed S1 surface without solvent effect (Method 6 in Table 3.3) and the values are listed in Table 3.3. These are the best-calculated transition wavelength values for the lowest electronic transitions, HOMO→LUMO in these three dyes. HOMO orbital of the ground state and LUMO orbital of the first excited states are shown in Figure. 3.3. As it can be noticed, participation of chromophore atoms B and F is minimal in both orbitals. Thus, boron centre in the Bodipy core offers another option for substitution with no electronic effect on the dye core because the changes in the π-electron density on the fluorine atoms in the S0 and S1 states are very low.

Table 3.3: Comparison of calculated optical transition wavelength (λ) of PM567, PM580 and PM597 dyes with the experimental values. Time dependent density functional theory (TDDFT) with functionals, B3LYP and PBE0 + long range correction (LRC-µPBE0) are considered for the excited state calculations. Dunning correlated atomic basis functions, cc-PVDZ is adopted for all the atoms in these calculations.

<table>
<thead>
<tr>
<th>Theoretical Method</th>
<th>Calculated λ (nm) for dye</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM567</td>
</tr>
<tr>
<td>Method1: TD(PBE0) (S1)//B3LYP (S0)</td>
<td>415</td>
</tr>
<tr>
<td>Method2: TD(LRC-µPBE0) (S1)//B3LYP (S0)</td>
<td>431</td>
</tr>
<tr>
<td>Method3: TD(B3LYP)+PCM (S1)//B3LYP+PCM (S0)(^1)</td>
<td>439</td>
</tr>
<tr>
<td>Method4: TD(B3LYP) (S1)//TD(B3LYP) (S1)</td>
<td>539</td>
</tr>
<tr>
<td>Method5: TD(LRC-µPBE0) (S1)//TD(B3LYP) (S1)</td>
<td>454</td>
</tr>
<tr>
<td>Method6: TD(B3LYP) +PCM (S1)//TD(B3LYP) (S1)(^1)</td>
<td>528</td>
</tr>
<tr>
<td>Experiment(^1) (λ(^{\text{max}})(_{\text{abs}}))</td>
<td>518</td>
</tr>
</tbody>
</table>

\(^1\)Ethanol Solvent
Studies on photophysics and laser properties of important pyrromethene dyes.

Figure 3.3: Plot of (a) HOMO and (b) LUMO orbital in the ground $S_0$ state and the first excited $S_1$ state of the dye (i) PM567, (ii) PM580 and (iii) PM597 with the maximum contour value of 0.1.

3.3.2 Experimental Approach:

3.3.2.1 Photophysical Properties:

A typical illustration of observed linear fluorescence intensity plots for all three PM dyes in methanol solvent is shown in Figure 3.4. The gradient of the plot for each dye
solution is taken as proportional to the fluorescence quantum yield of that sample. Refer to section 2.3.1 (Chapter 2).

Figure 3.4: Integrated Fluorescence Intensity ($I_{FL}$) Plot for (▲) PM567, (●) PM580 and (■) PM597 dyes using methanol solvent (PM567 and PM597 were considered as reference).

The measured photo-physical properties of PM and RH dye solutions, such as absorption maximum ($\lambda_{\text{abs}}^{\text{max}}$), fluorescence maximum ($\lambda_{\text{em}}^{\text{max}}$), fluorescence quantum yield ($\Phi$) and fluorescence lifetime ($\tau$) etc., are summarized in Table 3.4. It also includes values for radiative ($k_r$) and non-radiative ($k_{nr}$) rates of dyes, computed from the measured $\Phi$ and $\tau$ values. Photo-physical properties of both the PM567 and PM580 dyes show close resemblance and these agree with the previously reported data\textsuperscript{6,19,21}. The absorption and fluorescence spectra of PM597 dye were observed to shift to longer wavelengths with respect to those of PM567 and PM580 dyes which agree with earlier report\textsuperscript{9}. However, the shift is much higher in the fluorescence (~28 nm) than in the absorption (~5 nm) spectra, and thus produced a large Stokes shift, $\Delta\nu$ (~1389 cm$^{-1}$). The large bathochromic shift of absorption and particularly, emission bands for PM597 originates from higher electron donating capability of the bulky alkyl groups at C2 and C6 carbon atom positions, which is substantially higher for tert-butyl groups in PM597 than for n-butyl groups in PM580 and ethyl groups in PM567. The electronic charge density at C2 and C6 carbon positions of
PM597 dye show positive values, in comparison to negative values for PM567 and PM580 (refer Table 3.2).

**Table 3.4:** Photo-physical properties of PM and RH dyes in methanol and ethanol solvents.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Solvent</th>
<th>$\lambda_{\text{abs}}^{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{em}}^{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{a}}^{\text{max}}$ ($10^4$ M$^{-1}$cm$^{-1}$)</th>
<th>$\Delta\nu$ (cm$^{-1}$)</th>
<th>$\Phi_f$</th>
<th>$\tau$ (ns)</th>
<th>$k_r$ (10$^8$ s$^{-1}$)</th>
<th>$k_{nr}$ (10$^8$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM567</td>
<td>MeOH</td>
<td>516</td>
<td>535</td>
<td>7.9</td>
<td>688</td>
<td>0.84</td>
<td>6.37</td>
<td>1.31</td>
<td>0.251</td>
</tr>
<tr>
<td>PM567</td>
<td>EtOH</td>
<td>518</td>
<td>536</td>
<td>8.3</td>
<td>648</td>
<td>0.83</td>
<td>6.27</td>
<td>1.32</td>
<td>0.271</td>
</tr>
<tr>
<td>PM580</td>
<td>MeOH</td>
<td>517</td>
<td>537</td>
<td>7.5</td>
<td>721</td>
<td>0.86</td>
<td>6.23</td>
<td>1.38</td>
<td>0.224</td>
</tr>
<tr>
<td>PM580</td>
<td>EtOH</td>
<td>519</td>
<td>538</td>
<td>7.6</td>
<td>680</td>
<td>0.85</td>
<td>6.16</td>
<td>1.37</td>
<td>0.243</td>
</tr>
<tr>
<td>PM597</td>
<td>MeOH</td>
<td>522</td>
<td>562</td>
<td>7.3</td>
<td>1363</td>
<td>0.48</td>
<td>4.21</td>
<td>1.11</td>
<td>1.277</td>
</tr>
<tr>
<td>PM597</td>
<td>EtOH</td>
<td>523</td>
<td>564</td>
<td>7.4</td>
<td>1389</td>
<td>0.42</td>
<td>4.07</td>
<td>1.03</td>
<td>1.425</td>
</tr>
<tr>
<td>RH6G</td>
<td>EtOH</td>
<td>530</td>
<td>560</td>
<td>10.6*</td>
<td>1011</td>
<td>0.99#</td>
<td>4.5</td>
<td>2.17</td>
<td>0.04</td>
</tr>
<tr>
<td>RhB</td>
<td>EtOH</td>
<td>543</td>
<td>568</td>
<td>10.0*</td>
<td>811</td>
<td>0.7*</td>
<td>2.8</td>
<td>2.5</td>
<td>1.07</td>
</tr>
<tr>
<td>KRS</td>
<td>EtOH</td>
<td>555</td>
<td>574</td>
<td>11.9*</td>
<td>596</td>
<td>0.69*</td>
<td>3.8</td>
<td>1.82</td>
<td>0.82</td>
</tr>
</tbody>
</table>

*Taken from references: (') Ref. 39, (+) Ref. 40, (*) Ref. 41.*

Also, our calculation on geometrical parameters of first excited state ($S_1$) of these dyes show dihedral angles (C2BC1C3) of 14.2° in PM597 molecule, in comparison to 4.6° in PM580 and 6.8° in PM567. Thus, the observed large red shift, in the fluorescence spectrum of dye PM597, is related to the enormous distortion of its excited ($S_1$) state from aromaticity, which in turn, reduces the resonance energy of the emission band in the solvent environment. The observation of considerably smaller fluorescence yield ($\Phi$) and lifetime ($\tau$) of PM597 dye is also related to the large distorted geometry of PM597 from planarity in the excited state ($S_1$).
3.3.2.2 Laser Properties:

The observed narrow-band laser tuning curves for all three PM dyes using ethanol solvent, pumped by 532 nm of Nd-YAG laser, are shown in Figure 3.5. PM567 and PM580 dyes produced laser gain in similar region of spectra (545 nm to 580 nm) and had comparable peak efficiency (~22%) at similar wavelengths (~558 nm). However, in concurrence with absorption and fluorescence spectra, PM597(d) dye show lasing peak at significantly longer wavelength (578 nm) with wider tuning range in region 560 nm to 610 nm. The methanol solvent based PM dyes produced marginally higher (1-2%) laser efficiency than that with ethanol, which correlates with slightly superior photo-physical properties of these dyes in methanol (Table 3.4). The pump energy threshold ($L_T$) and slope efficiency ($\eta_s$) of each dye lasers at its respective peak laser wavelength were calculated by extrapolating the plot of dye laser power against pump power, which is illustrated for methanol solutions of PM dyes in Figure 3.6.

![Figure 3.5: Dye laser (DL) tuning curves for (a) PM567, (b) PM580, (c) RH6G and (d) PM 597 dyes using ethanol solvent. Pump wavelength: 532 nm, Pump Energy ~ 7 mJ/pulse.](image-url)
Figure 3.6: Dye Laser (DL) gain curves of (a) PM567, (b) PM580 and (c) PM597 dyes using methanol as solvent at their respective peak laser wavelengths.

Table 3.5: Laser Characteristics of PM and RH dye solutions

<table>
<thead>
<tr>
<th>Dye</th>
<th>Solvent</th>
<th>Conc. of Dye (mM)</th>
<th>Max. ( \lambda_L ) (nm)</th>
<th>Max. Eff. ( \eta ) (%)</th>
<th>Threshold ( L_T ) (mJ)</th>
<th>Slope Eff., ( \eta_s ) (%)</th>
<th>Tuning Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM567</td>
<td>EtOH</td>
<td>0.88</td>
<td>558.3</td>
<td>23</td>
<td>0.3</td>
<td>24.1</td>
<td>546-580</td>
</tr>
<tr>
<td>PM567</td>
<td>MeOH</td>
<td>0.97</td>
<td>556.2</td>
<td>24</td>
<td>0.27</td>
<td>25.1</td>
<td>546-578</td>
</tr>
<tr>
<td>PM580</td>
<td>EtOH</td>
<td>0.71</td>
<td>557.7</td>
<td>22</td>
<td>0.35</td>
<td>23</td>
<td>548-580</td>
</tr>
<tr>
<td>PM580</td>
<td>MeOH</td>
<td>0.77</td>
<td>561</td>
<td>23</td>
<td>0.28</td>
<td>22.9</td>
<td>547-580</td>
</tr>
<tr>
<td>PM597</td>
<td>EtOH</td>
<td>0.28</td>
<td>575.1</td>
<td>20</td>
<td>0.45</td>
<td>22.1</td>
<td>561-611</td>
</tr>
<tr>
<td>PM597</td>
<td>MeOH</td>
<td>0.29</td>
<td>576</td>
<td>22</td>
<td>0.39</td>
<td>24.2</td>
<td>561-611</td>
</tr>
<tr>
<td>RH6G</td>
<td>EtOH</td>
<td>0.15</td>
<td>565</td>
<td>16.5</td>
<td>0.15</td>
<td>17.7</td>
<td>555-575</td>
</tr>
<tr>
<td>RhB*</td>
<td>EtOH</td>
<td>0.18</td>
<td>586</td>
<td>13.6</td>
<td>0.23</td>
<td>14.6</td>
<td>578-601</td>
</tr>
<tr>
<td>KRS*</td>
<td>EtOH</td>
<td>0.2</td>
<td>587</td>
<td>9.5</td>
<td>0.15</td>
<td>9.9</td>
<td>580-596</td>
</tr>
</tbody>
</table>

(*) Taken from Ref. 41
Table 3.5 summarizes laser properties of PM dyes, using both ethanol and methanol solvents. The corresponding data for RH dyes using ethanol solvent are also included for comparison. All the three PM dyes gave substantially higher laser efficiency than even RH6G, the most efficient RH class dye. However, RH6G dye laser produced lower laser threshold, which was explained for PM567 and RH6G dyes using an analytical model in our earlier work\(^\text{22}\). The slightly lower peak (1-2%) lasing efficiency of PM597 dye was observed with respect to PM567 and PM580 dyes, using both the solvents. However, it is insignificant compared to the larger non-radiative rate (4.9 to 5.9 times) and smaller radiative rate (1.1 to 1.3 times) of PM597 dye in comparison to PM567 and PM580 dyes (Tables 3.4 and 3.5). This observation of high laser efficiency of PM597 dye, despite poor photo-physical properties, indicates that other mechanisms might be responsible.

The dye laser efficiency depends essentially on the net gain that depends, in turn, on radiative rate, non-radiative rate, ground and excited-state absorption (GSA, ESA) cross-sections at the laser wavelengths, as well as, on cavity losses and dynamic changes caused by time dependent saturation of the gain. PM597 dye has shown a larger Stokes shift in fluorescence. Additionally, lower concentration of dye PM597 (0.28 mM) was used in this study, on account of its higher absorption cross-section at the pump wavelength (532 nm). These two factors facilitated to reduce GSA at lasing wavelengths of PM597, and in turn, the cavity losses for dye laser photons. A low ESA at laser wavelengths may also facilitate to obtain the high efficiency of PM597 dye. Rhodamine dyes are known\(^\text{39}\) to have significant ESA at the relevant laser wavelengths. It may be noted that, our recent studies on high-repetition-rate (~6.3 kHz) dye lasers in oscillator-amplifier configuration, using ethanol solutions of PM567 and PM597 dyes with additive DABCO, carried out separately by pumping with green component (510 nm) of copper vapor lasers show excellent photo-stability and efficiency of these PM dyes.

3.3.2.3 Effect of lasing wavelength on photostability:

The tuning curve of PM567 dye laser was obtained in the spectral region 540 nm to 575 nm with a peak laser efficiency of 35% at 550 nm (Figure 3.7).
Studies on photophysics and laser properties of important pyrromethene dyes

Figure 3.7: Tuning curve of PM567 dye laser. Ethanol solution of dye was excited by 532 nm of a pulsed Nd-YAG laser with pump energy of 4.4 mJ. The dye laser (DL) was operated in Littrow configuration.

Figure 3.8: Decrease in normalized laser efficiency of PM567 dye at wavelengths 550nm (peak), 543 nm (blue-edge) and 571 nm (red-edge) during (a) lasing (L) and (b) non-lasing with cuvette window lasing conditions (WL). The dye laser efficiency was observed to decrease at a faster rate in non-lasing with window lasing (WL) than that in presence of lasing (L) condition.

While monitoring dye laser power at maxima (550 nm) as a function of cumulative pump energy, the dye laser efficiency was observed to decrease at a faster rate in non-lasing with window lasing (WL) than that in presence of lasing (L) condition. Similar observations
were also noticed at two other periphery wavelengths 543 nm and 571 nm of the dye tuning curve, which are illustrated in Figure 3.8. This may be understood as follows. The visible excitation of PM567 dye is a single electron promoted transition from $S_0$ to $S_1$ state. In case of non-lasing condition, the residence time of PM567 dye molecules at the excited singlet state ($S_1$) was predominantly depending upon spontaneous emission lifetime ($\tau_s$) of the dye, which was measured as 6.27 ns in ethanol. However, during lasing process the rate of emission (R) at the emission wavelength from the excited $S_1$ state is the sum of the rates of stimulated ($R_{st}$) and spontaneous ($R_s$) emissions. Therefore, under steady-state approximation

$$R = R_{st} + R_s$$

or,

$$R = \sigma_e(\nu) I_\nu + 1/\tau_s$$

Thus, the average time that each excited dye molecule resides in the $S_1$ state during lasing condition may be expressed as

$$T = 1/R = \tau_s/[\sigma_e(\nu) I_\nu \tau_s + 1]$$

where $I_\nu$ and $\sigma_e(\nu)$ are intra-cavity signal intensity and stimulated emission cross-section of dye at laser frequency ($\nu$), respectively. Hence, for given values of $\sigma_e$ and $\tau_s$, an increase of the signal intensity $I_\nu$ reduces average residence time $T$ of dye molecules in the excited $S_1$ state on account of a higher stimulated emission rate. Thus, residence time of dye molecules at the excited state is much shorter during stimulated emission (lasing process) than that at spontaneous emission (non-lasing) condition.

Photo-degradation studies reported 22-25, 29-31 so far suggested that degradation of dyes was largely initiated by reactions involving dye molecules in the excited singlet and triplet states. Triplet state population of dye molecules were generally small on account of slow rate of singlet ($S_1$) to triplet ($T_1$) intersystem crossing, when excited by such low-repetition-rate (10 Hz), short pulse width (6 ns) laser. Consequently, population and residence time of dye molecules in $S_1$ state largely determined the effective photo-degradation rate of such dye lasers, whether in presence or in absence of laser action. Thus, shorter residence time of dye molecules in the excited $S_1$ state during lasing process facilitated observation of higher photo-stability of dye in comparison to non-lasing condition.
Figure 3.9: Decrease in normalized laser efficiency of PM567 dye under lasing condition when dye laser was operated at (a) 550 nm, (b) 543 nm, and (c) 571 nm.

To understand the effect of emission wavelength on the rate of dye photo-stability, the dye laser was tuned to a set wavelength and gradual decrease in dye laser efficiency was monitored as a function of cumulative pump exposure time with similar pump energy. The decrease in dye laser efficiency was found to be slowest at peak wavelength 550 nm followed by 543 nm and 571 nm, which are illustrated in Figure 3.9. These results also pointed to the influence of stimulated emission cross-section ($\sigma_e$) at different emission wavelengths and hence different stimulated emission rate of dye on residence time of dye molecules at the excited $S_1$ state and thus its photo-stability. The dye gain profile at Figure 3.7 showed that the stimulated emission rate of PM567 dye increased in the same order 550 nm > 543 nm > 571 nm. This was also supported by observations of faster evolution of dye laser pulse at peak wavelength (550 nm), followed by at 543 nm and 571 nm, which is illustrated in Figure 3.10. The faster drop in dye laser efficiency under non-lasing with window lasing (WL) in comparison to lasing (L) condition was also confirmed by measuring rate of photo-stability of dye at these three wavelengths, calculated by measuring concentrations of dye solutions before and after known irradiation period (Table 3.6) with similar pump energy. Increase in the rate of photo-stability of dye laser, upon lasing (L) to non-lasing with window lasing (WL) condition, was observed to be higher at peak wavelength (550 nm) in comparison to other two extreme wavelengths, in otherwise identical pump condition.
Studies on photophysics and laser properties of important pyrromethene dyes

Figure 3.10: Temporal evolution of the PM567 dye laser pulses are shown at different wavelengths (A) 550 nm (peak), (B) 543 nm (blue-edge), and (C) 571 nm (red-edge) of the tuning curve. The different laser pulses are indicated as (a) Pump laser, 2nd harmonic of Nd-YAG (b) initial dye laser pulse and (c) dye laser pulse after a known period of exposure.

Also, it was found to be higher at shorter (543 nm) than that at longer (571 nm) wavelength of the dye gain curve. The photo-stability rate ($Q_{PS}^{NL}$) of dye under total non-lasing condition (NL) was found to be the lowest (Table 3.6). To get an insight of the process these experimental results were theoretically simulated using a time dependent rate equation model.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Exposure Period (min)</th>
<th>Lasing Condition (L)</th>
<th>Non-lasing with window lasing condition (WL)</th>
<th>Non-lasing condition (NL)$^#$</th>
<th>Increase in $Q_{PS}$ with lasing ($Q_{PS}^{L}/Q_{PS}^{NL}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>543</td>
<td>180</td>
<td>4.3</td>
<td>3.7</td>
<td>4.1</td>
<td>3.8</td>
</tr>
<tr>
<td>550</td>
<td>240</td>
<td>4.2</td>
<td>4.1</td>
<td>3.6</td>
<td>3.8</td>
</tr>
<tr>
<td>571</td>
<td>120</td>
<td>5.2</td>
<td>3.3</td>
<td>4.8</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 3.6: Photo-stability ($Q_{PS}$) of PM567 dye solution at various conditions, pumped by 532 nm of a pulsed Nd-YAG laser. Concentration of dye solutions for exposure was 0.77 mM with initial O.D value of 6.4 at $\lambda_{abs}^{max}$, measured using 1 mm cell. $^\#$ For Non-lasing condition ($Q_{PS}^{NL}$) the exposure period was 120 min.
3.4. Conclusions:

The superior laser performance of Pyrromethene (PM) dyes in comparison to Rhodamine (RH) dyes is clearly demonstrated. Comparative photo-physical, laser properties and molecular structures of three important Pyrromethene dyes, PM567, PM580 and PM597 show that all the three PM dyes are highly efficient. Particularly, PM597 dye produced wider tuning range and lasing in longer wavelength region, in spite of very low fluorescence yield and high non-radiative decay rate. A likely reason for observing higher efficiency with PM dyes in comparison to RH6G dyes, are low GSA and presumably, low ESA of the PM dyes at the laser wavelengths. ESA, followed by rapid non-radiative relaxation to the excited laser level, acts as an intracavity photon loss mechanism that significantly reduces dye laser efficiency. DFT/TDDFT calculations on ground and excited (S1) states of all three PM dyes show large distortion from the planarity of the two-pyrrole rings in the excited state of PM597 molecule. This, in turn, produced large Stokes shift and presumably, low loss of laser photons due to GSA and ESA processes and thus make PM597 an efficient laser dye when used in laser cavity. Further studies to quantify GSA and ESA losses at pump and laser wavelengths of the dyes are required to understand the complex interplay between their molecular structures, photo-physical properties and laser performances. The longest wavelength absorption maximum of three PM dyes calculated by the DFT/TDDFT formalism are close to the experimental values, and could adequately reproduce the spectral shift induced by the different alkyl substitutions at C2 and C6 carbon positions of dyes along the long molecular axis. We plan to apply this theoretical combination (B3LYP/TDDFT + PCM solvent model) for calculating emission and other photo-physical properties of PM dyes for its utilization in designing new PM dye molecules having desired photo-physical properties.

Putting a step ahead to achieve a long service life of narrow band dye laser operation we observed improvement in photo-stability of PM567 dye laser, while it was operated at the peak over edge wavelengths of its tuning curve and was compared with theoretically calculated trends obtained following a rate equation based theoretical approach. Two factors that critically affected the decrease in laser efficiency with time were the stimulated emission cross-section at the laser wavelength and the decay time of the resonator cavity, essentially intra-cavity losses. The largest effect of enhanced stimulated emission rate on
improving dye photo-stability was observed at the maximum of the tuning curve i.e. for the laser when operated at the peak of its tuning range. Consequently, effect of stimulated emission rate improving the photo-stability of the lasing dye at different emission wavelengths and thus enhancing the operation life time of the system was most prominent in this case. Thus, it can be inferred that the maximum photo-degradation rate occurred when stimulated emission rate was the weakest during evolution of lasing in the oscillator. Hence, stability of dye is expected to be higher when operated in an amplifier mode with higher stimulated emission rates.

3.5. References:

Studies on photophysics and laser properties of important pyrromethene dyes


