CHAPTER-2

RATIONAL DESIGN AND SYNTHESIS OF SOME PHOTOSTABLE BODIPY LASER DYES
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2.1. Preamble

As discussed in the previous chapter (1.6.1) improvement of the photochemical stability of the Bodipy dyes is a central theme in dye laser research for their commercial applications. It is well established the photodegradation of the Bodipy dyes is primarily mediated by their reaction with singlet oxygen ($^1$O$_2$), generated in situ from the excited states of the dye molecules.\textsuperscript{38b,42a,h,43c,56b} The methods adopted to enhance the lasing operating lifetimes of these dyes, such as the use of deoxygenated dye solutions\textsuperscript{43c} or the addition of a high concentration (ca. 100 mm) of $^1$O$_2$ quenchers, such as Tin770, TBP,\textsuperscript{56b} or DABCO,\textsuperscript{38b,42a} are practically non-viable for the large scale operations, where large amounts (several L) of dye solutions are used. Also, high concentrations of the $^1$O$_2$ quenchers reduce the laser efficiency by quenching the dye fluorescence significantly.

It was anticipated that a systematic variation in the substitution pattern of the Bodipy dyes might provide a photostable laser dye with better spectral and lasing properties. In this regard, several efforts by structural modification such as alteration of the pyrrole rings-alkyl substituents or incorporation of different substituents at C-8 and/or C-2 + C-6 positions of the pyrromethene moiety have been attempted. But their long term photostability in liquid dye lasers has neither been clearly established nor rationalized.\textsuperscript{42b,56b} The most stable Bodipy dye, PM650 (with a C-8 CN substitution instead of the Me group of PM567, 21), reported so far is unsuitable for lasing due to its low fluorescence yield.\textsuperscript{42b} Previously incorporation of an electron-rich aryl substituent at the C-8 (meso-) position improved the photostability of the dyes without compromising their lasing efficiency.\textsuperscript{56a} For example, the photostability of the meso-(2,4,6-trimethoxyphenyl)-substituted congener (54a, Figure 2.1.1) was twice that of 21.\textsuperscript{56a} The substituent prevented photochemical degradation by reducing the generation of $^1$O$_2$ as well as the
reaction probability of the dye with $^1\text{O}_2$, but had no electronic interaction with the Bodipy chromophore.

The boron centre in the Bodipy core offers another option for substitution with no electronic effect on the dye core because the changes in the $\pi$-electron density on the fluorine atoms in the $S_0$ and $S_1$ states are very low.$^{56c}$ The substitution at the boron centre has been used to increase Stokes’ shift,$^{28d,29}$ solubility and chemical stability of the Bodipy dyes.$^{58}$ However, the lasing performance of the B-substituted Bodipy dyes has not been tested so far. Presently, two different approaches viz. substitution of the F atoms at the B-centre with an oxygenated alkyl group as such, and in combination with incorporation of a bulky group at the meso-position were adopted to improve the photo-stability. To this end, in this study, two B-substituted Bodipy dyes (54b and 54c, Scheme 2.2.1.1) were synthesized, and examined for their photophysical and lasing properties, as well as their photochemical stabilities. The results were rationalized by analyzing their redox potentials (using cyclic voltammetry, CV), and triplet state life times and absorption spectra (by pulse radiolysis) as well as quantum chemical calculations.
2.2. Studies on the B-Substituted Bodipy Dyes

2.2.1. Synthesis

The low solubility of the Bodipy dyes restricts their use especially in polar solvents like methanol, ethanol and water. Previously, laser experiments on different B-aryl- and B-alkyl-substituted Bodipy dyes could not be performed from this laboratory because of the poor solubility of the dyes in these solvents. Hence, in this study the 2,5-dioxaoct-7-yn moiety was judiciously chosen for substituting the B-fluoro atoms of the Bodipy dyes 21 and 54a.56a Such a replacement was envisaged to improve the solubility of the resultant dyes in polar solvents. Previously, the Bodipy dye 54a was found to be an efficient and photochemically stable laser dye.56 Hence, it was envisaged that a new dye possessing the structural combinations of the dyes 21 and 54a, namely substitutions at the meso position and the boron centre, might have improved lasing performance.

For the formulation of boron substituted dyes first, the alkyne diethylene glycol derivative 55 was synthesized by a base-catalyzed alkylation of the glycol with propargyl bromide (Scheme 2.2.1.1).58 Appearance of a triplet at $\delta$ 2.41 for the alkyne proton and a doublet at $\delta$ 4.18 for the propargylic protons confirmed the propargylation (Figures 2.2.1.1 a-b). This
was converted to the corresponding Grignard reagent by reaction with EtMgBr and subsequently reacted with 21 to afford the new dye 54b. The $^1$H NMR of compound 54b showed characteristic peak of propargylic $\text{OCH}_2$ protons at $\delta$ 4.16. Appearance of a singlet at $\delta$ -13.4 in place of the triplets at $\delta$ 3.87 for the BF$_2$ group in the $^{11}$B NMR spectrum confirmed its formation (Figures 2.2.1.2 a–b and 2.2.1.3).

**Scheme 2.2.1.1 Synthesis of the compounds 54b and 54c**
Figure 2.2.1.1 The NMR spectrum of 55 (a) $^1$H NMR, (b) $^{13}$C NMR.
Figure 2.2.1.2 The NMR spectrum of 54b (a) $^1$H NMR, (b) $^{13}$C NMR.
The synthesis of compound 54c started by nitrosation of ethyl acetoacetate at low temperature with NaNO₂/MeCO₂H followed by in situ tandem reduction of the resultant product with Zn-dust and condensation with acetyl acetone to furnish the pyrrole 56. Its alkaline hydrolysis under heating directly furnished the ketone 57. This was subjected to reduction with LiAlH₄ to furnish 58 via direct conversion of its CO functionality to the CH₂ moiety. A trifluoroacetic acid (TFA)-catalyzed condensation of the pyrrole derivative 58 with 2,4,6-trimethoxybenzaldehyde, followed by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation and subsequent reaction with BF₃·Et₂O furnished 54a.⁵⁶a All the intermediates and compound 54a were characterized from their known ¹H and ¹³C NMR spectra. Figures 2.2.1.4 a-b show the NMR patterns of 54a.

The dye 54c was obtained by nucleophilic substitution of the F atoms of 54a with the Grignard reagent prepared from 55 as above (Scheme 2.2.1.1). Formation of compound 54c was also confirmed from the disappearance of the ¹¹B NMR triplets at δ 3.87 (BF₂) and appearance of
a $^{11}$B NMR singlet at δ -13.2. Besides, the characteristic $^1$H and $^{13}$C NMR resonances due to the Bodipy core and –OCH$_2$/–OCH$_3$ appendages, the peaks for the alkyne–CH$_2$–O moieties at δ 4.19 in the $^1$H NMR and at δ 90.6 in $^{13}$C NMR were also observed (Figures 2.2.1.5 a-b).

Figure 2.2.1.4 The NMR spectrum of 54a (a) $^1$H NMR, (b) $^{13}$C NMR.
Figure 2.2.1.5 The NMR spectrum of 54c (a) $^1$H NMR, (b) $^{13}$C NMR.
2.2.2. Photophysical characteristics

The measured photophysical parameters (longest-wavelength absorption maxima ($\lambda_{\text{abs}}$), emission maxima ($\lambda_{\text{em}}$), fluorescence quantum yields ($\Phi_f$), fluorescent lifetimes ($\tau$), maximum molar absorptivities ($\varepsilon_{\text{max}}$) along with the calculated Stokes’ shifts ($\nu$) and the radiative ($k_r$) and non-radiative ($k_n$) decay constants of the dyes 54a–c relative to those of the dye 21 in EtOH solvent are presented in Table 2.2.2.1. The normalized absorption and emission spectra of the dyes in EtOH solvent are also shown in Figure 2.2.2.1 for comparison. All the compounds showed similar absorption spectra with features typical of the Bodipy dyes, such as strong $S_0\rightarrow S_1$ transitions with clear maxima ($\lambda_{\text{max}}$) between 510 and 530 along with vibronic transitions on the higher-energy side evident as a shoulder, and ill-defined, weak bands corresponding to the $S_0\rightarrow S_2$ transitions at about 420 nm.59 Each dye showed small fwhm that is characteristic of the
cyanine type of chromophores. The $S_0 \rightarrow S_1$ absorption band of the dye 54c was red shifted by 10 nm relative to that of the corresponding meso-methyl dye 54b.

Figure 2.2.2.1 Normalized absorption and fluorescence spectra of dyes 21 and 54a–c in EtOH.
Table 2.2.2.1: Photophysical parameters of the dyes 21 and 54a–c in EtOH

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{abs}}$ [a]</th>
<th>$\varepsilon_{\text{max}}$ [b]</th>
<th>$\lambda_{\text{em}}$ [c]</th>
<th>$V$</th>
<th>$\Phi_{\text{fl}}$ [d]</th>
<th>$\tau$ [e]</th>
<th>$k_r$ [f]</th>
<th>$k_{nr}$ [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>517</td>
<td>8.3</td>
<td>534</td>
<td>616.0</td>
<td>0.84 [h]</td>
<td>6.43</td>
<td>1.31</td>
<td>0.25</td>
</tr>
<tr>
<td>54a</td>
<td>528</td>
<td>10.4</td>
<td>537</td>
<td>317.4</td>
<td>0.85</td>
<td>6.98</td>
<td>1.22</td>
<td>0.21</td>
</tr>
<tr>
<td>54b</td>
<td>513</td>
<td>8.4</td>
<td>529</td>
<td>589.6</td>
<td>0.84</td>
<td>6.22</td>
<td>1.35</td>
<td>0.26</td>
</tr>
<tr>
<td>54c</td>
<td>523</td>
<td>9.4</td>
<td>533</td>
<td>358.7</td>
<td>0.81</td>
<td>6.61</td>
<td>1.22</td>
<td>0.29</td>
</tr>
</tbody>
</table>

[a] Error: ± 0.2 nm. [b] Extinction coefficients for the corresponding $\lambda_{\text{max}}$. [c] Error: ± 0.3 nm. [d] The fluorescence of all the dyes was measured at the excitation wavelength 490 nm. The fluorescence quantum yields of 54a–c are reported relative to that of 21 ($\Phi_{\text{fl}} = 0.84$). [e] Fluorescence lifetime. [f,g] Radiative and non-radiative decay rates.

The fluorescence spectra of the dyes were almost mirror images of the respective absorption spectra, with minimum energy loss. All the dyes were found to be highly fluorescent ($\Phi_{\text{fl}} > 0.8$) but the absorption and emission spectra of the compounds 54a and 54c were relatively sharper and stronger compared to that of the meso-methyl dyes 21 and 54b, reflecting a significantly higher polarizability of those dye chromophores due to the increased $\pi$ electron clouds. Also, the absorption and emission spectra of the B-substituted new dyes 54b and 54c showed a smaller blue shift (~5 nm) compared to the corresponding parent dyes 21 and 54a. The dye 54c had a higher $\varepsilon_{\text{max}}$, but smaller Stokes’ shift relative to those of 21 and 54b. The photophysical data clearly revealed that substitution of the F-atoms at the boron centre had insignificant effect on the spectral properties of the Bodipy chromophore. Overall, the photophysical properties of the two new Bodipy dyes 54b and 54c appear favorable for use as laser dyes.

2.2.3. Lasing characteristics
The narrow-band lasing data of all the Bodipy dyes in EtOH are presented in Table 2.2.3.1 and their lasing characteristics shown in Figures 2.2.3.1 and 2.2.3.2. The narrow-band lasing profiles of all the dyes followed an expected pattern, showing a maximum efficiency at a particular wavelength ($\lambda_L$), characteristic of the dye (Figure 2.2.3.1). The maximum lasing efficiency values ($\eta$) of the dyes 21 (21.8%) and 54b (20.4%) at their respective $\lambda_L$s (Table 2.2.3.1) revealed a marginal reduction on replacing the F-atoms at the boron atom with the 2,5-dioxaoct-7-yne moiety. The lasing efficiency of dye 54b in the highly viscous diethylene glycol dimethyl ether solvent was comparable to that in EtOH, when the chosen dye concentrations had similar optical density (O. D. = 1.2) at the pump wavelength (532 nm). This suggested that the torsional motion of the flexible 2,5-dioxaoct-7-yne moieties at the boron centre do not contribute to the non-radiative processes for energy dissipation. Thus, the marginal loss of the lasing efficiency of 54b compared to that of 21 may be due to its slightly higher triplet extinction coefficient (Table 2.2.7.1). The excited $S_1$–$S_n$ absorption process may also contribute to this, although the excited-state absorption cross-sections for the Bodipy derivatives are very low.\(^6\) It is noteworthy that the loss of the lasing efficiency on going from the dye 21 to 54b was more than compensated by incorporating the electron rich aryl substitution at the meso-position of the Bodipy chromphore. Thus, consistent with the expectation, the maximum lasing efficiency of the dye 54c (22.0%) was found to be even higher than that of 21 at their respective $\lambda_L$s (Table 2.2.3.1). The spatial profile of the lasing output for each dye was circular at the respective maximum lasing efficiency. This would ensure uniform propagation of the laser light over a longer distance, which is beneficial for different types of laser applications.
Table 2.2.3.1: Lasing characteristics of the Bodipy dyes 21 and 54a–c in EtOH

<table>
<thead>
<tr>
<th>Dye</th>
<th>( \lambda_L ) [nm]</th>
<th>( \eta^{[a]} ) [%]</th>
<th>( \eta_s ) [%]</th>
<th>GSA ( [10^{-18} \text{ cm}^2] ) at ( \lambda_L )</th>
<th>( \Phi_{pd} )</th>
<th>( \Phi_{pd}^{-1} ) of 54b and 54c /( \Phi_{pd}^{-1} ) of 21</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>552</td>
<td>21.8</td>
<td>24</td>
<td>5.1</td>
<td>6.0 ( \times 10^{-4} )</td>
<td>--</td>
</tr>
<tr>
<td>54b</td>
<td>552</td>
<td>20.4</td>
<td>21</td>
<td>1.1</td>
<td>2.8 ( \times 10^{-4} )</td>
<td>2.1</td>
</tr>
<tr>
<td>54c</td>
<td>546</td>
<td>22.0</td>
<td>30</td>
<td>10.0</td>
<td>2.1 ( \times 10^{-4} )</td>
<td>2.9</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Error: \( \pm 1.0\% \).

The comparative laser slope efficiencies (Figure 2.2.3.2) of the Bodipy dyes clearly demonstrated an enhanced laser performance of dye 54c compared to the dyes 21 and 54b, irrespective of the pump energy. The threshold pump energy values (L\(_T\)) of the dyes 54b (0.19 mJ) and 54c (0.26 mJ) are also much smaller than that of dye 21 (0.36 mJ). The laser tuning range of 54c was similar to those of 21 and 54b, but its \( \lambda_L \) (546 nm) was blue-shifted by 6 nm relative to those (552 nm) of 21 and 54b.

Despite these positive attributes, the maximum lasing efficiency of 54c was achieved at a higher O. D. (1.8) than that (O. D. 0.7) with the dyes 21 and 54b. This implied that a higher concentration of dye 54c is required for its optimum performance as a laser dye, and suggested higher ground state absorption (GSA) of 54c at the lasing wavelength that would reduce the laser photons. This was confirmed by the triplet states studies carried out by pulse radiolysis (PR) experiments. Since the results of PR studies were also important in explaining the relative photostabilities of the Bodipy dyes, these will be discussed later.
Figure 2.2.3.1 Narrow band lasing efficiencies of the Bodipy dyes 21, 54b and 54c in EtOH, determined by pumping at 532 nm radiation of a Q-switched pulsed Nd-YAG laser.

Figure 2.2.3.2 Comparative slope efficiencies of Bodipy dyes 21, 54b and 54c at their respective λ_{LS} in EtOH solutions, determined by pumping at 532 nm radiation of a Q-switched pulsed Nd-YAG laser.
2.2.4. Photostability characteristics

Initially, the quantum yields of photodegradation ($\Phi_{pd}$) of the dyes 21, 54b and 54c in air-equilibrated EtOH solutions were measured under non-lasing conditions. Consistent with the fact that the degradation of the dyes at the olefinic site would produce non-fluorescent products, the longest wavelength absorption bands ($S_0 \rightarrow S_1$) of the dye solutions did not show any shape change, but the peak heights were reduced after photoexposure. Analyses of the absorption intensities, from the peak area (Table 2.2.3.1, higher $\Phi_{pd}^{-1}$) clearly revealed impact of the substitutions at boron on the enhanced photostabilities of the new dyes in EtOH solution. The meso-(2,4,6-trimethoxyphenyl) substitution increased the photostability further, rendering dye 54c as the most photostable of the four dyes. The increased stabilities of the dyes 54b and 54c after irradiation at 532 nm for 4 h under non-lasing conditions were also confirmed by HPLC analyses (Table 2.2.4.1).

Table 2.2.4.1: Quantification of photodecomposition of Bodipy dyes 21, 54b and 54c.[a]

<table>
<thead>
<tr>
<th>Dye</th>
<th>% Photo-decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>85</td>
</tr>
<tr>
<td>54b</td>
<td>45</td>
</tr>
<tr>
<td>54c</td>
<td>35</td>
</tr>
</tbody>
</table>

[a] The individual dyes were irradiated under non-lasing conditions by the 532 nm output of a pulsed Nd:YAG laser for a period of 4 h. The extents of degradation were quantified from the integrated area of the respective HPLC chromatogram using a standard graph, prepared separately with the individual dyes. The values are mean of three independent similar experiments.
Figure 2.2.4.1 Normalized profiles of the lasing efficiencies of the Bodipy dyes 21, 54b and 54c as a function of irradiation time.

In separate experiments, the photostabilities of the dyes 21 and 54b and 54c under lasing conditions were evaluated by assessing their respective lasing efficiencies in EtOH solution a function of irradiation time. A time-dependent decrease in the lasing efficiencies (Figure 2.2.4.1) was observed with all the dyes. However, the decrease was very rapid for 21 compared to that of 54b and 54c, confirming better photostabilities of the new B-substituted dyes even under lasing conditions. Typically after exposure for 4 h, the lasing efficiencies of 54b and 54c decreased by 21 and 15%, respectively, whereas that of 21 was reduced by 36% of its initial value. Overall, the comparative results of the lasing efficiencies and photostabilities of the Bodipy dyes (Figure 2.2.4.2) clearly showed the supremacy of the new B-substituted dyes, especially 54c over the commercial dye 21.
Given that the *in situ* generated $^1\text{O}_2$ is responsible for the photodegradation of the dyes, the higher stabilities of $54b$ and $54c$ may be due to their lower 1) reaction rates with $^1\text{O}_2$ and/or 2) $^1\text{O}_2$ generation capacities. Hence, these factors were investigated in comparison with dye $21$ and the results are discussed below.

### 2.2.5. Electrochemical characteristics

Cyclic voltammetric analysis of Bodipy dyes $21$, $54b$ and $54c$ showed a reversible peak in each case in the anodic portion of the cyclic voltammograms (Figure 2.2.5.1), which was assigned to one-electron oxidation of the Bodipy unit. The corresponding oxidation potentials ($E_{\text{ox}}$) reveal that the boron substitution has a negative effect on the oxidation potentials. Dye
54b \( (E_{\text{ox}} = 0.95 \, \text{V}) \) was more easily oxidised than 21 \( (E_{\text{ox}} = 1.02 \, \text{V}) \) by 70 mV and the presence of the electron-donating aryl group at the meso position further reduced the \( E_{\text{ox}} \) of dye 54c \( (E_{\text{ox}} = 0.83 \, \text{V}) \), making it more prone to oxidation than 54b by 120 mV. The above data suggest the trend in probability of oxidation of the dyes increases in the order 21 < 54b < 54c, which is opposite to that observed experimentally. Other factors, like the rate of reaction with \( ^1\text{O}_2 \) and the \( ^1\text{O}_2 \) generation capacity of the dyes might play a predominant role in the relative photostabilities of the dyes. To investigate these, we carried out theoretical calculations on the ground and excited states of the dyes as well as \( ^1\text{O}_2 \), and characterised the triplet states of the dyes by pulse radiolysis.

![Figure 2.2.5.1 Cyclic voltammograms of the Bodipy dyes 21, 54b and 54c in CH₂Cl₂ at room temperature.](image)

2.2.6. Theoretical interpretations

The ground-state \( (S_0) \) minimum-energy structures 21-R, 54b-R and 54c-R (Figure 2.2.6.1) of the Bodipy dyes 21, 54b and 54c, respectively, were optimised by carrying out DFT
calculations. These conformers were subsequently used to study the excited-state structures and properties of the dyes in the lowest singlet (S\textsubscript{1}) and triplet (T\textsubscript{1}) states. After characterising all the ground-state features, the reaction course of the dyes with \textsuperscript{1}O\textsubscript{2} was investigated by placing the \textsuperscript{1}O\textsubscript{2} in the proximity of the most vulnerable position, the C7'=C8 double bond, of each dye (Figure 2.2.6.1). The transition-state (TS) structures were identified as 21-TS, 54b-TS and 54c-TS, and the peroxides 21-P, 54b-P and 54c-P were identified as the reaction products obtained from 21, 54b and 54c, respectively (Figure 2.2.6.1). In all the reactions, the TSs are formed by partial cleavage of the C7'=C8 \pi bond and formation of the C7'=O2 bond as the initial events, as supported by the bond lengths (Table 2.2.6.1). With dye 21, the C8=C7' (1.41 Å) and O1O2 (1.21 Å) bond lengths increase to 1.53 and 1.41 Å, respectively, in the TS. The distance between C7' and O2 (1.46 Å) indicated formation of a σ bond between them. The C8 and O1 atoms are too far apart (2.64 Å) to form a stable bond, but gradually move closer for bond formation (bond length = 1.51 Å), furnishing the peroxide compound 21a-P. Charge density calculations further established the mechanism. According to the calculations, in the TS, the electron density at O1 is more than that at O2, whereas the electron density at C8 is less than that in 21a-R. This is consistent with the proposed mechanism (Figure 2.2.6.1). After the formation of the C8–O1 bond, O1 and O2 become electronically similar, as is evident from the charge densities on the two atoms. However, most importantly, the model suggests a much higher (more than two-fold) activation energy for the reaction between \textsuperscript{1}O\textsubscript{2} with 54b (5.86 kcal mol\textsuperscript{-1}) or 54c (5.35 kcalmol\textsuperscript{-1}) than for 21 (2.45 kcal mol\textsuperscript{-1}) (Figure 2.2.6.2). This would make dye 1a the most vulnerable to oxidation by singlet oxygen, which explains the observed trend in the photostabilities of the dyes: 21 << 54b ≈ 54c.
Figure 2.2.6.1 Reaction mechanism of the Bodipy dyes 21, 54b and 54c with $^1$O$_2$. 
Table 2.2.6.1: Changes of bond lengths and atomic charges during the reaction of the dye 21 with \(^1\text{O}_2\).

<table>
<thead>
<tr>
<th>Dye</th>
<th>Bond length (Å)</th>
<th>Atomic charge (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C8-O1)</td>
<td>(C7'-O2)</td>
</tr>
<tr>
<td>21-R</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>21-TS</td>
<td>2.64</td>
<td>1.46</td>
</tr>
<tr>
<td>21-P</td>
<td>1.51</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Figure 2.2.6.2 Change of potential energies during the reaction of the Bodipy dyes 21, 54b and 54c with \(^1\text{O}_2\).

2.2.7. Pulse radiolysis studies

The triplet states determine 1) the amount of \(^1\text{O}_2\) generated by the dyes through energy transfer to dissolved \(\text{O}_2\) and also 2) the reduction in the lasing efficiency by absorbing the lasing
photons. Hence, triplet-state studies can provide valuable information on the lasing characteristics and photostabilities of the Bodipy dyes. Triplet state spectroscopy and the energy-transfer processes of the dyes \textbf{21}, \textbf{54b} and \textbf{54c} were investigated by pulse radiolysis in benzene solutions. Radiolysis of benzene gives a high yield of the triplet state \((G = 4.2/100 \text{ eV})\) with an energy of 82 kcal mol\(^{-1}\), which can generate dye triplets by energy transfer. However, owing to the low lifetime \((\tau = 3 \text{ ns})\) of the benzene triplet, a high concentration of solute is required. This limitation can be overcome by using a triplet sensitizer such as biphenyl \((E_T = 65 \text{ kcal mol}^{-1})\) along with the solute. The triplet states of the laser dyes \textbf{21}, \textbf{54b} and \textbf{54c} in benzene solution were generated by pulse radiolysis in the presence of biphenyl. Under these conditions, biphenyl triplets are initially formed, which, in turn, transfer energy to generate the triplet states of the Bodipy dyes. The triplet states of the dyes show absorption at 550–750 nm. The spectra consist of a single peak with the \(\lambda_{\text{max}}\) at around 720 nm for \textbf{21} and \textbf{54b}, however, the \(\lambda_{\text{max}}\) (640 nm) of the triplet species of \textbf{54c} was blueshifted by 80 nm (Table 2.2.7.1). Thus, the T–T absorption spectrum of dye \textbf{54c} overlaps considerably with its fluorescence spectrum. This would increase the reabsorption loss of the lasing photons, which explains the requirement of dye \textbf{54c} to have a higher optical density for an equivalent lasing efficiency to that of dye \textbf{21}. The other noticeable feature of the spectra is the appearance of a bleaching signal (negative signal) immediately after the pulse. The bleaching signal obeys a first-order decay law (at low doses) at wavelengths at which light absorption by the ground state is much higher than the transient absorption. The triplet-state extinction coefficients at \(\lambda_{\text{max}}\) and the rate constants for energy transfer from the biphenyl triplet to the dye \((k_{\text{et}})\) and from the dye \((\textbf{21}, \textbf{54b} \text{ and } \textbf{54c})\) to \(^3\text{O}_2 \) \(k (^3\text{Dye} \rightarrow \text{O}_2)\) were calculated from experimental data and are presented in Table 2.2.7.1. Interestingly, the value of \(k (^3\text{Dye} \rightarrow \text{O}_2)\) decreases gradually from \textbf{21} to \textbf{54c}. The values of \(k (^3\text{Dye} \rightarrow \text{O}_2)\) for the dyes
54b and 54c are two- and four-fold less than that of 21. This suggests that relative to dye 21, dyes 54b and 54c generated two and four times less $^1$O$_2$. Thus, according to the $^1$O$_2$ generation capacity, the stabilities of the dyes would be as follows: $21 < 54b < 54c$. Taken together, the above data reveal that despite being more prone to oxidation, dyes 54b and 54c are more photostable than 21 due to their lower reaction rates with $^1$O$_2$ and lower $^1$O$_2$ generation capacity.

**Table 2.2.7.1:** Triplet state data of Bodipy dyes 21, 54b and 54c.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ (LM$^{-1}$cm$^{-1}$)</th>
<th>$k_{\text{et}}$ ($^3$B.P$\rightarrow$Dye) (LM$^{-1}$s$^{-1}$)</th>
<th>$k$ ($^3$Dye$\rightarrow$O$_2$) (LM$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>720</td>
<td>7880</td>
<td>$4.1 \times 10^9$</td>
<td>$1.9 \times 10^9$</td>
</tr>
<tr>
<td>54b</td>
<td>720</td>
<td>8020</td>
<td>$7.7 \times 10^9$</td>
<td>$1.0 \times 10^9$</td>
</tr>
<tr>
<td>54c</td>
<td>640</td>
<td>8900</td>
<td>$2.8 \times 10^9$</td>
<td>$0.5 \times 10^9$</td>
</tr>
</tbody>
</table>
2.3. Red-shifted BODIPY dyes

In this part, we aimed to design and synthesize a new series of dyes emitting in the red spectral region for lasing application. There are few red emitting fluorescent dyes are commercially available such as, Rhodamine dyes, Texas Red ($\lambda_{em} = 615$ nm), Alexa 594 ($\lambda_{em} = 617$ nm) and Alexa 663 ($\lambda_{em} = 647$ nm) etc. But a very few red emitting dyes are available from Bodipy class of fluorophores for lasing application. The research is aimed to shift emission of the dyes to the red region while keeping their suitable properties for lasing application. There are reports, to shift the emission band of green emitting dye to longer wavelengths by attaching electron-donating groups to the Bodipy core, by rigidifying the structure, and by extending the conjugation of the chromophore. But there are no any solid reports whether their fluorescence emission is of utility for the generation of laser emission. Also, these structural changes can lead to sometimes to molecules with undesired photo-physical properties. To this end, a new red shifted Bodipy dye was synthesized by incorporating a mono-styryl group at the C-3 position of the commercially available PM567 dye 21 followed by appending an ethyleneglycol moiety at the B-centre and their lasing action as well as photostability were studied. The structures of the dyes are shown in Figure 2.3.1.

Figure 2.3.1 Chemical structures of dyes 21, 60a and 61a.
2.3.1. Synthesis

The 3-styryl substituted dye 60a was synthesized from PM567 dye 21 via the Knoevenagel-type condensation with p-anisaldehyde in a mixture of toluene and piperidine (Scheme 2.3.1.1). Since, 3,5-methyl protons are equally prone for the reaction leading to formation of distyryl 60b derivative along with monostyryl derivative 60a. Therefore, to improve the yield of monostyryl product, the effects of reaction time and aldehyde concentrations were studied, and the results are shown in Table 2.3.1.1. Introduction of one styryl group at C-3 as in the dye 60a reduced its solubility in EtOH. Hence its lasing efficacy could not be studied. To overcome the problem, dye 61 was synthesized by subjecting the dye 60a for nucleophilic substitution of the fluorine atoms by reaction with the Grignard reagent prepared from 2,5-dioxaoct-7-yne (Scheme 2.3.1.2). The \(^1\)H NMR of compound 61a showed characteristic peak of propargylic protons at \(\delta\) 4.10 (Figure 2.3.1.1 a-b). The Bodipy dyes with such modifications at B-centre are known to be chemically more stable than the corresponding BF\(_2\) congeners.

Scheme 2.3.1.1 Synthesis of compounds 60a and 60b.
Table 2.3.1.1: Effect of concentration of corresponding aldehyde in the reaction

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Amount</th>
<th>Equivalent</th>
<th>Time</th>
<th>% Yield of 60a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 mg</td>
<td>1:1</td>
<td>3 h</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>100 mg</td>
<td>1:1</td>
<td>5 h</td>
<td>Degraded</td>
</tr>
<tr>
<td>3</td>
<td>100 mg</td>
<td>1:1.5</td>
<td>3 h</td>
<td>7.0</td>
</tr>
<tr>
<td>4</td>
<td>100 mg</td>
<td>1:1.8</td>
<td>3 h</td>
<td>14.7</td>
</tr>
<tr>
<td>5</td>
<td>100 mg</td>
<td>1:2</td>
<td>3 h</td>
<td>13.1</td>
</tr>
<tr>
<td>6</td>
<td>100 mg</td>
<td>1:2.5</td>
<td>3 h</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Scheme 2.3.1.2 Synthesis of compound 61
Figure 2.3.1.1 The NMR spectrum of 61 (a) $^1$H NMR, (b) $^{13}$C NMR.
2.3.2. Photophysical characteristics

The photophysical parameters of all the dyes are listed in Table 2.3.2.1. The shapes of the absorption spectra of the dyes 60a, 60b and 61a were similar to that of the commercially available dye 21 but the maxima were bathochromically shifted by 56.5 nm, 56 nm (for 60a and 61a respectively) and much higher 122 nm (for 60b) with extension of conjugation (Figure 2.3.2.1). The fluorescence spectra of the dyes were also identical throughout the series, and entirely consistent with fluorescence from the Bodipy subunit. The spectral shifts to higher wavelengths are a result of the extension of the delocalized electronic π-system to the styryl group. The non-conjugating effect of substitution at B-centre was evident from the similarities of the absorption and fluorescence spectra of the dyes 60a and 61. For compound 60a, 60b and 61 the strong absorption band centered near 350 nm can probably be assigned to the π→π* transition of the styryl moieties and the overlapped S0→S2 (π→π*) transition band of the Bodipy core.

![Normalized absorption spectra](a)
![Fluorescence spectra of dyes](b)

**Figure 2.3.2.1** (a) Normalized absorption spectra, (b) Fluorescence spectra of dyes 21, 60a, 60b and 61 in CH2Cl2.
Table 2.3.2.1: Photo-physical properties and photo-degradation data in ethanol

<table>
<thead>
<tr>
<th>Dye</th>
<th>λ_{abs} (nm)</th>
<th>λ_{fl} (nm)</th>
<th>ε_{max} (M⁻¹cm⁻¹)</th>
<th>Φ_{fl}[^a]</th>
<th>Δλ (nm)</th>
<th>Max. laser Efficiency η (%)</th>
<th>Degradation, (Q_{pd})</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>518.0</td>
<td>532</td>
<td>8.1 × 10⁴</td>
<td>0.84</td>
<td>14.0</td>
<td>47</td>
<td>6.8 × 10⁻⁴</td>
</tr>
<tr>
<td>60a</td>
<td>574.5</td>
<td>592</td>
<td>8.0 × 10⁴</td>
<td>0.66</td>
<td>17.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>60b</td>
<td>640.0</td>
<td>669</td>
<td>9.4 × 10⁴</td>
<td>0.60[^a]</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>61</td>
<td>574.0</td>
<td>590</td>
<td>9.5 × 10⁴</td>
<td>0.67</td>
<td>16.0</td>
<td>5</td>
<td>3.8 × 10⁻⁴</td>
</tr>
</tbody>
</table>

[^a]The fluorescence quantum yields of the dyes refer relative to that of the dye Rh101 (Φ_{fl} = 1 in EtOH).

Figure 2.3.2.3 Dyes 21, 60a and 60b (i) under visible light, (ii) under UV light.

2.3.3. Lasing characteristics and photo-degradation

The comparative lasing performances of dyes 21 and 61 were studied in ethanol. The lasing efficiencies of the dyes 21 and 61 were determined under an optically matched condition (O. D. = 0.24 at 532 nm with 1 mm cell). The lasing efficiency of dye 61 was significantly less than that of the dye 21. This was surprising, given the fluorescence quantum yield of 61 was not
appreciably less than that of 21. It is possible that the pumping wavelength (532 nm) was far from the $\lambda_{\text{max}}$ (574 nm) of 61 to excite the dye efficiently. This may reduce the lasing efficiency. However, it was gratifying to note that dye 61 was much photostable than the dye 21 (Figure 2.3.3.1).

![Figure 2.3.3.1](image)

**Figure 2.3.3.1** Comparative lasing efficiency and photostability of dyes 21 and 61.

2.4. Summary

We have designed and synthesised two different congeners of the commercially available Bodipy dye PM567 by substitution at the boron centre and/or at both the boron centre and the meso position. The two congeners show high lasing efficiencies and increased photostability. The better photostabilities of the boron-substituted dyes 54b and 54c have been rationalised by theoretical calculations and pulse radiolysis studies. The substitution at the boron centre reduced the $^1$O$_2$ generation capacity of the dyes and their reaction rates with $^1$O$_2$, enhancing the lifetimes of these dyes under lasing conditions. These findings will be helpful for the future development of photostable Bodipy dyes. The lasing efficiency of the new red shifted dye 61 was very less, although its photostability was better than that of the precursor dye.

2.5. Experimental
2.5.1. General details

Laser grade PM567 (Exciton), rhodamines 101 and 6G (Lambda Physik) were used without any further purification. Spectroscopic and chromatographic analyses revealed their purities to be >99%. All other chemicals and spectroscopic grade solvents were purchased from Aldrich, Merck or Sigma, and used without any further purification. The IR spectra were recorded as thin films with a JASCO Model A-202 FT-IR spectrophotometer. Unless otherwise mentioned, the 1H NMR (200 MHz) and 13C NMR (50 MHz) spectra were recorded in CDCl3 with a Bruker AC-200 instrument and the data are presented in terms of chemical shift in δ (ppm), coupling constant (J in Hz) and multiplicities. The mass spectra (70 eV) were recorded with a MD-80 Fission instrument. The electrochemical analysis was done in Autolab PGSTAT 302N instrument. CHN analyses were carried out using Thermo Finnigan Flash EA1112 series. The spectrophotometric analyses were carried out at 25 °C with a Jasco V-550 UV-vis spectrophotometer and a Jasco FP 6500 spectrofluorometer using quartz cells of 1 cm path length. All anhydrous reactions were carried out under Ar using freshly dried solvents. The column chromatography and thin layer chromatography (TLC) were performed using column grade silica gel (40-63 μm) and silica gel-coated aluminum plates with fluorescent indicator respectively.

2.5.2. Synthesis

4,7-Dioxaoct-1-yne (55). To a stirred suspension of NaH (0.288 g, 12.0 mmol) in THF (100 mL) was added ethyleneglycol monomethyl ether (0.760 g, 10.0 mmol) in THF (50 mL). After stirring the mixture for 3 h, propargyl bromide (1.19 g, 10.0 mmol) was added into it and the mixture stirred for another 12 h. The mixture was diluted with H2O (50 mL) and extracted with CH2Cl2 (50 mL). The organic layer was dried, concentrated, and the residue distilled (60 °C/ 30
mm) to furnish 55. Yield: 0.855 g (75%); colorless liquid; IR: 2925, 2175 cm\(^{-1}\); \(^1\)H NMR: \(\delta\) 2.41 (t, \(J = 2.4\) Hz, 1H), 3.38 (s, 3H), 3.52-3.59 (m, 2H), 3.64-3.73 (m, 2H), 4.18 (d, \(J = 2.4\) Hz, 2H); \(^13\)C NMR: \(\delta\) 57.8, 58.3, 68.4, 71.1, 74.3, 79.2; EI-MS (m/z): 114 [M]\(^+\). Anal. Calcd. for C\(_6\)H\(_{10}\)O\(_2\): C, 63.14; H, 8.83%. Found: C, 63.25; H, 8.79%.

**Ethyl 4-Acetyl-3,5-dimethyl-1H-pyrrrole-2-carboxylate (56).** To a stirred cooled (0 °C) solution of ethyl acetoacetate (4.9 g, 0.038 mol) in acetic acid (10 mL) was added a cold solution of NaNO\(_2\) (2.8 g, 0.041 mol) in H\(_2\)O (10 mL). After stirring the mixture for 24 h at 25 °C, acetyl acetone (3.8 g, 0.038 mol) and zinc dust (5.3 g) were added, and the mixture was stirred at 60 °C for 1 h. The mixture was brought to room temperature and extracted with CHCl\(_3\) (3 × 10 mL) Concentration of the extract in vacuo followed by crystallization from CHCl\(_3\) gave 56. Yield: 6.35 g (80%); white solid; mp: 142 °C (lit.\(^{64}\) mp: 143-144 °C); IR: 3302, 1678, 1646 cm\(^{-1}\); \(^1\)H NMR: \(\delta\) 1.36 (t, \(J = 7.1\) Hz, 3H), 2.43 (s, 3H), 2.51 (s, 3H), 2.57 (s, 3H), 4.34 (q, \(J = 7.1\) Hz, 2H), 9.41 (broad s, 1H, NH); \(^13\)C NMR: \(\delta\) 12.5, 14.1, 14.6, 30.9, 60.2, 117.8, 123.1, 129.3, 138.9, 162.0, 195.4; MS (m/z): 209 [M]\(^+\).

**2,4-Dimethyl-3-acetyl-1H-pyrrole (57).** A mixture of 56 (3.0 g, 0.014 mol) and KOH (1.5 g, 0.027 mol) in ethylene glycol (10 mL) was heated at 160 °C for 4 h. After cooling, the mixture was extracted with CHCl\(_3\) (3 × 10 mL), and the extract was washed with H\(_2\)O (2 × 10 mL) and brine (1 × 5 mL) and dried. Removal of solvent gave pure 57. Yield: 1.86 g (97%); white solid; mp: 96 °C; IR: 3300, 1680 cm\(^{-1}\); \(^1\)H NMR: \(\delta\) 2.26 (s, 3H), 2.43 (s, 3H), 2.50 (s, 3H), 6.36 (s, 1H), 8.52 (broad s 1H, NH); \(^13\)C NMR: \(\delta\) 13.7, 15.2, 30.7, 115.0, 120.5, 120.7, 136.2, 195.9; MS (m/z): 137 [M]\(^+\). Anal. Calcd. for C\(_8\)H\(_{11}\)NO: C, 70.04; H, 8.08; N, 10.21%. Found: C, 70.10; H, 8.02; N, 10.17%.
2,4-Dimethyl-3-ethyl-1H-pyrrole (58). To a stirred suspension of LiAlH₄ (0.333 g, 8.76 mmol) in dry THF (20 mL) was added 57 (1.0 g, 7.30 mmol) in THF (10 mL). The mixture was refluxed for 4.5 h and brought to room temperature, and the excess hydride was decomposed with aqueous saturated Na₂SO₄. The mixture was extracted with CHCl₃ (2 × 10 mL), and the extract was concentrated in vacuo. The residue was subjected to column chromatography (neutral Al₂O₃, hexane-EtOAc) to furnish 58. Yield: 0.673 g (75%); brown liquid; IR: 3377, 1689, 1644 cm⁻¹; ¹H NMR: δ 1.23 (t, J = 7.4 Hz, 3H), 2.18 (s, 3H), 2.28 (s, 3H), 2.54 (q, J = 7.4 Hz, 2H), 6.48 (s, 1H), 7.51 (broad s, 1H, NH); ¹³C NMR: δ 10.1, 10.9, 15.5, 17.3, 112.8, 117.4, 120.1, 123.1; MS (m/z): 123 [M]⁺.

2,6-Diethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(2’,4’,6’-trimethoxyphenyl)-4-bora-3a,4a-diaza-s-indocene (54a). A mixture of 58 (0.450 g, 3.7 mmol), 2,4,6-trimethoxybenzaldehyde (0.363 g, 1.85 mmol) and TFA (0.012 g, 0.10 mmol) in CH₂Cl₂ (20 mL) was stirred at room temperature for 24 h. DDQ (0.420 mg, 1.85 mmol) was added to the resulting deep-red solution and stirring continued for 4 h. The mixture was treated with Et₃N (0.5 mL), stirred for another h, BF₃·Et₂O (0.762 mL, 4.6 mmol) was added in portions over 4 h and stirred at room temperature overnight. The resulting dark mixture was washed successively with aqueous saturated NaHCO₃ (2 × 10 mL), H₂O (2 × 10 mL) and brine (5 mL), and dried. Removal of the solvent in vacuo followed by column chromatography of the residue (silica gel, hexane/EtOAc) furnished 54a. Yield: 0.19 g (22%); orange needles (hexane); mp: 157 °C; ¹H NMR: δ 1.05 (t, J = 7.6 Hz, 6H), 1.57 (s, 6H), 2.15 (s, 6H), 2.37 (q, 4H, J = 7.6 Hz), 2.48 (s, 6H), 3.76 (s, 3H), 6.08 (s, 1H), 6.93 (s, 1H); ¹³C NMR: δ 9.4, 12.5, 14.6, 17.3, 55.3, 92.9, 118.5, 131.6, 132.4, 136.6, 154.7,161.5; EI-MS: (m/z): 470 [M]⁺.
General procedure of synthesis of 54b, 54c and 61a. To a solution of 2,5-dioxaoctyne (4.08 mM) in THF (10 mL) was added EtMgBr (4.08 mM, 4.08 mL 1 M in Et₂O). The mixture was heated at 60 °C for 2 h followed by addition of the suitable Bodipy dye (0.82 mM) and further for 18 h at 60 °C. The resulted dark mixture was thoroughly washed successively with aqueous saturated NH₄Cl (1 X 20 mL), H₂O (1 X 20 mL), brine (1 X 20 mL) and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, hexane-EtOAc) furnished the respective B-substituted dyes. 54b. Yield: 62%; red squares (benzene/hexane); mp: 154 °C; IR: 2927, 2167 cm⁻¹; ¹H NMR: δ 1.00 (t, J = 7.6 Hz, 6H), 2.18 (s, 6H), 2.35 (q, J = 7.6 Hz, 4H), 2.59 (s, 3H), 2.66 (s, 6H), 3.34 (s, 6H), 3.49 - 3.55 (m, 4H), 3.59 - 3.65 (m, 4H) 4.16 (s, 4H); ¹³C NMR: δ 13.8, 14.5, 14.9, 17.1, 17.3, 58.8, 59.5, 68.4, 71.6, 90.7, 129.9, 132.3, 134.2, 139.5, 151.5; ¹¹B NMR (96 MHz): δ -13.4 (s); EI-MS (m/z): 506 [M]+; Anal. Calcd. for C₃₀H₄₃BN₂O₄: C, 71.14; H, 8.56; N, 5.53%. Found: C, 71.11; H, 8.52; N, 5.51%.

54c. Yield: 70%; red needle (CH₂Cl₂/cyclohexane); mp: 149 °C; IR: 2948, 2835, 1632 cm⁻¹; ¹H NMR: δ 1.01 (t, J = 7.5 Hz, 6H), 1.44 (s, 6H), 2.30 (q, J = 7.5 Hz, 4H), 2.68 (s, 6H), 3.5 (s, 6H), 3.49-3.56 (m, 4H), 3.62-3.68 (m, 10H), 3.87 (s, 3H), 4.19 (s, 4H) 6.19 (s, 2H); ¹³C NMR: δ 10.8, 13.8, 14.7, 17.3, 55.3, 55.8, 58.8, 59.7, 68.3, 71.7, 90.6, 106.2, 129.4, 131.6, 135.3, 152.2, 158.1, 162.1; ¹¹B NMR (96 MHz): δ -13.2 (s); EI-MS (m/z): 659 [M+1]+, 658 [M]+; Anal. Calcd. for C₃₈H₅₁BN₂O₇: C, 69.30; H, 7.80; N, 4.25%. Found: C, 70.00; H, 7.65; N, 4.44%.

61a. Yield: 60%; mp: 225 °C; IR: 2959, 1636 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.05 (t, J = 7.5 Hz, 3H), 1.22 (t, J = 7.5 Hz, 3H), 2.35-2.43 (m, 8H), 2.64-2.70 (m, 8H), 3.25-3.28 (m, 10H), 3.49-3.50 (m, 4H), 3.83 (s, 3H), 4.10 (s, 4H), 6.91-6.97 (m, 3H), 7.54 (d, J = 7.0 Hz, 2H), 8.10 (d, J = 16.5 Hz, 1H); ¹³C NMR (125 MHz): δ 14.2, 14.5, 14.7, 14.9, 17.3, 17.4, 18.5, 55.3, 58.7, 59.4, 68.1, 71.6, 90.8, 114.2, 120.7, 128.1, 130.8, 131.0, 131.3, 131.4, 132.2, 133.3, 134.6, 135.1,
138.9, 146.9, 153.4, 159.6. EI-MS (m/z): 625 [M+1]+; Anal. Calcd. for C_{26}H_{31}BF_{2}N_{2}O: C, 73.01; H, 7.92; N, 4.29%. Found: C, 73.07; H, 7.91; N, 4.48%.

2,6-Diethyl-4,4-difluoro-3-p-methoxystyryl-1,5,7,8-tetramethyl-4-bora-3a,4a-diaza-s-indene 60a. A mixture of 21 (1.0 mmol), p-anisaldehyde (1.1 mmol), glacial acetic acid (0.5 mL) and piperidine (3.5 mL) was refluxed in toluene (35 mL) with simultaneous azeotropic removal of water formed during the reaction. After the consumption of 21, H_{2}O (100 mL) was added into the reaction mixture, which was extracted with CHCl_{3} (3 × 20 mL). The organic layer was dried and concentrated in vacuo to give a residue, which on column chromatography (silica gel, hexane-EtOAc) furnished the respective styryl derivatives. pink cuboidals (CH_{2}Cl_{2}/cyclohexane). Yield: 13%; mp: 235 °C; IR: 2961, 1635, 1606, 1478 cm\(^{-1}\); \(^1\)H NMR: δ 1.05 (t, \(J = 7.5\) Hz, 3H), 1.20 (t, \(J = 7.5\) Hz, 3H), 2.32-2.47 (m, 8H), 2.53 (s, 3H), 2.57-2.74 (m, 8H), 3.83 (s, 3H), 6.87 (d, \(J = 8.7\) Hz, 2H), 7.07 (d, \(J = 16.8\) Hz, 1H), 7.48-7.62 (m, 3H); \(^{13}\)C NMR: δ 12.5, 14.0, 14.4, 14.7, 17.1, 18.3, 55.3, 114.2, 118.1, 128.4, 130.5, 132.4, 132.7, 133.1, 134.2, 136.5, 136.7, 138.8, 148.0, 153.2, 159.9. EI-MS (m/z): 437 [M+1]+, 417 [M-19]+. Anal. Calcd. for C_{26}H_{31}BF_{2}N_{2}O: C, 71.57; H, 7.16; N, 6.42%. Found: C, 71.10; H, 7.21; N, 6.18%.

2.5.3. Photophysical studies

The absorption and emission spectra of the dyes (~10\(^{-6}\) M) in various solvents were measured using a 1 cm quartz cuvette. The fluorescence quantum yields (\(\Phi_f\)) of the dyes 21, 54b and 54c relative to that of the reference dye 21 and the molar extinction coefficients (\(\epsilon_{max}\)) were determined in ethanol. The excited state (\(S_1\)) lifetimes of 21, 54b and 54c in ethanol were determined by the time-resolved fluorescence measurements, carried out using an LED based time-correlated single-photon-counting (TCSPC) spectrometer. The fluorescence decays were measured with a 490 nm LED (1 MHz) excitation source and a TBX4 detection module coupled
with a special Hamamatsu PMT. The instrument response function was 1.2 ns at fwhm. Following deconvolution analysis of the fluorescence decays, the time resolution of the present setup was ~50 ps. All the measurements were carried out at ambient room temperature (298 ± 1 K) using a microprocessor based temperature controller.

2.5.4. Lasing studies

The lasing studies of the dyes 21, 54b and 54c in ethanol were carried out using a constructed narrow band dye laser set up, transversely pumped by the second harmonic (at 532 nm) output of a Q-switched pulsed Nd:YAG laser at a repetition rate of 10 Hz with ~7 mJ pulse energy and 5-7 ns FWHM pulses. All laser data for the dyes in ethanol were measured using the indigenously made dye laser set up, schematically shown in Figure 2.4.1. The dye laser was constructed in grazing-incidence-grating configuration (with a grating of 2400 lines/mm), with a 25X 4-prisms pre-expander. The pump and dye laser powers were measured by the same power meter (OPHIR). The tuning curve of each dye solution was obtained by scanning the wavelength of dye laser through the gain profile of dyes and measuring the average pump and dye laser powers with the power meter. For determining the pump laser threshold ($L_T$) and slope efficiency ($\eta_s$) of each dye solution, the input pump energy was varied and the lasing output of each of the dyes at peak of respective gain curves was plotted as a function of pump energy.
2.5.5. Photostability studies

The quantum yield of photo-degradation ($\Phi_{pd}$) of the dyes is defined as probability of decomposition of the dye molecules by the absorbed pump photons. Photostability is inverse of the $\Phi_{pd}$ value. A known quantity of dye solution (2 mL) in a dye laser cuvette was exposed to pump energy of 4 mJ at 532 nm. The concentration of the dye solution was chosen such that the pump beam was totally absorbed within the dye solution in the cuvette during the excitation of 4 h. The solution was stirred constantly by a teflon-coated magnetic stirrer to avoid local heating. The number of photo-degraded dye molecules in the exposed volume of the dye solutions was quantitatively estimated from the absorbances at the respective $\lambda_{max}$ before and after photo-exposure for a set period of time. The reflection loss of pump beam on incident surfaces of dye cell was considered in calculating the absorbed cumulative pump photons. The extent of photo-degradation of the dye molecules was also determined by HPLC analyses.
2.5.6. Electrochemical studies

Cyclic voltammetry was done at 25 °C in deoxygenated CH$_2$Cl$_2$ containing Bu$_4$NClO$_4$ (TBAP) (0.1 M), and a solute concentration of 1-5 × 10$^{-3}$ M. The redox potentials were standardized with ferrocene (Fc) as the internal reference, and converted to saturated Calomel electrode (SCE) assuming that $E_{1/2}$ (Fc/Fc$^+$) = +0.38 V SCE. The error in half-wave potentials was ±10 mV. All waves were monoelectronic.

2.5.7. Pulse radiolysis

The triplet states studies of the dyes were carried out using the nanosecond pulse radiolysis technique.$^{65a}$ The dose absorbed per pulse was determined using an aerated 0.01 mol dm$^{-3}$ KSCN solution, taking the value of $G\varepsilon$ of (SCN)$_2$ as 2.59 × 10$^{-4}$ m$^2$ J$^{-1}$ at 475 nm.$^{65b}$ The dose was kept at 15 Gray per pulse. The dye solutions (1 × 10$^{-4}$ M) were prepared in spectroscopy grade benzene and purged with high purity N$_2$ to remove dissolved oxygen. The pulse radiolysis experiments were carried out using biphenyl (5 × 10$^{-3}$ M) as the triplet sensitizer. Formation of the dye triplets and their extinction coefficients were determined by energy transfer from the biphenyl triplet to the dyes. For studying the reactions of the dyes at triplet state with O$_2$, the experiments were carried using a high concentration of the dye (5 × 10$^{-3}$ M) in the absence of a triplet sensitizer. The decay of the triplet states of the dyes were monitored at their respective $\lambda_{max}$. Concentration of oxygen in solutions was adjusted by mixing appropriate volumes of nitrogen purged dye solutions in benzene with aerated dye solutions in benzene.

2.5.8. Theoretical calculations

The minimum-energy structures of all the Bodipy dyes (21, 54b and 54c) in the ground state ($S_0$) were established by applying a correlated hybrid density function (B3LYP) using a Dunningtype correlation consistent atomic basis set (cc-pVDZ) for all the atoms. The quasi-
Newton–Raphson-based algorithm was used to carry out geometry optimisation on each of the dyes with various possible conformers as the initial structures. Time-dependent density functional theory (TDDFT) was used with the B3LYP density function to study the excited- state structures and the properties of the dyes in the lowest singlet ($S_1$) and triplet states ($T_1$) with the most stable ground-state ($S_0$) conformer as the starting structure. The same atomic basis set, cc-pVDZ, was used for all the excited-state calculations. The minimum-energy structures of these dyes taking the effect of medium into account were calculated by using the PCM model of macroscopic solvation. Excited state calculations were also carried out on these solvent-modified geometries to determine the effect of solvent by using TDDFT (B3LYP) coupled with the PCM solvent model. The minimum-energy structures of the transition states (TS) and products for the reaction of $^1$O$_2$ and the dyes were calculated by applying the GAMESS suite of program for ab initio electronic structure calculations. The calculated TS structures were confirmed by Hessian calculations having only one imaginary frequency. Single point energy calculations were also carried out with long-range corrections added to B3LYP functional adopting a smaller size basis function (6-31G**) and the reaction barriers were observed to be in the same order.