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Structure and solvent-induced tuning of laser property and photostability of a boradiazaindacene (BODIPY) dye

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Graphical Abstract:



Enhancement of photostability of BODIPY dye based on changes in its structure in conjunction with solvent polarity.

Highlights:

- Highly efficient B-substituted BODIPY laser dye was synthesized.
- The BODIPY dye was 34 times more photostable in non-polar 1,4-dioxane solvents than in polar ethanol.
- High photostability of the BODIPY dye in non-polar solvent is due to its lower reactivity with ¹O₂.
- Rationalization of the results by theoretical calculations.
- Besides alkyl substitution at the B-atom, use of less polar 1,4-dioxane medium in combination, can increase the photostability of the BODIPY dye immensely without compromising its laser property.
- The photostability of the new BODIPY dye in 1,4-dioxane is comparable to that of Rhodamine 6G in ethanol.

ABSTRACT. Boradiazaindacene (BODIPY) class of laser dyes are highly efficient but degrade rapidly in alcohol solution during lasing action, progressively reducing output power. Photodegradation of these dyes is mainly due to reaction with the *in situ* generated singlet oxygen ($^{1}O_{2}$). With the aim to increase the lasing lifetimes of these dyes, we have designed and synthesized a new congener of the widely used BODIPY dye (PM567) by substitution at its B-centre. The new dye was highly fluorescent, and showed comparable lasing efficiency, but better photostability relative to PM567 in both polar (ethanol) and non-polar (1,4-dioxane) solvents, when excited by 2nd harmonic (532 nm) of a pulsed Nd-YAG laser. More interestingly, the lasing efficiency and photostabilities of the dyes were much better in 1,4dioxane than in ethanol. The relative photostabilities of the dyes were rationalized by absorption spectroscopic analyses of their triplet state properties in the respective solvents in the presence of a $^{1}O_{2}$ generator or quencher as an additive, pulse radiolysis studies and quantum chemical calculations.

1. Introduction

Boradiazaindacene [1-6] (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, BODIPY) dyes are extensively used as efficient active media for solid as well as liquid dye lasers due to their high fluorescence yields, intense absorption profiles in the green spectral region and low triplet-triplet extinction coefficients over the fluorescence region [7-13]. However, their application in high-average-power liquid dye lasers remains limited due to the rapid photochemical degradation of the dyes. For example, after irradiation at 532 nm for 4 h under non-lasing conditions, the lasing efficiency of the commercially available BODIPY dye, PM567 (1a) was reduced by 36% of its initial value [12]. The degradation is primarily mediated by their reaction with singlet oxygen (¹O₂), generated *in situ* during photochemical excitation of these dyes [11,14,15]. Different strategies to enhance the laser photostability of these dyes such as the use of deoxygenated dye solutions [16] and/or addition of high concentrations of ¹O₂ quenchers (TIN770, TBP or DABCO) [14,17,18], are inconvenient for large-scale dye laser operation. Moreover, their laser efficiency may also reduce due to fluorescence quenching. The photophysics and photostability of dye solutions generally depend on the dye structure as well as nature of the chosen solvent, because of the specific and non-specific solute-solvent interactions. Change of chemical structures of the BODIPY

dyes has significant effect on their photostabilities [13]. We showed earlier that the PM567 analogues, synthesized by substitution at the (i) *meso* position, **1b**; (ii) boron centre, **2a**; and/or (iii) both the sites, **2b** were markedly more photostable than **1a** [11,12]. Earlier, solvent-dependent change in the photostability of BODIPY dye **1a** has been reported even under air saturated conditions [19]. More recently, our group has designed photostable BODIPYs based on changes in their structures as well as solvent polarities [20-22]. To this end, new BODIPYs with an N-ethyl carbazole at the *meso* position and Et or Bn groups at the 2- and 6-positions *viz*. **3a** and **3b** have shown good photostabilities in heptane solvent, albeit with reduced lasing efficiencies [20]. In a related study, the BODIPYs **4a-c**, possessing 2,6dibenzyl groups showed improved photostabilities in 1,4-dioxane solvent, irrespective of the *meso*-substituents (Me, Ph or H) [21]. The chemical structures of the BODIPY dyes **1-4** are shown in Figure 1. However, syntheses of the BODIPYs **3** and **4** required multiple steps that may impede their practical laser applications.

Earlier, we showed that the B-substituted dye **2a** has a significantly enhanced photostability than its BF₂-precursor, **1a** in polar ethanol ($\varepsilon = 24.5$ @ 25 °C) solvent [12]. Mechanistic investigation *via* a transition state (TS) model suggested higher activation energy for the reaction between ¹O₂ with **2a** than that of **1a**. This made dye **2a** less vulnerable to oxidation by singlet oxygen than **1a**. The TS model also suggested that the activation energy for the reaction between ¹O₂ with **2a** can be increased further by lowering the solvent polarity which may make the B-substituted dye more robust against oxidation. Thus, the aim of the present study was to evaluate the lasing efficiency and photostability of the B-substituted dye in a less polar solvent. In general, for laser studies, solvents such as water, methanol, ethanol and dioxane are best suited for their high specific heat capacity, low refractive index (RI) temperature coefficient, low viscosity, low inflammability, high thermal diffusibility etc. Amongst these, dioxane is the least polar ($\varepsilon = 2.25$ @ 25 °C) solvent. But unfortunately,

solubility of the dye **2a** in 1,4-dioxane was not enough to perform lasing experiments. Hence, we synthesized a new B-substituted BODIPY dye **5** (Scheme 1) and examined its photophysical and lasing properties in polar ethanol with respect to its precursor dye **1a**. Then we evaluated the photophysical and lasing properties of **1a** and **5** in 1,4-dioxane solvent to determine the relative utility of these dye-solvent combinations for high average-power dye lasers.



Figure 1. Chemical structures of PM567 and some BODIPYs developed by our group.

2. Materials and methods

2.1 Experimental Details

All the chemicals and spectroscopic grade solvents were purchased from Aldrich, Merck or Sigma and used without any further purification. The synthesis of the dye **5a** was carried out as shown in Scheme 1, and the experimental details are provided as the Supporting information. The spectrophotometry was carried out at 25 °C with a Jasco V-550 UV-vis spectrophotometer and Jasco FP 6500 spectrofluorometer respectively. The fluorescence spectra were corrected.

2.2 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 (Φ_{fl}) of the dye **5** relative to that of the reference dye **1a** [11] and the molar extinction coefficients (ϵ_{max}) were determined in ethanol and 1,4-dioxane. The following equation was used to determine the relative fluorescence quantum yield:

 $\phi(\mathbf{X}) = (\mathbf{A}_{\mathbf{S}}/\mathbf{A}_{\mathbf{X}})(\mathbf{F}_{\mathbf{X}}/\mathbf{F}_{\mathbf{S}})(\mathbf{n}_{\mathbf{X}}/\mathbf{n}_{\mathbf{S}})^2\phi(\mathbf{S})$

where A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve and n is the refractive index of the solvents (at 25 °C) used in the measurements. The subscripts S and X represent standard and unknown, respectively. The excited state (S₁) lifetimes of **1a** and **5** in ethanol and 1,4-dioxane 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 \pm 1 K) using a microprocessor based temperature controller.

2.3 Lasing studies

The lasing studies of the dyes **1a** and **5** in ethanol and 1,4-dioxane 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 ~6 mJ pulse energy and 5-7 ns FWHM pulses. A schematic of the dye laser set up is shown in Figure S1a. The dye laser was set up in grazing incidence grating (GIG) configuration (with a grating of 2400 lines/mm) with 25 X 4-prisms pre-expander. The pump and dye laser powers were measured by the same power meter (OPHIR).

The dye solutions of **1a** and **5** (O. D. = 7 at 532 nm, 1 cm cell) in ethanol and 1,4dioxane were used to determine the narrow band lasing efficiency. The tuning curves of the dye solutions were obtained by scanning the wavelength of dye laser through the gain profiles of the dyes, and measuring the dye laser wavelength by a wavemeter, average pump and dye laser powers with a power meter. For determining the pump laser threshold (L_T), the output power of dye lasers, while tuning the dye laser wavelength at the peak of the respective gain curves, were measured as a function of input pump power at 532 nm.

2.4 Photostability studies

The 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 period (4 h). The solution was constantly stirred with a teflon-coated magnetic stirrer to avoid local heating. The number of photodegraded dye molecules in the exposed volume of the dye solutions was estimated from the absorbances (at the corresponding λ_{abs}) before and after photoexposure for a set period of time. The reflection loss of the pump beam on incident surfaces of the dye cell was taken into consideration while calculating the absorbed cumulative pump photons.

2.5 Electrochemical studies

Cyclic voltammetry (CV) study was carried out at 25 °C in deoxygenated CH_2Cl_2 containing TBAP (0.1 M), and a solute concentration of $1-5 \times 10^{-3}$ M. The redox potentials were standardized with ferrocene (Fc) as the internal reference, and converted to 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. CV scans were recorded at a scan rate of 50 mVs⁻¹. All the electrochemical experiments were carried out using Potentiostat Autolab 100. A glassy carbon

electrode, cleaned by ultra-sonication and dried by dry air flow, was used as the working electrode.

2.6 Studies of relative ${}^{1}O_{2}$ generation of the dyes

A solution of 1,3-diphenylisobenzofuran (DPBF) (50 μ M) and dye **1a** or **5** (5 μ M each) in aerated ethanol (3 mL) taken in a 10 mm quartz cell was irradiated with a filtered visible light source (estimated intensity of 20 W/m² and wavelength >495 nm) at room temperature for 15 min. The 40 W lamp was operated using a voltage stabilized power supply to obtain steady power. The absorbances of the solutions were measured at λ_{abs} of DPBF (412 nm) at an interval of 2 min. The relative ¹O₂ generation capacities of dyes **1a** and **5** in ethanol were determined by measuring the time-dependent reduction of the DPBF absorbance. Solutions of DPBF (negative control) and of the dyes **1a** and **5** (positive controls) were also irradiated. Similar experiments were carried out in 1,4-dioxane to measure the relative ¹O₂ generation capacities of the dyes **1a** and **5** in 1,4-dioxane.

2.7 Pulse radiolysis

The triplet states studies of the dyes were carried out using the nanosecond pulse radiolysis technique [23]. The dose absorbed per pulse was determined using an aerated 0.01 mol dm⁻³ KSCN solution, taking (G. ϵ) of (SCN)₂⁻ as 2.59 × 10⁻⁴ m² J⁻¹ at 475 nm [24]. The dose was kept at 20 Gray per pulse. The dye solutions (1 × 10⁻⁴ mol dm⁻³) were prepared in spectroscopy grade 1,4-dioxane/benzene (9:1) and purged with high purity N₂ to remove dissolved oxygen. The pulse radiolysis experiments were carried out using 4,4,- dimethylbiphenyl (DMBP) (5 × 10⁻³ mol dm⁻³) as the triplet sensitizer. Formation of the dye triplets and their extinction coefficients were determined by energy transfer from the DMBP triplet to the dyes. For studying the reactions of the dyes at triplet state with O₂, the experiments were carried using a high concentration of the dye (3 × 10⁻³ mol dm⁻³) without any triplet sensitizer. The decays of the triplet states of the dyes were monitored at their

respective λ_{max} . Concentration of oxygen in solutions was adjusted by mixing appropriate volumes of nitrogen purged dye solutions in 1,4-dioxane/benzene (9:1) with aerated dye solutions in 1,4-dioxane/benzene (9:1).

2.8 Studies of ${}^{1}O_{2}$ reactivity with dyes

An aerated ethanol solution (3 mL) of methylene blue (MB) (10 μ M) and dye **1a** or **5** (each, 10 μ M) in 10 mm quartz cells was irradiated at 7.5 W/m² of filtered light source of wavelength > 590 nm at room temperature for 1.5 h. A 590 nm cut off filter was used during irradiation to ensure that the light was absorbed by the photosensitizer, MB only. Absorption at λ_{abs} of dye **1a** (518 nm) and λ_{abs} of dye **5** (515 nm) were measured at various fixed intervals (15 min.). Relative reactivities of the dyes **1a** and **5** with ${}^{1}O_{2}$ in ethanol were determined by measuring the reduction in absorbance of the respective dyes at their λ_{abs} over time. Irradiation of MB solution in the absence of dyes as a negative control and solution of dye **1a** and **5** in 1,4-dioxane/ethanol (1:4) to measure relative ${}^{1}O_{2}$ generation capacities of dye **1a** and **5** in 1,4-dioxane/ethanol (1:4). The experiments could not be done in 1,4-dioxane due to poor solubility of MB.

2.9 Theoretical calculations

The minimum energy structures in the ground (S₀) state of all BODIPY dyes (**5**) was established by applying a correlated hybrid density function (B3LYP), using 6-31G* basis sets for all the atoms. The Quasi Newton-Raphson based algorithm was used to carry out geometry optimization for each of these dyes with various possible conformers as the initial structures. The minimum energy structures of transition states (TS) and products for the reaction of ${}^{1}O_{2}$ and the dyes were calculated by applying the GAMESS suite of *ab initio* electronic structure program. TS structure was confirmed by Hessian calculation having only one imaginary frequency.

3. Results and discussion

3.1 Design and synthesis

For the present work, we designed the new dye **5** with a propargyl alcohol appendage at the B-centre. The appendage was chosen to keep a balance between the hydrophobicity and hydrophilicity of the dye to ensure its solubility in both ethanol and 1,4-dioxane for the lasing studies. Moreover, the electronic excitation energy of ${}^{1}O_{2}$ is comparable with the energy associated with the high frequency vibrations of C-H and O-H bonds. This energy matching may lead to an electronic-to-vibrational energy transfer between ${}^{1}O_{2}$ and the dye to increase the ${}^{1}O_{2}$ quenching rate ($k_{\Delta Q}$) [25]. Hence it was hypothesized that the extra C-H and especially the two O-H bonds of the dye **5** may assist physical quenching of ${}^{1}O_{2}$ and reduce the lifetime (τ^{Δ}) of ${}^{1}O_{2}$ in both the solvents. This appeared to be particularly crucial in 1,4-dioxane, as τ^{Δ} (27.0 µs) of ${}^{1}O_{2}$ in 1,4-dioxane is almost 3 times to that (9.7 µs) in ethanol [25,26].



Scheme 1. Synthesis of dye **5**. a) DHP, PPTS, CH₂Cl₂, 25 °C, 12 h. b) EtMgBr, THF, 50 °C, 2 h, **1a**, 24 h. c) PTS, MeOH/H₂O (9:1), 25 °C, 10 h.

For the synthesis (Scheme 1), the hydroxyl group of propargyl alcohol (**6**) was tetrahydropyranylated by a pyridinium *para*-toluenesulphonate (PPTS)-catalyzed reaction with 2,3-dihydropyran (DHP) to obtain **7**. The Grignard reagent, prepared from **7** was subsequently coupled with the dye **1a** to obtain the dye **8** [27]. Finally, its

depyranylation with *para*-toluenesulphonic acid (PTS) in aqueous MeOH furnished the dye **5**.

3.2 Photophysical properties

The photophysical properties of the dyes **1a** and **5** in ethanol and 1,4-dioxane were evaluated at room temperature (25 °C). The measured photophysical parameters (longest wavelength absorption maximum (λ_{abs}), emission maximum (λ_{em}), fluorescence quantum yield (Φ_{fl}), maximum molar absorptivity (ϵ_{max}) and fluorescence lifetime (τ_F)) and the calculated Stokes shift (ν), radiative (k_r) and non-radiative (k_{nr}) decay rates of the dye **5** relative to those of dye **1a** in both the solvents are presented in Table 1. The normalized (to keep the spectral heights similar for the individual) absorption and emission spectra of dyes **1a** and **5** in ethanol (Figure 2) and 1,4-dioxane (Figure S7) were similar, each showing a strong S0 \rightarrow S1 absorption band at about 520 nm, typical of the BODIPY dyes [11,12,28-31]. This indicated that the energy of the S1 states of **1a** and **5** are similar in these solvents. Both the dyes were highly fluorescent ($\Phi_{fl} > 0.78$). The λ_{abs} and λ_{em} of **5** were blue shifted by 3 nm than that of **1a** in both the solvents. Also, the λ_{em} values of **1a** and **5** were red shifted by 2 nm in 1,4dioxane than in ethanol. Thus, the Stokes shifts of the dyes were marginally more in 1,4-dioxane than in ethanol.

According to Strickler-Berg equation, the absorption coefficient (ε_{max}) and the radiative rate (k_r) are approximately proportional to each other. However, in the present studies, while the ε_{max} values for the dyes **1a** and **5** were found to decrease on changing the solvent from EtOH to 1,4-dioxane, their respective k_r values increased. This may be due to the specific interaction (hydrogen bonding) of solvent (ethanol) with the dye molecules. Similar observations in protic and aprotic solvents with dye **1a** and other BODIPY dyes have been reported previously [32-34].

Table 1. Photophysical properties of the BODIPY dyes **1a** and **5** in ethanol and 1,4-dioxane solvent at 25 °C.

Dye	Solvent	$\lambda_{abs}{}^{[a]}$	$\epsilon_{max}^{[b]}$	$\lambda_{em}^{[c]}$	ν	$\Phi_{fl}{}^{[d]}$	$\tau_{F}^{[e]}$	kr	k _{nr}
		[nm]	$[10^4 M^{-1} cm^{-1}]$	[nm]	[cm ⁻¹]		[ns]	(10^8 s^{-1})	(10^8 s^{-1})
	Ethanol	518.0	7.1	533.0	543.3	0.84 ^[f]	6.48	1.30	0.25
1a	1,4-dioxane	518.0	6.2	535.0	613.4	0.89	6.52	1.36	0.17
	Ethanol	515.0	8.6	530.0	549.6	0.78	6.77	1.15	0.32
5	1,4-dioxane	515.0	6.7	532.0	620.5	0.89	7.18	1.24	0.15

[a] Error: ± 0.2 nm. [b] Extinction coefficients at respective λ_{max} . [c] Error: ± 0.3 nm. [d] Error: ± 0.04 . The fluorescence of the dyes **1a** and **5** were measured at the excitation wavelength 505 nm. The fluorescence quantum yield of **5** is relative to that of **1a**, reported earlier [11]. [e] Error: ± 0.05 ns. [f] This data is taken from ref. [11].



Figure 2. Normalized absorption (bold lines) and emission (dotted lines) spectra of the dyes 1a (blue)and 5 (black) in ethanol.

The respective ε_{max} values of dye **5** in the chosen solvents were higher than that of dye **1a**. Interestingly, the Φ_{fl} values of both the dyes were similar in 1,4-dioxane, and more than those in ethanol. These data clearly revealed that substitution of the Fgroups at the B-atom with the propargyl alcohol appendage had little effect on the optical properties of the BODIPY chromophore [12]. Taken together, the photophysical properties of the dyes **1a** and **5** in the chosen solvents appeared favorable for their use as green wavelength (CVL- 511 nm or 2nd Harmonic of Nd:YAG – 532 nm)-pumped laser dyes. More importantly, superior lasing performances of **1a** and **5** were anticipated in 1,4-dioxane because of their better optical properties in it.

3.3 Lasing characteristics

For the laser experiments, the dye concentration needs to be optimized so that the pump beam (80-90% intensity) will be almost uniformly absorbed within the dye solution in the dye cell. Additionally, the spatial profile of the dye laser output should be approximately circular *i. e.*, divergence of the dye laser beam is similar in both horizontal and vertical

directions. If the solution is too dilute, then majority of the pump beam will mostly escape interaction with the dye solution. On the other hand, if it is too concentrated, then the pump beam will be absorbed by the dyes at the glass surface only. In that case, due to local heating of the dye solution, scattering of the laser beam will be increased, decreasing the laser output.

Presently, the absorption and emission spectra of **1a** and **5** showed substantial overlap, implying the existence of some homo-FRET that may lead to concentration-dependent nonradiative decay, reducing the fluoroscence quantum and laser efficiency. In the present studies, the optimum concentration of **1a** and **5** for the narrow-band lasing studies were first determined by the broad band lasing experiments. For this, the concentration-dependent broad band lasing efficiencies (η) of the respective dyes in ethanol solution were first determined, keeping other parameters, including cavity alignment unchanged. The concentrationdependent lasing efficiencies of the dyes followed an expected pattern, initially increasing with the dye concentration to reach a maximum before decreasing again (Figure S1b). The narrow band lasing studies were subsequently carried out at the concentrations where the respective dyes showed maximum η values. For each dye, the same concentration was used for both ethanol and 1,4-dioxane solutions.

The narrow band lasing characteristics of the BODIPY dyes **1a** and **5** in ethanol and 1,4-dioxane are shown in Table 2 and Figure 3. The narrow band lasing profiles of the dyes in both the solvents followed an expected pattern, showing a maximum efficiency at particular wavelengths (λ_L), characteristic of the dyes. Consistent with the observed photophysical properties, the laser tuning ranges and λ_L values of **1a** and **5** were similar in both ethanol and 1,4-dioxane. The maximum lasing efficiency values (η) of the dyes **1a** (15.3% in ethanol, 17.1% in 1,4-dioxane) and **5** (11.8% in ethanol, 15.3% in 1,4-dioxane) at the respective λ_L (Table 2) revealed insignificant reduction in the laser efficiency due to substitution at the B-centre. The threshold pump energy (L_T)

values (Table 2, column 6) of **1a** and **5** were larger in 1,4-dioxane than in ethanol. However, the L_T values of **5** were lesser than that of **1a** in the respective solvents. Despite this, both the dyes showed higher narrow band dye lasing (DL) efficiencies in 1,4-dioxane than in ethanol. This is in accordance with their larger radiative and smaller non-radiative decay rates in 1,4-dioxane (Table 1). The excited-state absorption (ESA, S₁–S_n and T₁-T_n processes) may also contribute to this, although the ESA cross-sections for the BODIPY derivatives are very low [35-37].

Table	Table 2. Lasing properties of the BODIPY dyes 1a and 5 in ethanol and 1,4-dioxane. Pump								
laser:	laser: 2 nd harmonic of Nd:YAG at 532 nm.								
Dye	Solvent	$\lambda_L^{[a]}$	Tuning range	$\eta^{[b]}$	$L_T[mJ]$	GSA			
		[nm]	[nm]	[%]		$[10^{\text{-18}}\text{cm}^2]$ at λ_L			
	Ethanol	553.8	541-583	15.3	0.29	1.34			
1a	1,4-dioxane	555.8	540-584	17.1	0.61	1.36			
	Ethanol	554.0	541-581	11.8	0.28	1.45			
5	1,4-dioxane	554.0	540-580	15.3	0.49	1.06			

[a] Error: ± 0.2 nm. [b] Error: ± 1.0 %



Figure 3. Narrow band dye laser (DL) efficiency of **1a** and **5** in ethanol and 1,4-dioxane, determined by pumping with 532 nm radiation of a Q-switched pulsed (10 Hz) Nd:YAG laser.

Next, the ground-state absorption (GSA) of both the dyes in the chosen solvents at the respective λ_L values were determined by absorption spectroscopy. The GSA cross-section (1.06) of dye **5** in 1,4-dioxane was much lower than that (1.45) in ethanol, as well as those (1.34 and 1.36 respectively) of dye **1a** in these solvents. Thus, the loss of laser photons with dye **5** would be less in 1,4-dioxane due to lower GSA. Nevertheless, its DL efficiency was slightly less than that of **1a**. This may be because various other factors such as effective stimulated emission cross-section, the cavity losses and dynamic changes caused by time-dependent saturation of the gain contribute to the net gain, hence, the DL efficiency. *3.4 Photostability*

The photostabilities (Φ_{pd}^{-1}) of the dyes **1a** and **5** were studied in air-equilibrated ethanol and 1,4-dioxane under non-lasing conditions by measuring the photodegradation quantum yields (Φ_{pd}) . Photo-cleavage of the dyes would take place at the olefinic site to produce smaller molecules that do not absorb visible light. Hence, no change in the λ_{max}

values and/ or additional peaks were seen in the absorption spectra of the photo-exposed dyes [11]. But, the photo-degradation was evident from the reduced peak heights of their longest wavelength absorption bands ($S_0 \rightarrow S_1$).

Dye	Solvent	$\Phi_{pd}{}^{[a]}$	Φ_{pd} -1 $_{dye}$ 5 /	Φ_{pd} -1 _{dioxane} /	$\Phi_{pdDABCO}^{[a]}$	Φ_{pd} -1 _{DABCO} /
			$\Phi_{pd}{}^{-1}$ dye 1a	$\Phi_{pd}{}^{-1}$ ethanol		Φ_{pd} -1
1a	Ethanol	6.7 x 10 ⁻⁴	-	-	1.5 x 10 ⁻⁴	4.5
	1,4-dioxane	3.1 x 10 ⁻⁵	-	21.6	1.5 x 10 ⁻⁵	2.1
5	Ethanol	3.2 x 10 ⁻⁴	2.1	-	1.4 x 10 ⁻⁴	2.3
	1,4-dioxane	9.4 x 10 ⁻⁶	3.3	34.0	8.1 x 10 ⁻⁶	1.2

[a] Error: ± 1 %.

Our results revealed that dye **5** was 2.1 fold more photostable than **1a** in ethanol (Table 3, column 4) which is comparable with the photostability of **2a** in ethanol [12]. But in 1,4-dioxane, the photostability of dye **5** was further increased (3.3 fold) compared to **1a** (Table 3, column 4) and was comparable to that of the established photostable laser dye, rhodamine 6G ($\Phi_{pd} = 1.8 \times 10^{-6}$) [38] in ethanol. Most importantly the dye **5** solution in dioxane was more photostable than that of our earlier developed dye **2a** in ethanol solution. Overall, the present data clearly established that substitutions of the F- atoms with the propargyl alcohol moieties at the B centre improved the photostability of the BODIPY, irrespective of the solvent used. We also showed that the solvent nature had a prominent role in the photostability of the BODIPY dyes. The dyes **1a** and **5** were 21.6 and 34.0 fold more photostable in 1,4-dioxane than in ethanol (Table 3, column 5). The results are surprising, given that ¹O₂

has a significantly higher lifetime in 1,4-dioxane than in ethanol. Interestingly, the effect of solvent polarity on stability enhancement was more predominant with dye **5** compared to dye **1a**.

Addition of the ${}^{1}O_{2}$ quencher, DABCO improved photostabilities of the dyes **1a** and **5** in both the solvents (Table 3, column 6), confirming that the generated ${}^{1}O_{2}$ is responsible for the dye degradation. It was noticed that photostability enhancement by the same molar concentration of DABCO (50 times to dye) was almost half in case of **5** than with **1a** in both the solvents (Table 3, column 7). Also, the effect of DABCO was more pronounced in ethanol than in 1,4-dioxane for both the dyes. Indeed DABCO has an insignificant effect on the photostability of **5** in 1,4-dioxane. Taken together, these data clearly indicated that ${}^{1}O_{2}$ generation capacity and/or reactivity with ${}^{1}O_{2}$ of (i) dye **5** are less than that of dye **1a** and (ii) both the dyes are less in 1,4-dioxane than in ethanol. These aspects were further investigated by a series of experiments as described below.

3.4 Cyclic voltammetry (CV)

The CV technique is conveniently used to assess the electrochemical properties such as the number of electrons per molecule oxidized or reduced, the diffusion coefficient, redox potential etc. of an analyte in solution. It involves a time-dependent increase of the working electrode potential at a specific rate to reach a set value, followed by reversing the sweep to the initial potential. In the present experiments, the potentials were scanned in the window of 0 to 1.6 V, the current was measured continuously during the potential scan, and plotted against the applied potentials to generate the current-voltage curves as shown in Figure 4. The relative oxidation potentials (E_{ox}) of the dyes **1a** and **5** and the effect of solvent polarity on the E_{ox} values were investigated by recording their CVs in highly polar acetonitrile (ACN) and less

polar dichloromethane (DCM). Each of the dyes showed a reversible peak in the anodic portion of the CVs (Figure 4), which was assigned to one electron oxidation of the BODIPY unit [39]. Substitution at the B-centre had a negative effect on the oxidation potential. Thus, compared to **1a**, dye **5** was more easily oxidizable by 70 mV and 60 mV in DCM and ACN, respectively (Table 4). Thus, the trend in oxidation probability of dyes in the chosen solvents was **1a** < **5**, which is opposite to the observed rate of their photodegradation (Φ_{pd} values, Table 3).



Figure 4. Cyclic voltammograms of the BODIPY dyes **1a** and **5** in DCM and ACN at room temperature.

Table 4. Electrochemical properties of 1a and 5 in DCM and ACN. ^[a]						
Dyes	Solvent	$E_{\rm ox}$ [V]	$E_{\text{ox}, \text{ DCM}}$ - $E_{\text{ox}, \text{ ACN}} [\text{mV}]$			
1a	DCM	1.00	20			
	ACN	0.98				

DCM	0.93	10
ACN	0.92	

5

[a] The E_{ox} values were determined by CV at a solute concentration of $1-5 \times 10^{-3}$ M in deoxygenated solvents containing TBAP (0.1 M), at 25 °C. The E_{ox} values were standardized with ferrocene (Fc) as the internal reference and converted to 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.

Nevertheless, decrease in the solvent polarity had a positive effect on the E_{ox} values of the dyes. The dyes **1a** and **5** were less oxidizable in DCM than in ACN by 20 mV and 10 mV, respectively (Table 4). Thus, both the dyes would be more resistant to oxidation in non-polar solvents than in polar ethanol, as observed experimentally. But the CV results could not explain the higher photostability of dye **5** than dye **1a**, and the much higher stability of both the dyes in 1,4-dioxane. Hence, we measured the relative ¹O₂ generation rates of both the dyes as well as their reactivity with ¹O₂, and rationalized the results by triplet state studies using pulse radiolysis and theoretical calculations of the ground and excited states of the dyes as well as of ¹O₂. These are sequentially discussed below.



Figure 5. Change in absorption spectra of DPBF (50 μ M) in 1,4-dioxane during dyesensitized photooxidation in presence of dye **1a** (5 μ M): (a) 0 min; (b) 15 min. A stabilized 40 W tungsten lamp, with a cutoff filter allowing exposure >495 nm was used for photoirradiation.

3.5 Relative ${}^{1}O_{2}$ generation by **1a** and **5**

The ${}^{1}O_{2}$ generation capacities of the dyes **1a** and **5** were determined by monitoring the dye-sensitized photooxidation of 1,3-diphenylisobenzofuran (DPBF) [40-42]. For this, the ethanol and 1,4-dioxane solutions of DPBF and 1a or 5 were irradiated over a time period of 900 s, using a stablized tungsten lamp with a wavelength cut off filter >495 nm. Under these conditions, only the BODIPY dyes were excited to generate ¹O₂, which would primarily react with DPBF because the reaction rate of ¹O₂ is significantly higher with DPBF than the BODIPY dyes [43,44], and also, DPBF was taken at 50 times higher molar concentration in comparison to the BODIPY dyes. Therefore, the absorption bands of the dyes 1a and 5 remained unchanged, but the absorption peaks of DPBF decreased gradually (Figure 5 and Figures S9-S11). The plots of the time-dependent DPBF consumption in the presence of the photoexcited dyes 1a and 5 in ethanol and 1,4-dioxane solutions are shown in Figure 6. The relative rates of DPBF consumption, obtained from the slopes of the plots corresponded to the efficiency of ¹O₂ generation by the dyes. It was seen that both the dyes generated ${}^{1}O_{2}$ in ethanol and 1,4-dioxane significantly. The higher rate of consumption of DPBF in 1,4-dioxane may be due to longer life of ${}^{1}O_{2}$ in this solvent.

Possibly, the reactivity of ${}^{1}O_{2}$ with both the dyes is much less in 1,4-dioxane. Hence, when DABCO is added in dioxane, it merely quenches the unreacted ${}^{1}O_{2}$ without showing much effect on the photostabilities of the dyes, especially **5**. But in ethanol, the reactivity of ${}^{1}O_{2}$ with the dyes, especially **1a** is more. Hence, in this

solvent, besides directly quenching ${}^{1}O_{2}$, DABCO may also prevent its reaction with the dyes to improve their photostabilities in ethanol. Overall, the CV and DPBF photooxidation results could not explain the higher photostability of **5** over **1a** which may be explained as follows.





The triplet state studies of the BODIPY dyes are important as we can get valuable information about the lasing characteristics and the photostabilities of the dyes. The triplet states decide (i) the extent of ${}^{1}O_{2}$ generation by the dyes via energy transfer to the dissolved O_{2} in solvents, and also (ii) the reduction in the lasing efficiency due to triplet (T₁)-triplet (T_n) absorption loss of the dye laser photons. Presently, the triplet state spectroscopy and the energy transfer processes of the dyes **1a** and **5** were investigated by carrying out their pulse radiolyses in 1,4-dioxane/benzene (9:1) solutions, using 4,4'-dimethylbiphenyl (DMBP) (E_T = 65 kcal mol⁻¹) as a triplet sensitizer. Radiolysis of benzene gives a high yield of the triplet state

(G = 4.2 /100 eV) with energy of 82 kcal mol⁻¹, but with low lifetime (τ = 3 ns).

Hence, DMBP was used for efficient generation of the dye triplets.



Figure 7. Triplet state absorption spectra of **1a** and **5** $(1 \times 10^{-4} \text{ mol dm}^{-3})$ in 1,4dioxane/benzene (9:1) mixture in presence of DMBP (5 × 10⁻³ mol dm⁻³).

The triplet state absorption spectra of the dyes **1a** and **5** were similar, showing broad absorption at 600-800 nm with λ_{max} at 710 nm for **1a** and at 720 nm for **5** (Figure 7). The triplet state extinction coefficients (ε^{T}_{max}) at λ_{max} , the rate constants for the energy transfer from DMBP triplet to the dyes (k_{et}) and from the dyes (**1a** and **5**) to ${}^{1}O_{2}$ (k (${}^{3}Dye \rightarrow O_{2}$)) were calculated from the experimental data, and shown in Table 5. The k (${}^{3}Dye \rightarrow O_{2}$) value for **5** was ~3 fold less than that of **1a**. This suggested that the ${}^{1}O_{2}$ generation capability of **5** is less than that of **1a**, contrary to our dye-sensitized DPBF photooxidation results (previous section). Other factors like a higher singlet to triplet intersystem crossing rate (k_{isc}) for dye **5** than dye **1a** may be responsible for this anomaly.

Table 5. Triplet-state data for the dyes 1a and 5 in 1,4-dioxane/benzene (9:1).							
Dye	λ_{max}	$\epsilon^{T}_{max}{}^{[a]}$	k _{et} [³ DMBP→Dye]	$k[^{3}Dye \rightarrow O_{2}]$			
	[nm]	$[M^{-1}cm^{-1}]$	$[10^{9}M^{-1}S^{-1}]$	$[10^8 M^{-1} S^{-1}]$			
1a	710	2440	2.0	8.7			
5	720	2830	3.7	3.2			

[a] Extinction coefficients at the respective λ_{max} .

3.7 Relative reactivity of ${}^{1}O_{2}$ with dye **1a** and **5**

The reactivity of ${}^{1}O_{2}$ with dyes **1a** and **5** in ethanol and 1,4-dioxane/ethanol (1:4) were examined by measuring the decrease of their absorbances (at respective λ_{abs}) on photo-irradiation in the presence of methylene blue (MB), a known efficient ${}^{1}O_{2}$ generator under visible light (tungsten lamp) illumination [45,46]. The experiment could not be done in neat 1,4-dioxane because of the poor solubility of MB. Under these conditions, only MB is excited to generate ${}^{1}O_{2}$. Individual illumination (λ >590 nm) of ethanol solution of MB, **1a** or **5** did not induce substantial changes in their respective absorption spectra. This also confirmed that MB is stable towards ${}^{1}O_{2}$. But illumination of **1a** or **5** and MB together in ethanol led to a time-dependent decrease in the respective dye absorbances, although there was no change in the nature of the absorption bands of the dye (Figure S12-S14).

As before, the relative rates of degradation of the dyes were obtained from the slopes of the O. D. *vs* irradiation time plots (Figure 8). The reactivity of ${}^{1}O_{2}$ with dye 5

was less than that with dye **1a** in both the media. Typically, a 90 min illumination led to 50% and 37% degradation of **1a** and **5** respectively in pure ethanol. While the degradations of **1a** and **5** in 1,4-dioxane/ethanol (1:4) were 47% and 35% respectively. These results confirmed that dye **5** is more photostable than dye **1a** due to its lower reactivity with ${}^{1}O_{2}$ and the activity of ${}^{1}O_{2}$ with these dyes is decreased on lowering the solvent polarity. Both these explain the exceptionally high photostability of dye **5** in 1,4-dioxane.



Figure 8. Time-dependent changes in the ODs of the dyes at their respective λ_{max} during photo-excitation in presence of MB in ethanol and 1,4-dioxane-ethanol (1:4).

3.8 Theoretical interpretations

To further explain the reactivity of ${}^{1}O_{2}$ with the dyes in solvents of different polarities, we carried out the theoretical calculations of the reaction of ${}^{1}O_{2}$ with the dye 5. Earlier we characterized the photodegradation products of the BODIPY dyes to confirm that the C7'-C8 double bond of the BODIPY core is the most vulnerable

position for 1,2-cycloaddition of ${}^{1}O_{2}$ [11]. Hence the reaction course of dye **5** with ${}^{1}O_{2}$, was theoretically calculated by placing the ${}^{1}O_{2}$ in proximity to the C7'-C8 double bond of **5** (Figure 9, **5a**). The transition state (TS) and the product structures were assigned as **5b** and the peroxide **5c** respectively (Figure 9).



Figure 9. Mechanism of the reaction of the BODIPY dye 5 with $^{1}O_{2}$.



Figure 10. Energy-minimized ground state structures (**5a**) of the dye **5**, and the structures of the transition state (**5b**) and product (**5c**) of the reaction between **5** and ${}^{1}O_{2}$.

The ground-state (S₀) minimum-energy structure **5a** of the BODIPY dye **5** was optimized by DFT calculations (Figure 10). The calculated bond lengths and charge density values of **5a**, **5b** and **5c** are presented in Table 6. The TS **5b** is formed by partial cleavage of the C7'-C8 π -bond and formation of the C7'-O2 bond as the initial events, as supported by the calculated bond lengths (Table 6). The C7'-C8 (1.41 Å) and O1-O2 (1.21 Å) bond

lengths in **5a** increased to 1.52 Å and 1.41 Å, respectively, in the TS **5b**. The distance between C7' and O2 (1.50 Å) indicated that a single bond is formed between them. The C8 and O1 atoms were too far apart (2.71 Å) to form a stable bond, but gradually moved closer for the bond formation (bond length = 1.51 Å), furnishing the peroxide **5c**. The charge density calculations further established the mechanism. Consistent with the proposed mechanism (Figure 9), the calculated electron density at O1 is more than that at O2 in **5b**. 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 (Table 6). However, most importantly, the calculated charge density values suggested that the charge separation in the TS 5b is more than that in the dye 5a and the peroxide 5c. Thus, the energies of the initial and final products will not change much with the change in solvent polarity, but the energy of the TS 5b will be very high in non-polar 1,4-dioxane. The polar solvent, ethanol will stabilize the TS 5b. This will make the activation energy of the reaction higher in 1,4-dioxane, compared to that in ethanol. Thus, the reaction rate of ${}^{1}O_{2}$ with the dye will be much lower in 1,4-dioxane than in ethanol. This explains the higher photostabilities of the dyes in 1,4-dioxane. This is consistent with our previous theoretical calculation that revealed lower E_{act} for the reaction between ${}^{1}O_{2}$ and **1a** than that with its another B-subtituted analog [12].

	Bond Length (Å)				Atomic charge (a.u.)		
Dyes	C8-O1	C7'-O2	C7'-C8	01-02	O1	O2	
5a	-	-	1.41	1.21	0.000	0.000	
5b	2.71	1.50	1.52	1.41	-0.411	-0.254	
5c	1.51	1.45	1.54	1.49	-0.298	-0.289	

Table 6. The DFT-calculated bond lengths and charge density values of 5a, 5b and 5c.

4. Conclusions

In short, a new BODIPY dye 5 containing two propargyl alcohol moieties at the B-centre was synthesized. The dye 5 showed comparable lasing efficiency as that of the commercial dye 1a but was photo-chemically more stable than 1a in both polar (ethanol) and non-polar (1,4-dioxane) solvents. Both the dyes 1a and 5 had similar ${}^{1}O_{2}$ generation capacities, and the oxidation potential (E_{ox}) of 5 was lower than that of 1a. Despite these, dye 5 is more photostable than dye 1a due to its lower reactivity with ¹O₂, particularly in the non-polar solvent 1,4-dioxane, as reflected by our MB-induced photo-degradation results, and rationalized by theoretical calculations. Earlier, we found that the B-substituted dye 2a was more photostable than the commercial dye 1a. The key finding of the present investigation is that we showed for the first time that besides alkyl substitution at the B-atom, use of less polar 1,4-dioxane medium in combination, can increase the photostability of the BODIPY dye immensely without compromising its laser property. The excellent photostability of the dye 5 in 1,4dioxane, comparable to that of Rhodamine 6G in ethanol, makes it a potential photostable new BODIPY dye for further exploration. Also, the new dye 5 may be an efficient photosensitizer for PDT applications due to its high singlet oxygen generation capacity. Moreover, since the dye 5 shows higher photostability in less polar environment, and is highly fluorescent, it may also be useful for fluorescence microscopy in living cells.

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