

Photophysical and laser characteristics of pyrromethene 567 dye: Experimental and theoretical studies

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Abstract. Narrow-band laser performance of alcohol solutions of pyrromethene 567 (PM567) and rhodamine 6G (RH6G) dye was investigated using a home-made GIG-configured dye laser, excited by the second-harmonic radiation (at 532 nm) of a pulsed Nd:YAG laser. Higher laser efficiency was observed with PM567 dye (~23% peak) in comparison to the commonly used RH6G dye (16.5%), in spite of much lower fluorescence quantum efficiency of the PM567 (0.83) *vis-à-vis* RH6G (0.98) dye solutions in ethanol. First principle-based electronic structure calculations were performed on PM567 dye in the ground (S_0) and excited states (S_1) using density functional theory to elucidate the structure and photophysical properties of the dye.

Keywords. Laser dye; pyrromethene 567; rhodamine 6G; electronic structure calculation.

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1. Introduction

Several chromophores of highly fluorescent organic compounds are now known, but the pyrromethene family of dyes, particularly pyrromethene 567 (PM567) dye, has attracted interest as being one of the most versatile fluorophores over the past decade [1]. The high laser efficiency of PM567 dye with low-repetition-rate (~10 Hz) solid-state [2,3] and liquid dye lasers [4] has led to several investigations on PM dyes recently. Faster rate of photochemical degradation of pyrromethene dyes in aerated liquid solution remain a cause of primary concern for use in liquid dye lasers, especially in high-repetition rate dye lasers. But, studies on high-repetition-rate dye laser performances with PM567 dye are very limited [5,6]. PM567 dye, with an absorption maximum at ~518 nm, possesses good absorption cross-section at green region of wavelengths, and thus, suitable for efficient pumping with high-repetition rate pump lasers, such as green component (at 510 nm) of copper vapour laser (CVL) or diode-pumped solid-state green (515 nm, 532 nm) lasers (DPSSGL).

We have carried out comparative laser performances of PM567 dye and widely used rhodamine 6G (RH6G) dye with a pulsed Nd:YAG (532 nm) pumped home-made narrow band dye laser in grazing-incidence-grating (GIG) configuration. Low-repetition-rate Nd:YAG/dye laser system facilitated quantitative comparison of laser efficiency, tuning range and quantum yield of photodegradation in dye solutions. Further information on correlation between structural properties and photophysical properties of PM567 dye was generated by first principle-based electronic structure calculations for the ground and the first excited states of the dye using density functional theory.

2. Experimental

Laser-grade dyes PM567 and RH6G were procured from M/s. Radiant (Germany) and used as received. Absorption and emission spectra of dilute dye solutions ($\sim 1 \times 10^{-6}$ M) were recorded with commercial absorption and fluorescence spectrophotometers. Fluorescence lifetime for each dye solution was measured by a time-correlated single-photon counting method. Fluorescence decay curves were fitted as single exponential decay and the fluorescence lifetime (τ) was calculated from the slope.

A narrow-band (spectral width = ~ 3 GHz) dye laser oscillator with an uncoated (4% reflectivity) output coupler, transversely pumped by second harmonic (532 nm) of a Q-switched Nd:YAG laser (PRF = 10 Hz, pulse width = ~ 6 ns) was set up in a grazing-incidence-grating configuration (with a grating of 2400 lines/mm), with a 25×4 -prisms pre-expander. The green pump laser beam was line focussed onto a flow through dye cell by a combination of plano-concave ($f = -50$ cm) and cylindrical ($f = 15$ cm) lenses. A dye cell of 2 mm width \times 20 mm length (Lambda Physik, Germany make) and its pump were used for dye laser. The fringe pattern of the dye laser output was monitored using a Fabry–Perot etalon and linewidth was calculated. For comparing the dye laser efficiencies, the concentrations of both the dye solutions were optimized for similar gain depth of the pump beam (at identical OD ~ 7 for 1 cm path) at 532 nm pump wavelength. The tuning curves of each dye solution were obtained by scanning the wavelength of the dye laser through the gain profile of the dye and measuring the average pump and dye laser powers with power meters. The pump power for obtaining the tuning curves was always kept well above the lasing threshold.

3. Theoretical method

Ground state (S_0) geometry optimization of dye PM567 was carried out by applying a correlated hybrid density functional, namely, B3LYP using a Dunning-type correlation consistent atomic basis set, cc-pVDZ for all the atoms following all electron molecular electronic structure theory. Time-dependent density functional theory (TDDFT) with B3LYP and PBE0 density functional was applied to study the excited state structure of the dyes in the first excited state (S_1) with appropriate long-range corrections. PBE0 DFT functional with long-range correction,

Table 1. Photophysical and laser properties of PM567 and RH6G dye solutions.

| Dye/Solvent | λ_{\max}^a (nm) | λ_{\max}^e (nm) | Peak λ_L (nm) | Φ_f | τ (ns) | k_r (10^8 s^{-1}) | k_{nr} (10^8 s^{-1}) | η (%) | η_s (%) |
|-------------|----------------------------|----------------------------|--------------------------|----------|----------------|------------------------------------|---------------------------------------|---------------|-----------------|
| PM567/EtOH | 516 | 535 | 558.3 | 0.84 | 6.37 | 1.31 | 0.25 | 23 | 24.1 |
| PM567/MeOH | 518 | 536 | 556.2 | 0.83 | 6.27 | 1.32 | 0.27 | 24 | 25.1 |
| RH6G/EtOH | 530 | 556 | 565 | 0.95 | 4.03 | 2.35 | 0.12 | 16.5 | 17.7 |

LRC- μ PBE0 was shown to predict accurate absorption and fluorescence properties of oligothiophene biomarkers [7]. Note that Dunning-type correlation consistent atomic basis set, cc-pVDZ for all the atoms was also used for all the excited state calculations. The effect of macroscopic hydration was tested by searching the ground state minimum energy structures of these dyes including PCM model with B3LYP functional. Excited state calculations were also carried out to test the COSMO affect on the excitation energies only via the Kohn–Sham orbital energies. All electronic structure calculations were carried out by applying the GAMESS suite of *ab initio* program system on BARC ANUPAM parallel computer system [8].

4. Results and discussion

The calculated most stable structure of the PM567 dye in the ground (S_0) and the first excited states (S_1) applying B3LYP functional under DFT/TDDFT procedure including C-PCM solvent model is shown in figures 1a and b. There is not much change in the geometrical parameters of the excited state compared to that in the ground state; the ring of the dye loses its planarity though. However, a significant change in atomic charge of the chromophore atoms is observed in the excited state. The atomic charges (in a.u.) of N(1), N(2), B, F(1) and F(2) in S_0 state are -0.21 , -0.22 , 0.21 , -0.24 and -0.23 , respectively. The atomic charges in the first excited state (S_1) of PM567 are -0.16 , -0.15 , 0.02 , -0.13 and -0.14 , respectively showing considerable electronic change. The strongest optical absorption band of the dye was predicted as 539 nm in the gas phase due to HOMO-to-LUMO electronic transition. When the excited state calculation was carried out by including macroscopic solvent effect through C-PCM solvent model for ethanol, the absorption maximum was 528 nm compared to 517 nm by experimental measurement. Performance of long-range corrected DFT functional, namely LRC- μ PBE0 under TDDFT formalism is very poor in the present case and largely blue-shifted by ~ 90 nm. Application of macroscopic model like conductor-like polarizable continuum model (C-PCM) does not improve the calculated transition wavelengths for this DFT functional.

The experimental data on photophysical properties of PM567 and RH6G dye solutions, using ethanol and methanol solvents, are summarized in table 1. The rate constants for the radiative (k_r) and non-radiative (k_{nr}) decay of the respective dye solutions were calculated using: $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$. Visible absorption

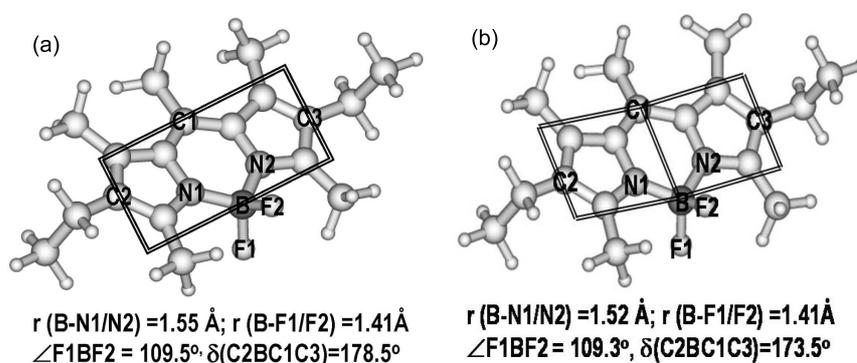


Figure 1. Optimized structure of PM567 dye in the (a) ground state (S_0) and (b) first excited state (S_1). The ground state structure was optimized by applying B3LYP/cc-pVDZ level of theory including C-PCM model. The first excited state structure was optimized at TDDFT(B3LYP)+C-PCM/cc-pVDZ level of theory.

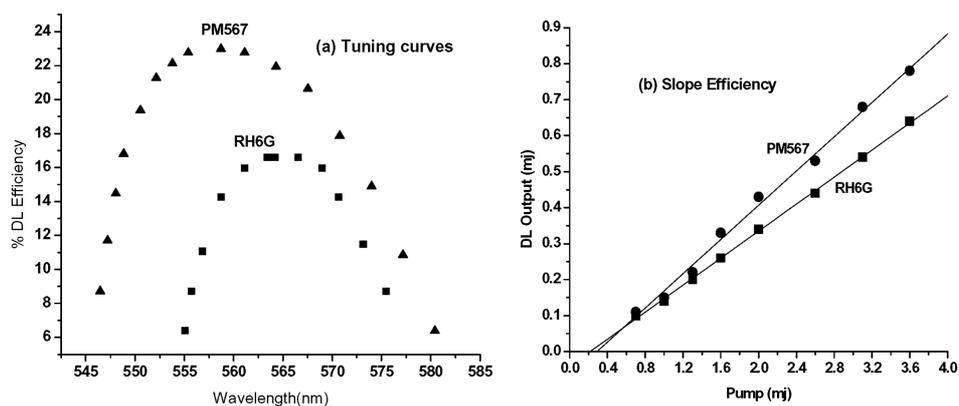


Figure 2. Narrow-band laser performances of PM567 and RH6G dyes using ethanol solvent. (a) Laser tuning curve at 4.7 mJ pump energy and (b) slope efficiency plot at respective laser peak wavelengths.

maximum (λ_{max}^a), fluorescence maximum (λ_{max}^e), fluorescence quantum yield (Φ_f) and fluorescence lifetime (τ) of dyes shows close resemblance to the previously reported [7] data. PM567 dye gave much lower fluorescence yield (Φ_f) and smaller fluorescence lifetime (τ) than that of RH6G (table 1), causing significantly smaller radiative rate (k_r) and larger non-radiative rate (k_{nr}) for the former dye. The observed laser tuning curves and slope efficiencies at respective laser peak for the two dyes, with pumping by the 532 nm radiation of the Nd:YAG second harmonic, are shown in figures 2a and 2b, respectively. The peak efficiency of the PM567 and RH6G dyes, using ethanol as solvent, were 23% centred at 558 nm and 16.5% at 555 nm, respectively, and respective tuning ranges are 546–580 nm and 555–577 nm for PM567 and RH6G dye lasers. As seen from figures 2, PM567 dye solution provides higher peak efficiency, as well as, wider tuning range when compared to

RH6G dye solution, but RH6G had much lower laser threshold, which was explained in our earlier work [9]. Table 1 includes laser properties of PM567 and RH6G dyes.

5. Conclusion

Pyrromethene 567 gave much higher laser efficiency and wider tuning range when compared with the commonly used rhodamine 6G dye in green–yellow spectral region. Experimental results and theoretical calculations on photophysical properties of the dye produced close resemblance showing the predictability of the present theoretical procedure. We plan to design new dye molecules having better laser efficiency and stability making structural modification of PM567 dye by applying similar theoretical procedure of molecular modelling.

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