PRAMANA — journal of physics

Vol. 82, No. 2
February 2014
pp. 277–281

Taming fluorescence yield of dye insensitive to temperature by non-covalent complex with the host CB[7] for aqueous dye lasers

MONIKA GUPTA[1,*], KRISHNA K JAGTAP[1], V SUDARSAN[2] and ALOK K RAY[1]

[1]Laser & Plasma Technology Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[2]Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
*Corresponding author. E-mail: monikaatgupta@gmail.com

DOI: 10.1007/s12043-013-0676-3; ***e*Publication:** 12 February 2014

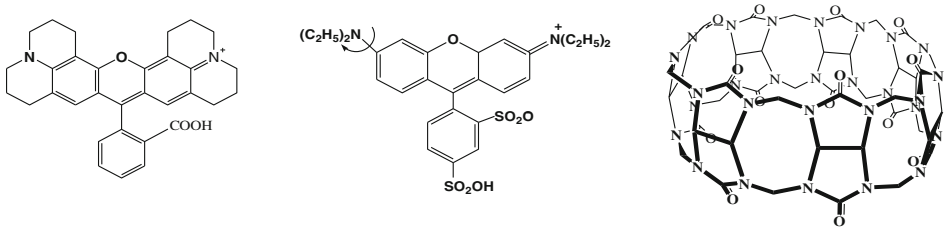
Abstract. Quantum yield of fluorescence (QYF) of widely used Rhodamine (RhB) dye in ethanol and water was observed to decrease rapidly with increase in temperature of the dye solutions, which was correlated to enhanced torsional motion of its flexible diethylamino groups. This is harmful for its use in high-average power dye lasers, pumped by copper vapour laser (CVL) or diode-pumped solid-state green laser (DPSSGL), in which bulk temperature of the dye solution was found to increase due to the heat generated by circulation pumps and non-radiative decay processes of excited dye molecules. The QYF of RhB dye in water was found to be not sensitive to temperature in the practical operating region 16–25°C of dye laser by adopting supramolecular route to form an inclusion complex of RhB with the container molecule cucurbit[7]uril (CB[7]).

Keywords. Temperature-dependent fluorescence; Rhodamine B; cucurbit[7]uril; host–guest complex; dye laser.

PACS Nos 36.20.kd; 83.60.pq; 87.64.kv

1. Introduction

Rhodamine B (RhB) is an efficient and photostable laser dye in the visible region, belonging to the xanthene family, and has been widely used in dye lasers pumped by second harmonic of a low-repetition-rate (10–20 Hz) Nd:YAG or high-repetition-rate (several tens of kHz) DPSSGL or yellow component (578 nm) of CVLs. However, unlike other xanthene dyes such as Rhodamine 101, its molecular structure is not rigid (figure 1) due to flexible diethyl amine groups ($-N(C_2H_5)_2$) of the dye molecule which enhance non-radiative rate of decay of excited molecules by vibrational and rotational motions. Thus, quantum yield of fluorescence (QYF) of RhB dye was found to depend sensitively on



(a) (b) (c)

Figure 1. Molecular structures of (**a**) Rhodamine 101, (**b**) Rhodamine B and (**c**) cucurbit[7]uril.

environmental conditions like temperature of the dye solutions, particularly for low viscous solvents such as water, ethanol or methanol [1]. For example, literature reports on QYF values of RhB dye were found to vary widely in the region 0.41 to 0.97.

Recently, we have carried out systematic studies on supramolecular route to form host–guest complexes of fluorescent dyes [2] with the macrocyclic container molecule cucurbit[7]uril (CB[7]) (figure 1) through non-covalent interactions for increased laser efficiency and photostability in aqueous media. In this context, QYF values of RhB dye solutions were determined using a fluorescence spectrophotometer and were observed that unlike in ethanol and pure water, the aqueous solutions of RhB dye, in the presence of the host CB[7], showed negligible reduction in QYF values when temperature of the dye solutions was increased from 289 K to 298 K.

2. Experimental

The laser-grade RhB dye was procured and high-purity (>98%) CB[7] sample was synthesized locally. Their purity was checked by HPLC and high resolution (500 MHz) ^{1}H NMR and MALDI-TOF mass spectrometry. The absorption and emission spectra of the RhB dye (ca.10^{-6} M) in ethanol and water were obtained using UV–vis absorption and steady-state fluorescence spectrophotometers. The quantum yield of fluorescence (QYF, Φ_{fl}) values of RhB dye in ethanol and water, in the absence and presence of the host CB[7] were measured and calculated relative to that of the ethanol solution of Rhodamine 101 dye as reference. The QYF value of aqueous RhB dye was found to increase with concentration of additive CB[7], and saturated at molar ratio of concentration of dye:CB[7]$\sim$1:5. It may be noted that QYF (Φ_{fl}) of the reference dye Rhodamine 101 in ethanol is reported as 0.9 and insensitive to increase in temperature [3]. The QYF values of RhB dye using ethanol and water, in the absence and presence of the additive CB[7], were measured in the temperature range of 279–298 K by calculating area under the fluorescence spectra with a step of change in temperature by 4 or 5 K. The uncertainty in the calculated values of QYF of RhB dye at different temperatures was $\pm$0.05. Liquid nitrogen cooling and thermoelectric heating were used to maintain and stabilize each value of temperature within $\pm$0.5 K. For each temperature setting, sufficient time (about 30 min) was allowed to maintain steady temperature of the dye solutions, before measuring the fluorescence spectra.

3. Result and discussion

The fluorescence spectra of RhB dye in water were found to shift bathochromically to longer wavelength region than that in ethanol (figure 2). This is because RhB is a polar molecule and possesses larger dipole moment at the excited state (S_1), and stabilizes its energy by interacting with the polar and protic water solvent. The measured fluorescence spectra of RhB dye in ethanol, water and water with CB[7] (molar ratio 1 : 5) in the temperature range 279–298 K were shown in figures 3a, b and c, respectively. These results showed sharp reduction in peak fluorescence intensity of the dye

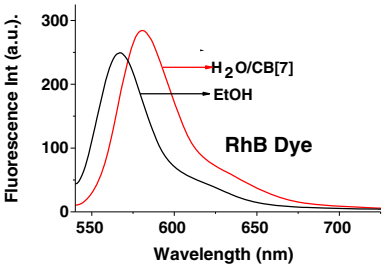


Figure 2. Comparative fluorescence spectra of RhB dye in ethanol and water with additive CB[7].

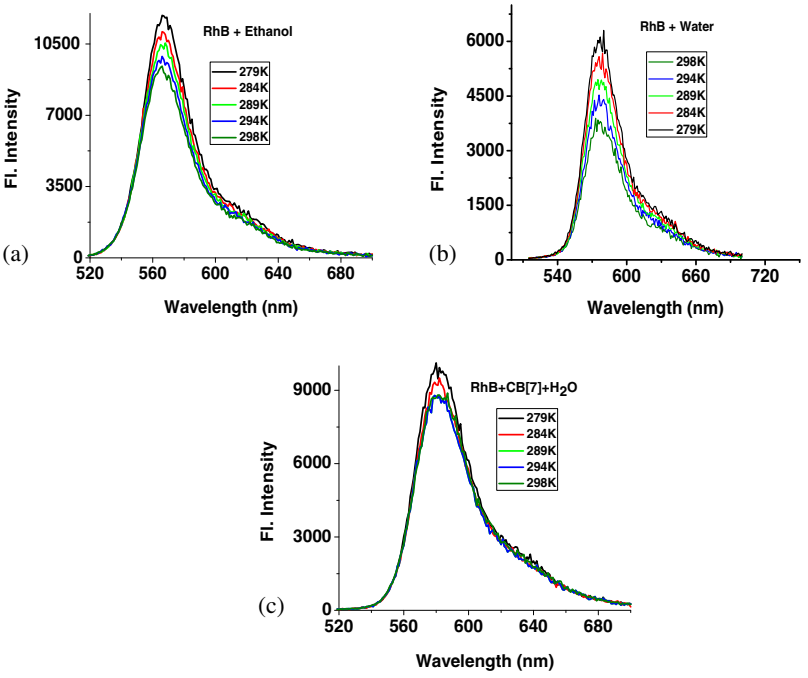


Figure 3. Fluorescence spectra of RhB in (**a**) ethanol, (**b**) water and (**c**) water with CB[7] at different temperatures in the region 279 K to 298 K.

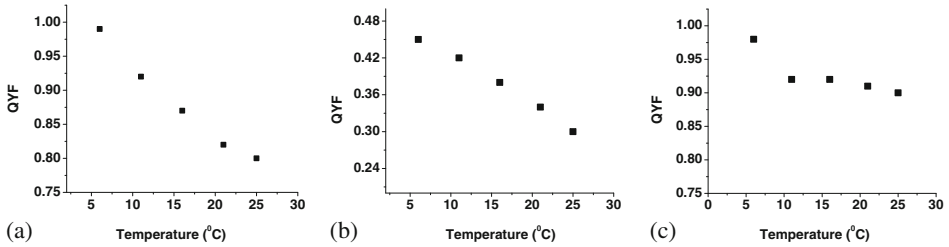


Figure 4. Plots of QYF vs. temperature for RhB in (**a**) ethanol, (**b**) water and (**c**) water with additive CB[7].

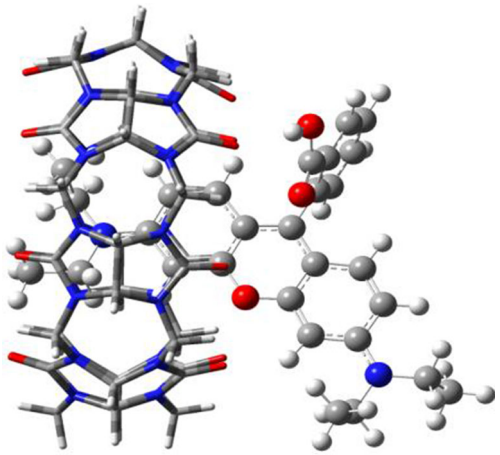


Figure 5. DFT-based model structure of the complex of RhB with CB[7] (taken from ref. [5]).

in ethanol and water with increase in temperature. However, fluorescence intensity of aqueous solutions of the dye, in presence of the host CB[7], was found to be independent of temperature in the region 283 K to 298 K (figure 3).

In the latter case, the fluorescence intensity was found to increase when temperature of the dye solution was decreased to 279 K. Figure 4 shows the plot of QYF values of RhB dye vs. temperature of the dye solutions in all the three cases. The container molecule CB[7] possesses electron-rich portals on both sides facilitating tighter binding of the RhB dye molecule through its positively charged diethylamine group ($-N^+(C_2H_5)_2$). The formation of the dye–CB[7] complex with 1 : 1 stoichiometry was confirmed by H NMR, polarization anisotropy spectroscopy and modelling studies [2,4,5]. The formation of supramolecular complex of the dye molecule (figure 5, taken from ref. [5]), in the presence of the host CB[7], may retard the torsional motions of the $-N(C_2H_5)_2$ groups of the dye molecule and hence its rate of non-radiative decay with increase in temperature. Thus, in the latter case, QYF was observed to be almost independent of temperature (figure 4).

4. Conclusion

In conclusion, the detrimental decrease in fluorescence intensity of the RhB dye with increase in temperature of dye solutions, in the practically operating region of 16 to 25°C, was largely arrested by using the macrocyclic host CB[7]. Thus, such aqueous active media is expected to deliver superior laser performances when used in high-repetition-rate dye lasers pumped by CVL or DPSSGL.

References

[1] K H Drexhage, Structures and properties of laser dyes, *Topics in applied physics* edited by F P Schafer, 147–152, 171–172, and references cited therein
[2] M Gupta, D K Maity, M K Singh, S K Nayak and A K Ray, *J. Phys. Chem. B* **116**, 5551 (2012)
[3] K Knut Rurack and Monika Spieles, *Anal. Chem.* **83**, 1232 (2011)
[4] J Mohanty, H Pal, A K Ray, S Kumar and W M Nau, *Chem. Phys. Chem.* **8**, 54 (2007)
[5] J K Khedkar, K K Jagtap, R V Pinjari, A K Ray and S P Gejji, *J. Mol. Model.* **18**, 3743 (2012)