J Fluoresc (2014) 24:895–898
DOI 10.1007/s10895-014-1369-0

ORIGINAL PAPER

Measurement of Absolute Fluorescence Quantum Yield of Basic Fuchsin Solution Using a Dual-Beam Thermal Lens Technique

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Received: 13 November 2013 / Accepted: 24 February 2014 / Published online: 8 March 2014

Abstract The dual beam thermal lens technique is an effective method for the measurement of fluorescence quantum yield of dye solutions. The concentration-dependent quantum yield of a novel dye of triaminotriphenylmethane family in ethanol is studied using this technique. The absolute fluorescence quantum yield is measured and is observed that the reduction in the quantum yield is due to the non-radiative relaxation of the absorbed energy.

Keywords Thermal blooming · Dye · Basic Fuchsin · Thermal lens · Fluorescence quantum yield

Introduction

Thermal blooming of laser beam was first observed by Gordon et al. [1]. Absorption of laser beam followed by non-radiative de-excitation of a sample leads to a localized heating of the sample, resulting a change in refractive index. For most of the liquids, the temperature coefficient of refractive index is negative and hence the thermal lens signal generated is divergent.

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There are several methods for calculating Fluorescence Quantum Yield (FQY) of a substance [2–6]. Most popular of them is the comparative method of FQY calculation by using a standard sample [7]. In this method two samples are investigated using the same experimental set up. The integrated areas under their corrected fluorescence spectra $S_1$and S_2 are related by

$$\frac{S_1}{S_2} = \frac{\Phi_2 A_2}{\Phi_1 A_1} \tag{1}$$

where Φ_1 and Φ_2 are the Quantum Yields and A_1 and A_2 are the corresponding absorbance of the two samples at a particular excitation wavelength. This method requires standard materials most commonly adopted method for the calculation of FQY is photothermal techniques that has high accuracy and reproducibility is the. The absolute value of FQY is very important as it is required for the calculation of thresholds of laser action. The present paper describes the determination of FQY of a novel dye-Fuchsin Basic in ethanol by dual beam thermal lens technique.

In order to evaluate FQY the radiative and non-radiative processes in the medium have to be considered. The thermal lens spectroscopy together with the fluorescence spectroscopy results in the measurement of absolute FQY. The former defines the rate of non-radiative decay whereas the later defines the rate of radiative decay. Because the contribution from non-radiative processes is not directly measurable using the traditional optical detection methods, thermo-optic techniques have been adopted recently for this purpose.

Basic Fuchsin (BF) a triaminotriphenylmethane dye with molecular formula $C_{20}H_{20}ClN_3$ (Fig. 1) is inflammable in nature and also known as Magenta II. Because of its anesthetic, bactericidal, and fungicidal properties it is used as coloring

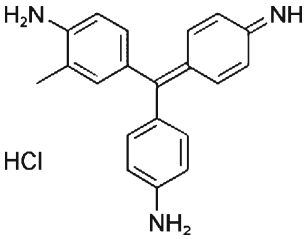

Fig. 1 Molecular structure of Basic Fuchsin

agent for textile and leather materials, staining of collagen, muscle, mitochondria, and tubercle bacillus.

Experimental Set-Up & Sample Preparation

The experimental set up (Fig. 2) used is the similar to the one reported by Fang and Swofford [8]. A diode pumped solid state laser of 532 nm having a maximum intensity of 100 mW is used as the heating source and a low power Helium-Neon laser (10 mW, 632 nm) is used as the probe beam. The intensity modulated pump beam (using a chopper of frequency 3 Hz) and the probe beam are made collinear and passed through the quartz cuvette containing sample solution through an assembly of dichroic mirror and a convex lens. The absorption coefficient of basic fuchsin at 632 nm is very narrow as compared to that of the pump beam and hence the perturbation in refractive index due to probe beam can be neglected. The thermal lens (TL) signal that is generated is filtered which passes only 632 nm. After filtering, the thermal lens signal is then collected through the tip of an optical fiber to the monochromator-PMT assembly and then to the Digital Storage Oscilloscope.

An accurately weighed amount of Fuchsin dye was dissolved in spectroscopic grade ethanol to get a concentration of $3*10^{-2}$ mol/L (the quenching concentration). From this stock solution, sample solutions with different concentrations were prepared and are used for FQY measurement.

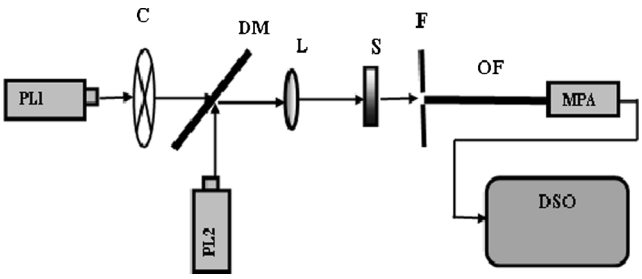

Fig. 2 Schematic representation of the experimental set-up *PL1* pump laser (DPSS, 532 nm), *C* chopper, *L* lens, *DM* dichroic mirror, *S* sample cell, *OF* optical fiber, *PL2* probe laser (He-Ne, 632 nm), *MPA* monochromator and PMT assembly, *DSO* digital storage oscilloscope

Results and Discussions

Fluorescence is the emission of photons produced by the transition of the molecule from electronically excited singlet state to the ground state [9]. Fluorescence quenching is the process, which decreases the fluorescence intensity of a given substance and increases the non-radiative transitions. The fluorescence quantum yield, Q_f is the ratio of the number of photons emitted to the number of photons absorbed through fluorescence. The method is based on the principle of energy conservation. The quantum efficiency can be calculated by Eq. (2)

$$Q_f = \left(\frac{\lambda_f}{\lambda}\right)\left(1-\frac{\eta}{\eta_\infty}\right) \tag{2}$$

The ratio of the fluorescence wavelength λ_f to the excitation wavelength λ corresponds to the Stokes shift. The thermal power degraded to heat, P_{th} is directly proportional to the TL signal η and P_α is proportional to TL signal η_α corresponding to the concentration at which the fluorescence intensity is quenched completely [10]. The thermal lens signal η has been measured using the standard technique as described [11].

The FQY of a dye medium depends on solute–solvent interaction, intersystem crossing, excited state absorption (ESA), two-photon absorption (TPA) and radiative and non-radiative relaxation cross sections. Most of these parameters depend critically on dye concentration and pump intensity. The ground state molecule reabsorbs the fluorescence from the excited state. This increases with increasing concentration resulting in a decrease in fluorescence and hence fluorescence

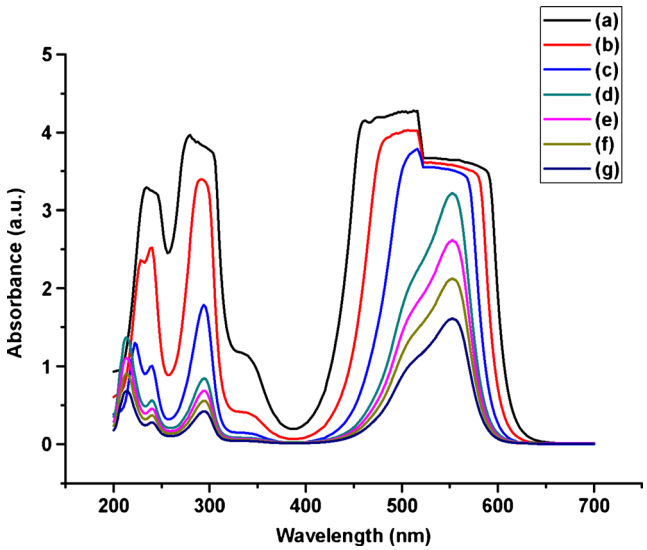

Fig. 3 Absorption spectrum for Basic Fuchsin in ethanol for concentrations: **a** $4*10^{-3}$ mol/L; **b** $1*10^{-3}$ mol/L; **c** $5*10^{-4}$ mol/L; **d** $3*10^{-4}$ mol/L; **e** $2*10^{-4}$ mol/L; **f** $8*10^{-5}$ mol/L; **g** $2*10^{-5}$ mol/L

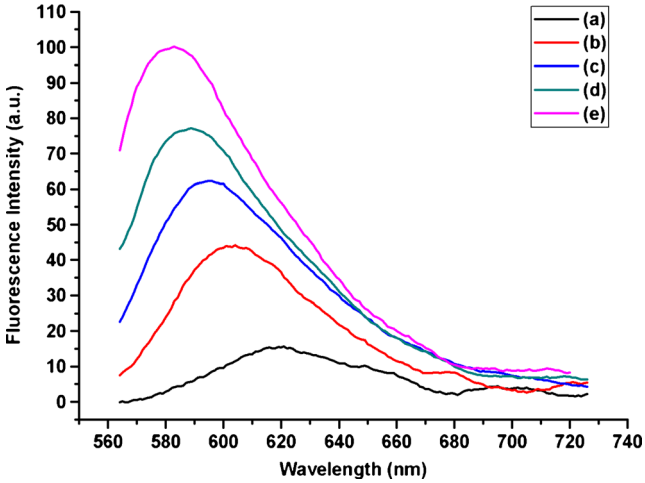

Fig. 4 Fluorescence spectrum of Basic Fuchsin in ethanol for an excitation wavelength of 532 nm for concentrations: **a** $4.5*10^{-4}$ mol/L; **b** $3*10^{-4}$ mol/L; **c** $2*10^{-4}$ mol/L; **d** $8*10^{-5}$ mol/L; **e** $4*10^{-5}$ mol/L

peak is shifted to smaller energies [12–16]. The absorption spectrum of BF in ethanol for various concentrations is taken using a Jasco U-570 UV/VIS/NIR spectrophotometer. The absorption spectrum is given in Fig. 3 and the absorption peak resides around 550 nm. As the concentration is increased there is a broadening of the spectrum because of the formation of higher aggregates. From this spectrum it is clear that absorption at 632 nm is very small and hence any perturbation due to the probe beam can be neglected. The fluorescence spectrum of BF for various concentrations is given in Fig. 4. The excitation wavelength used was 532 nm and the spectrum was measured using a Varian Cary Eclipse fluorescence spectrophotometer. The TL signal strength was measured in the dye solution in the concentration range 10^{-2} mol/L to 10^{-5} mol/L.

The concentration-dependence of the peak fluorescence wavelength (Fig. 5), shows a Stokes shift [17]. The red shift

Table 1 Properties of the ethanol

Solvent	Dielectric constant	Refractive index	Polarity	Dipole moment	Viscosity (at 0 °C)
Ethanol	24.3	1.35	5.2	1.69D	1.720 mPa.s

in the peak fluorescence wavelength implies a loss of energy of the emitted photons or an increase in Stokes shift with concentration. This is because of the energy losses due to dissipation of vibrational energy, redistribution of electrons in the surrounding solvent molecules, reorientation of the solvent molecules, and interactions between the fluorophore and the solvent or the solute. The solvent used in the present study is a polar protic solvent which participates in hydrogen bonding. These also have high dielectric constants and high dipole moments and possess O-H or N-H bonds. The solvent properties are given in Table 1. The FQY and fluorescence spectra are dependent on solvent polarity, viscosity, temperature, rate of solvent relaxation, probe conformational changes, rigidity of the local environment, internal charge transfer, proton transfer and excited state reactions, probe–probe interactions, changes in radiative and non-radiative decay rates etc [18, 19]. An increase in the solvent polarity increases the red shift because of the solvent relaxation effects. Like solvent polarity, the temperature also plays a major role in Stokes shift. The effects of high temperature are similar to those of high polarity solvents. At low temperatures the solvent is more viscous and hence the time required for solvent reorientation is higher. In a highly viscous environment the decay is radiative since the molecule is not able to display internal rotation as needed for charge transfer whereas in case of less viscous environment the molecule displays internal rotation and charge transfer resulting in radiationless decay. The dipole moment, refractive index (n) and dielectric constant (ε) also

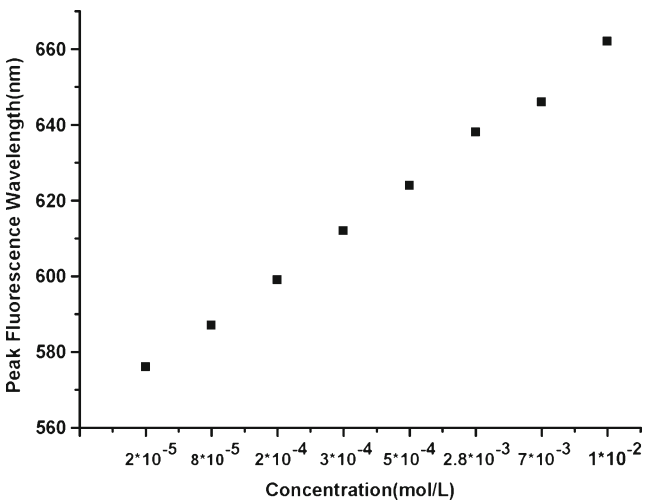

Fig. 5 The dependence of peak fluorescence wavelength of Basic Fuchsin in ethanol with varying concentration

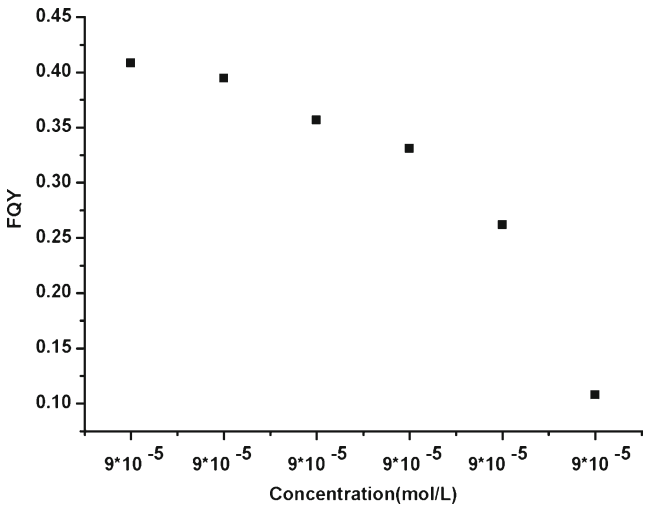

Fig. 6 Variations in the quantum yield of Basic Fuchsin in ethanol with varying concentration

plays a major role in the fluorescence spectrum and FQY. The refractive index (n) is an instantaneous high-frequency response that occurs by light absorption and depends on the motion of electrons within the solvent molecules whereas the dielectric constant (ε) is a static property, which depends on both electronic and molecular motions. An increase in n and ε result in stabilization of the ground and excited states by the redistribution of electrons and hence the refractive index and dielectric constant have a minor effect on the Stokes shift. Most fluorophore have nonzero dipole moments in the ground and excited states. If the solvent is polar then the stokes shift is increased which is a consequence of the increased dipole moment [19].

The variation of quantum yield obtained in TL measurements using Eq. (2) for Basic Fuchsin in ethanol as a function of concentration is given in Fig. 6. The FQY is decreased as the concentration is increased. This reveals that non-radiative processes become significant at higher concentrations resulting in enhanced thermal lensing. The rapid decrease in Q_f at higher concentrations can be due to the formation of dimers and aggregates which have zero or very small fluorescence quantum yield [13]. The role of triplet state absorption is also to be considered as an important factor.

The quantum yield closely depends on the environment of the fluorescing molecule, internal non-radiative conversion (S1› S0), intersystem crossing (S1› T1), excited singlet state absorption (ESA), aggregation of dye molecules etc. These are strongly dependent on excitation source, solvent characteristics and the concentration of the dye solution [17]. In the present case a significant reduction in fluorescence quantum yield can be expected due to dimerization at higher concentrations. The results show such a decrease in quantum yield as the concentration is increased and finally reaches the limit corresponding to fluorescence quenching.

Conclusion

Dual-beam thermal lens technique has been found to be an effective and useful method to study the concentration-dependence of the quantum yield of Basic Fuchsin dye in ethanol. The results clearly show that the quantum yield decreases with increasing concentration within the range 10^{-2} mol/L to 10^{-5} mol/L. The thermal lens method is suitable for quantum efficiency calculation of the present dye since no standard reference sample is required. The method seems very convenient and useful, especially at higher concentrations near fluorescence quenching.

Acknowledgments The author is grateful to the University Grant Commission, New Delhi for the research fellowships. DST is also acknowledged for the financial assistance.

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