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Effect of Host Medium on the Fluorescence Emission Intensity of Rhodamine B in Liquid and Solid Phase

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Abstract In this work, we study the effect of concentration, host medium, PH and phase states on the fluorescence emission from the laser dye Rhodamine B pumped by UV laser as exited source. The polymethylmethacrylate PMMA is used as a host medium in case of solid phase samples while, ethanol and Tetrahydrofuran (THF) are used in case of a liquid one. Laser Induced Fluorescence (LIF) technique was used to study the fluorescence properties of both cases of liquid and thin film solid-state samples. In addition, the Dual Thermal Lens (DTL) technique was used to study the quantum yield of these samples. The concentrations of Rhodamine B in ethanol as solvent between 2×10^{-2} M and 5×10^{-6} M were studied. The maximum fluorescence emission is observed at concentration of Rhodamine B $C=3\times10^{-4}$ M. Comparison studies were investigated for different host medium such as ethanol, THF, PMMA in liquid phase state and PMMA in solid phase state. The measurements revealed that, the behavior of both phases state was analogous. Rhodamine B/PMMA thin film sample by ratio of 4:1 and thickness 0.12 mm was found to have the best photostability sample with a quantum yield about ≈0.82.

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Introduction

Recently, electroluminescent devices based on organic thin layers have attracted much interest due to their potential application as large area light-emitting displays. Organic dyes are also candidates for making LEDs. Also, the semiconductor and conductor polymer with the fluorescent dye were found to enhance the emission the dye lasers [1–3].

The fluorescent dyes itself can be used to quantify fluid mixing in aqueous solution. The general technique involves rationing optically separable fluorescence from two fluorescent dyes. Fluorescence intensity ratios can be used to either measure the inherent variation in the dyes temperature fields [4].

The Rhodamine dyes are self-associated in different liquid crystal (Anisotropic solvent) host materials like ethanol (isotropic solvent) and this is very important in the display and electronic technology [5].

Solar cells based on dye-sensitized mesoporous films of TiO_2 are low-cost alternatives to conventional solid-state devices. This dye is also used as a sensor [6], nonlinear optical material, photosensitizer, malarial protease labels, active laser element, passive Q-switches and optical waveguide [7, 8].

From the early days of development of dye lasers, attempts were made to overcome the problems associated with dye solutions by incorporating dye molecules into solid matrices. A solid-state dye lasers avoid the problem of toxicity, flammability, compact, versatile, easy to operate, maintain and have high photostability properties. The photodegradation of the dye molecules under cw laser excitation is also studied [9].

In recent years, the synthesis of high performance dyes into the solid matrix using the polymer as a host present

advantages as better compatibility with organic laser dyes, inexpensive fabrication and high efficiency [10].

Hence, thermal and optical properties of dye-doped polymers are important in identifying suitable laser media, as Rhodamine B having the highest photostability ≈9,000 GJ/mol. In addition, Polymethylmethacrylate PMMA is one of the most highly amorphous network stretcher polymers. T. H. Nhung et al. [11] used the laser dyes Rhodamine B and Perylene Red incorporated at different relative concentrations into hybrid matrices synthesized using the sol–gel process. Energy transfer from Rhodamine B-donor to Perylene Red-acceptor molecules was observed. Using the different co-doped samples, solid-state dye laser systems with a tuning band control and higher efficiency were achieved in comparison with materials using solely one type of dye.

In addition, C. V. Bindhu et al. used the dual beam thermal lens (DTL) technique as a quantitative method to determine absolute fluorescence quantum yield and effect of concentration of Rhodamine B in different solvents. They investigated the absolute fluorescence quantum yield of Rhodamine B excited by cw argon ion laser (514 nm) as well as a pulsed Q-switched Nd:YAG laser (532 nm) [12].

Experimental

Materials

Rhodamine B (Rh B) of M.wt 479.02 g/mol from Merck is used as the fluorescent laser dye material. Polymethylmethacrylate (PMMA) of M.wt 100,000 g/mol from Aldrich is used as a polymer host for the dye while preparing thin films of Rhodamine B. The tetrahydrofuran (THF) from Aldrich is used as a common solvent for both (PMMA) and (Rh B) as well to reduce the problems of non-miscibility and non-homogeneity of the different solvent in each others. The absolute ethanol (99.9%) from Chema.jet is used as a common solvent for Rhodamine B.

The pH of samples is changed by adding the acidic or basic components such as NaOH and NH_4OH or NH_4Cl and HCl respectively to Rhodamine B in ethanol or THF of concentrations which have Maximum Fluorescence Emission Intensity (MFEI).

Preparation of thin film

Different concentrations of Rhodamine B in THF and PMMA in THF are prepared. Then, the two solutions are then mixed with continuous stirring for at least 5 min. This mixture is left in dishes inside oven at constant temperature 30 °C for 24 h to evaporate the solvent with constant rate to produce homogenous thin film [13]. The thin film of

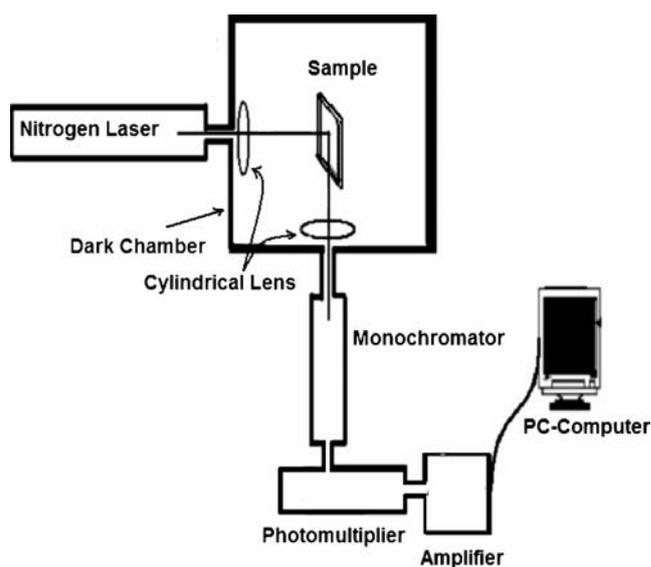thickness = 0.12 mm is removed from the dish and it is fixed inside double fiber frames as a sample holder.

LASER induced fluorescence (LIF)

A pulsed N_2-laser beam (337 nm) is delivered to the sample at incident angles of 45° and 90° on the thin film of dye sample and the liquid sample respectively. The pulsed laser beam from a N_2 laser is having a wavelength of 337±2 nm, pulse duration 15±1 ns and energy per pulse of 15±1 mJ. The laser beam is focused on the central bore by a quart cylindrical lens of focal length (156 mm) in a dark chamber to dimensions of 500×700 μm² spot providing target irradiance of 0.25±0.05 GW/cm² per pulse. To effectively eliminate Photodegardation processes, both energy and exposure time of nitrogen laser are reduced. Moreover, samples must be kept clean away from any photocatalytic materials [9, 10].

In addition, the emission spectra during the irradiation process is collected by a similar lens to a monochrometer having an input slit width of 3.5 mm and output slit width of 2.5 mm. The spectrum signals are detected by a photomultiplier (face type). An acquisition card is used to analyze the fluorescence spectra with pc-computer software specially written to scan the wavelength using a stepper motor as shown in Fig. 1. The experimental data is measured repeatedly at similar laser shots. The measurements data is already averaged using the controlling computer software.

Dual thermal lens (DTL)

The experimental set-up of the dual beam thermal lens technique is shown in Fig. 2. In the dual beam technique,
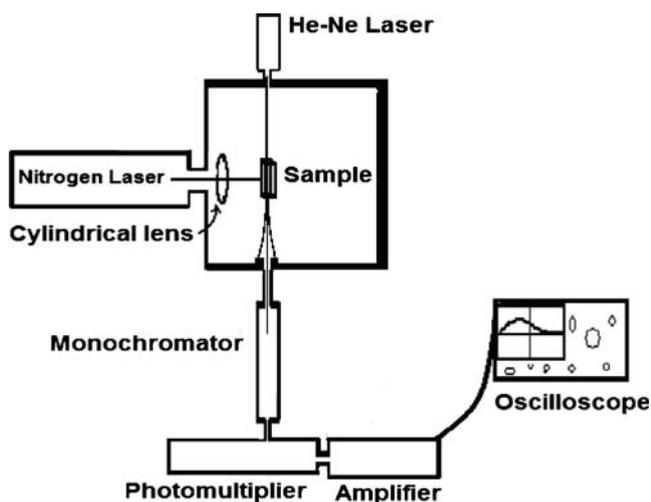

Fig. 1 Laser Induced Luminescence (LIF) set-up

Fig. 2 Dual beam thermal lens technique

Fig. 4 The effect of concentration on the maximum fluorescence emission intensity of Rhodamine B in ethanol

separate lasers are used, nitrogen laser (337 nm) as an exiting source and He–Ne laser (635 nm) as a probe beam. This technique is more advantageous, since only a single wavelength of the probe beam is always detected. The excitation source generates the thermal lens in the samples of dye medium. The beam of low intensity of He–Ne is diverted due to the thermal lens generated by the exiting source. This produced thermal lens signal depends on the type of samples. The probe beam is made collinear while passing through the samples. The thermal lens signal is detected by sampling the intensity at the center portion of the probe beam. This signal is transmitted only through the monochromator and detected by the photomultiplier which is connected to the oscilloscope.
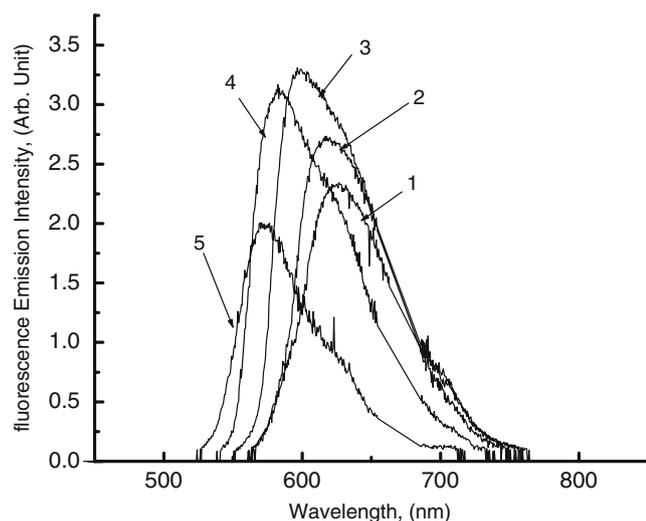
Results and discussion

The fluorescence emission spectra of the Rhodamine B samples at different concentrations of Rhodamine B in ethanol are shown in Fig. 3. From this figure, we find that the fluorescence emission spectra of Rhodamine B at different concentrations have a band tuneability of wavelengths from 520 nm to 765 nm. Moreover, it turns out that it exhibits a broader band at higher concentration. This is attributed to the favourable formation of monomers and aggregates of dye molecules. Figure 4 show the variation of Maximum fluorescence emission intensity as a function of Rhodamine B concentrations in ethanol. The fluorescence emission intensity increases with the concentration of Rhodamine B up to $C=3\times10^{-4}$ M, where it attains its climax. At low concentration $C=5\times10^{-6}$ M, the dye–dye molecules interaction was reported to be negligible due to the large average distance between them due to the increase the monomers and aggregates in agreement with A. Kurian et al., C. V. Bindhu et al., A. Santhi et al. and L. Z. Ismail et al. [9, 12–14].

However, at higher concentration $C=3\times10^{-4}$ M, the fluorescence emission intensity tends to decrease for concentrations from 10^{-4} M up to 10^{-2} M. This reduction is associated with non radiative energy transfer processes ending up with the formation of monomer dimers and higher aggregates. It also includes the relaxation processes between various vibronic levels of dye [9, 12].

In addition, the fluorescence emission intensity of Rhodamine B is found to not only get broader with concentration, but also shifts to higher wavelengths as shown in Fig. 5.This peak shift is pronounced up to 2×10^{-3} M and then level off at higher concentrations. This

Fig. 3 The fluorescence emission intensity of Rhodamine B in ethanol as a function of wavelengths at different concentrations in curves, (1) $C=7\times10^{-3}$ M, (2) $C=3\times10^{-3}$ M, (3) $C=3\times10^{-4}$ M, (4) $C=5\times10^{-5}$ and (5) $C=1\times10^{-5}$ M
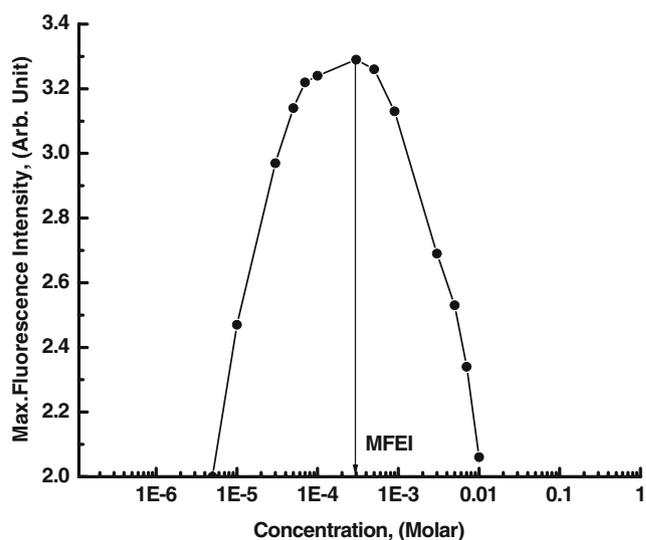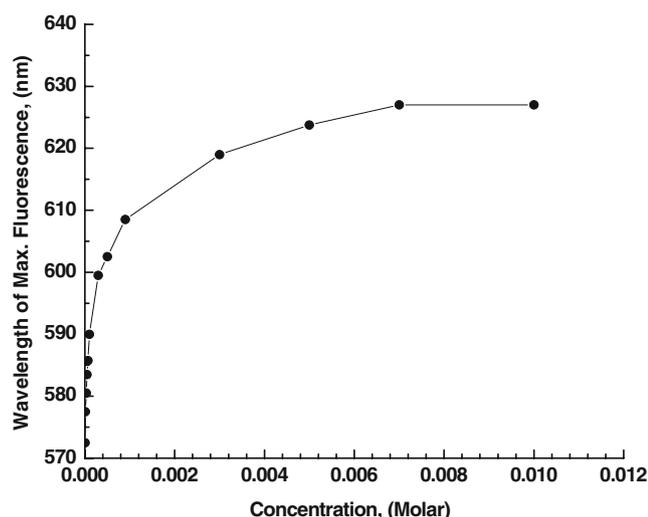
Fig. 5 The effect of concentration on the wavelength of the maximum fluorescence emission of Rhodamine B in ethanol
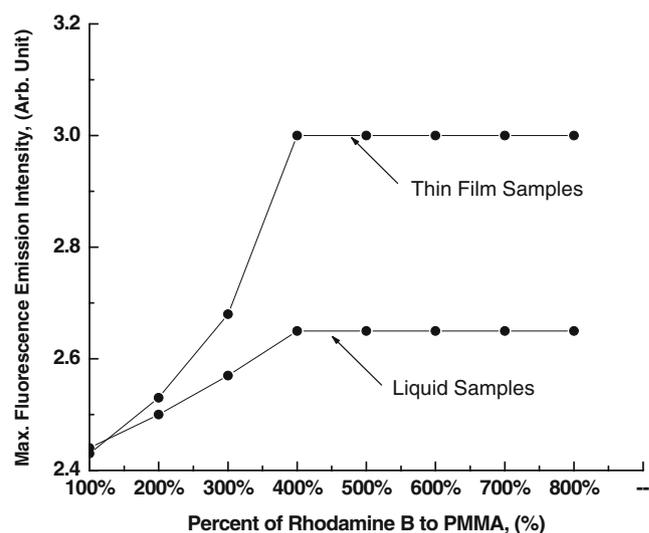
effect has to do with re-absorption and re-emission processes due to the overlap between the low frequency tail of the absorption spectrum of the dye molecule and the high frequency end of its fluorescence emission spectrum. The fluorescence from the excited state dye molecule reabsorbed by the ground state molecule would shift the fluorescence peak to lower energies [9]. Secondly, absorption saturation would lead to a similar peak shift. The molecules having closely lying levels of different absorption cross sections would therefore lead to wavelength shift. Besides, at high concentrations, the aggregation formation restricts the peak shift [12].
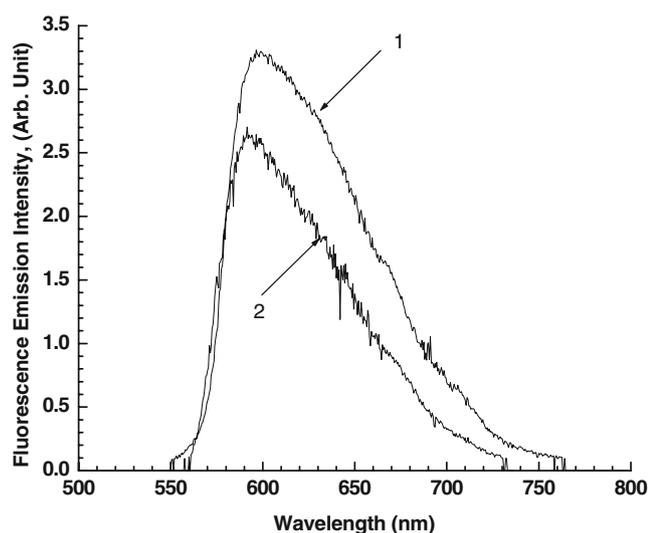
The role of the type of solvent and polarity of the medium on the fluorescence emission intensity of Rhodamine B in THF was also investigated as shown in Fig. 6. This figure shows higher fluorescence emission intensity and broader band of Rhodamine B dissolved in ethanol than Tetrahydrofuran (THF). Since ethanol is an alkaline polar medium according as the Rhodamine B has zwitterionic form and therefore absorbed more intensity of nitrogen pumped laser. Besides, it has higher viscosity and refractive index than Tetrahydrofuran (THF). Having smaller dye–dye molecular distances, Rhodamine B in ethanol permits the formation of aggregates which are responsible for the reduction of laser beam absorption [9, 16].

The polymethylmethacrylate (PMMA) with a concentration $C=8\times10^{-4}$ M is used as matrix for the Rhodamine B which has concentration $C=3\times10^{-4}$ M. Rhodamine B and PMMA with different ratios of Rhodamine B to PMMA are dissolved in THF. Figure 7 illustrates the comparison between the maximum fluorescence emission intensity of the thin film samples and the liquid samples of the ratio of Rhodamine B to PMMA at different ratios. The maximum fluorescence intensity is found to be higher in thin film samples than in liquid samples at all ratios. At low dye ratios, the maximum fluorescence intensity increases linearly with Rhodamine B to PMMA ratios up to a ratio about ≈4:1≈(400%) where it reaches its utmost value and any further increase in the dye ratios of Rhodamine B has no effect. This would indicate a phase change of Rhodamine B from a monomer to dimmer macromolecule forms at 4:1 ratio [9, 10, 11, 12]. In addition, the maximum of the fluorescence emission peak shifts with increasing the ratios of Rhodamine B to PMMA. After a certain ratio about 2:1≈

Fig. 6 The effect of solvent on the maximum fluorescence emission intensity of Rhodamine B with concentration 3×10^{-4} M. Curve (1) in ethanol and curve (2) in THF

Fig. 7 The maximum fluorescence intensity of Rhodamine B (C=3× 10^{-4} M) to PMMA (C=8×10^{-4} M) for thin film and liquid samples at different ratios
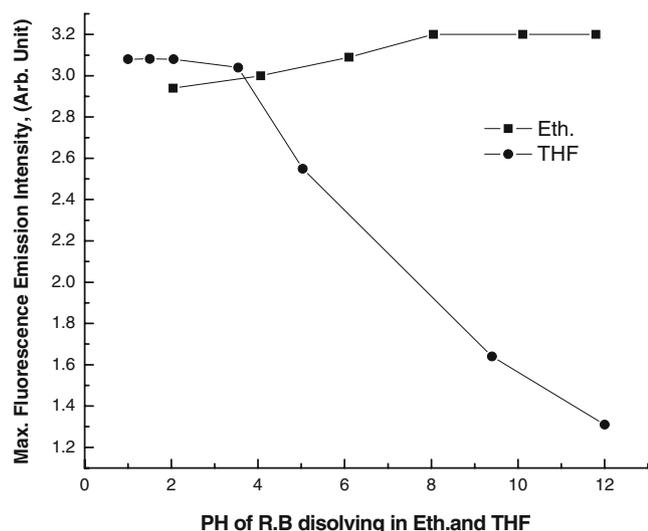
Fig. 8 The effect of pH on the fluorescence emission intensity of Rh B C=3×10^{-4} M dissolving in ethanol and in THF

200%, the shift is negligible. This is related to the phenomenon of re-absorption and re-emission [9].

The fluorescence emission spectra of the thin film samples of Rhodamine B/PMMA is found to show similar behavior by the liquid phase samples with different ratios. Also, the fluorescence emission spectra of Rhodamine B thin film of thickness=0.12 mm with different ratio of Rhodamine to PMMA is found exhibit a band tuneability of wavelengths from 520 nm to 750 nm. This result is in agreement with L. Z. Ismail et al. [13] and Kurian et al. [9].

Figure 8 illustrates the effect of PH on the fluorescence emission intensity of Rhodamine B dissolved in ethanol (polar solvent) and THF (non-polar solvent). At a PH value of about 3.75, the maximum fluorescence intensity of Rhodamine B in ethanol increases slightly with PH variation. This is due to the
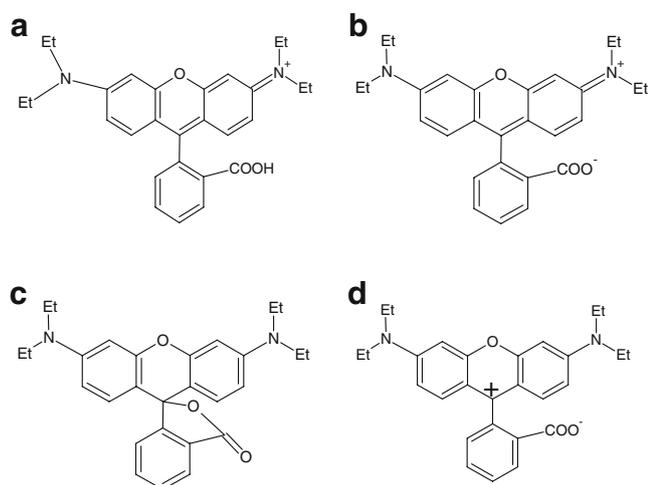
Fig. 9 Different formula of Rhodamine: a cationic, b quinonic, c Lactonic and d zwitterionic
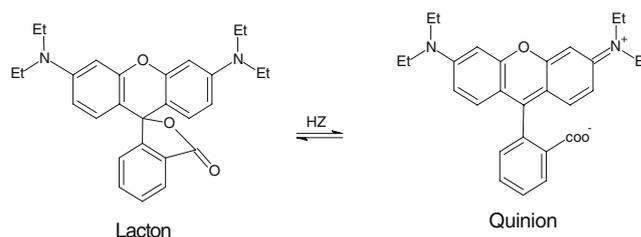
Fig. 10 Equilibrium between lactone and quinone form in the polar solvent

fact that Rhodamine B exists in a number of possible molecular forms such as cationic, zwitterionic, quinonic and lactonic [10] as shown in Fig. 9. In contrast in Rhodamine B in THF, the maximum fluorescence intensity falls rapidly with increasing PH value.

In the non-polar solvent (THF), at low pH the cation and quinone forms are present. On the other hand, by increasing the PH, the lactone form appears and this leads to the colorless of the dye solution due to the transfer of the cation and quinone to lactone as shown in Fig. 10 [17–19]. Then, the effect of PH on fluorescence emission intensity of Rhodamine B dissolved in ethanol and THF proved to have an impact in the variation of fluorescence emission intensity.

Quantum yield (Q) can be estimated by knowing the ratio between the thermal lens signal amplitude (η) of Rhodamine B concentrations in different host medium to that at which the fluorescence emission intensity is completely quenched (η_α) by using the dual thermal lens technique [9, 22]. The quantum yield and the ratios of η to η_α of Rhodamine B samples in different host media (Ethanol, THF, PMMA in THF and PMMA thin film) are shown in Table 1.

The quantum yield of Rhodamine B in ethanol is less than in the PMMA thin film. This means that the best lasing samples are the Rhodamine B in PMMA thin film, where they show the highest quantum yield. From the results, the Rhodamine B/PMMA with ratio about 4:1 has the highest quantum yield $\Phi \approx 0.82$ and good lasing properties.

Conclusion

By using the Laser Induced Fluorescence (LIF) technique, the effect of concentrations on the laser dye Rhodamine B

Table 1 Quantum yield values and the ratios of η to η_α of Rhodamine B in different host medium

Sample type	η/η_α	Q
1. Rhodamine B in ethanol	0.792	0.36
2. Rhodamine B in THF	0.81	0.31
3. Rhodamine B and PMMA in THF	0.834	0.27
4. Rhodamine B and PMMA thin film	0.529	0.82

dissolved in ethanol was studied. Fluorescence emission intensity of Rhodamine B gets broad and shifts to higher wavelength with concentration. It also depends on the type of solvents and polarity of the host medium. Besides, Rhodamine B in ethanol exhibit high fluorescence emission intensities than in THF. Besides, the effect of PH on fluorescence emission intensity of Rhodamine B dissolved in ethanol and THF proved to have an impact in the variation of fluorescence emission intensity.

However, the measurements revealed that, the fluorescence emission spectrum of thin film of Rhodamine B/PMMA samples are grater than liquid samples of Rhodamine B/PMMA dissolved in THF. Rhodamine B/PMMA thin film sample by ratio of 4:1 and thickness 0.12 mm was found to have the best photostability sample with a quantum yield about ≈0.82.

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