OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 11, No. 3-4, March-April 2017, p. 246 - 250

Spectroscopic analysis of fluorescent dye Rhodamine-6G in $Al(NO_3)_3$-SiO_2 sol-gel glasses

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In search of luminescent host-guest materials, $Al(NO_3)_3$-SiO_2 sol-gel glasses are investigated as host for dye Rhodamine-6G.Glass samples are fabricated with varying Rhodamine-6G concentrations and are characterized by absorption and photoluminescence studies. The efficiencies of absorption and photoluminescence of the glasses are quantified in comparison to the dyes doped in methanol. Radiative parameters viz. peak emission wavelength, intensity and quantum yields etc. are evaluated for the glass samples as a function of dye concentration, which confirms$1x10^{-4}$ M as the optimum Rhodamine-6G concentration in $Al(NO_3)_3$-SiO_2 sol-gel glasses. The results are discussed with the help of Single Exciton theory.

(Received June 30, 2016; accepted April 6, 2017)

*Keywords:*Rhodamine 6G, Photoluminescence, Quantum yield, Optical material

1. Introduction

Organic dyes now-a-days are gaining importance among the researchers from both scientific as well as technological point of view. These dyes form a very interesting class of quantum system among different atomic and molecular matters and are capable of emission in a very broad spectral range covering near infrared, visible and ultraviolet. These have wide applications as gain media in laser materials, non-linear optical materials, optical memories etc. due to their high fluorescence quantum yields, large cross sections for absorption and emission, low threshold power for laser action and attractive gain characteristics [1- 4]. In the field of laser, dye lasers were the fulfillment of the experimenters dream to have a laser that was easily tunable over a wide range of frequencies or wavelengths. Apart from tunability, dye lasers also possess the quality of efficient conversion of the flash lamp excitation into laser light due to the broad and strong absorption bands [5]. Also, the concentration and hence absorption as well as gain of optical medium containing dye can be readily controlled as the dyes can be used in both solid and liquid phases. The large oscillator strength and broad tunable emission of organic dyes, combined with the advantageous thermal and mechanical properties of the solid state hosts, make the laser dyes incorporated inorganic and inorganic-organic hybrid solid hosts very interesting candidates for photonics and integrated optics. Though the dye lasers based on liquid hosts are much developed and used in many laboratories as well as in technical applications, these possess inherent disadvantages like need of large volume of organic solvents, flow fluctuation, evaporation of solvents etc[6]. The use of dyes in solid hosts helps to overcome the problems related to fluid media such as elimination of translational freedom by avoiding intermolecular interaction, immunization of optical properties from high concentration interfaces, reduction of rotational relaxation of the excited state of laser dyes, elimination of inherent problems with physical pumping [7, 8] etc. The solid state dye lasers are also easy to handle, safe, compact and reliable [1]. The added advantages like low production cost as well as ability to fabricate in the desired shape make the solid state lasers potential candidate in the field of optoelectronics. So the study of modern materials based on laser dye incorporated in solid hosts is an area that bears potential technological significance. Based on the current status of the literature, mesoporous xerogels and glasses obtained via sol-gel methodology, with high surface areas and easy functionalization, appear to be promising host matrices for developing stable, highly transparent and highly efficient optical bulk materials[9]. Over the years, a number of studies on the incorporation of Rh-6G in different matrices have been taking place such as polymers[10-13], sol-gel derived silicas and related systems[14-17]. To our knowledge no such study on the spectroscopic behavior of Rhodamine-6G (Rh-6G) in $Al(NO_3)_3$- SiO_2 glasses have been done so far.

Among the organic dyes, Rh-6G is a popular and very efficient laser dye in the liquid state. In order to harness the advantages of the solid hosts as well as the efficiency of the Rh-6G, study of the behavior of Rh-6G in different solid hosts bears a significant technological potential. In the present work, therefore, we have fabricated the Rh-6G doped $Al(NO_3)_3$-SiO_2 sol-gel glasses and investigated its spectroscopic behavior with the help of UV-Visible absorption and Photoluminescence (PL) measurements. The efficiencies of the glasses were evaluated in comparison to the dyes doped in methanol medium. The optimum concentration of Rh-6G for maximum efficiency is evaluated for the studied glass host which is very crucial for the device applications.

2. Experimental

Five sets of glass samples for Rh-6G (Exciton, USA) doped $Al(NO_3)_3$-SiO_2 sol-gel glasses were fabricated by changing the dye concentrations. Tetra ethyl ortho silicate (TEOS) (Merck > 98%) as organo metallic precursor, methanol(Merck > 99%) as solvent, doubly distilled water for hydrolysis, dilute HNO_3(Merck 75%)as catalystwith their volumetric ratio16:70:10:4 and $Al(NO_3)_3.9H_2O$ (Merck > 95%) as co-dopant were used for the fabrication of glass samples. This results in themolar ratio between SiO_2 and $Al(NO_3)_3$in the glass samples as 94.7:5.3 to 95.7:3.9 for the studied concentration range of Rh-6G. The details of the preparation technique was as explained in earlier papers [18-20].Following dye concentrations were used for the fabrication of the glass samples.

Sample A: Rh-6G (5×10^{-5} M)
Sample B: Rh-6G (1×10^{-4} M)
Sample C: Rh-6G (5×10^{-4} M)
Sample D: Rh-6G (1×10^{-3} M)
Sample E: Rh-6G (5×10^{-3} M)

The dye loaded samples were obtained with high optical quality, free of cracks and striations. The thicknesses of the samples were found to be ~ 3mm. For the comparative analysis of the PL efficiency of the glass samples, Rh-6G in methanol medium with varying dye concentrations were also prepared. The concentration of Rh-6G was varied from 2.5×10^{-6}M to 1×10^{-3}M in the methanolic medium. Absorption spectra of the glass samples were recorded by Schimadzu UV 2600 UV-Visible spectrophotometer with a resolution of 1 nm using undoped glass as reference. PL measurements for the samples were conducted by Horiba Jobin Yvon Fluoromax 4P spectrofluorometer (spectral resolution of 1 nm) equipped with a photomultiplier detector and 500W xenon lamp as excitation source. The PL recording was done in front face configuration to minimize the re-absorption effects. All the measurements were done at room temperature.

3. Results and discussions

3.1. Absorption study

Fig. 1 shows the absorption spectra for Rh-6G doped in methanol. The spectra were recorded by considering the absorbance of undoped methanol as baseline. The samples were kept in a 1cm path length quartz cuvette in the path of the incident beam. Typical broadband spectrum for the methanolic solution of Rh-6G is observed around 530 nm, which is attributed to the monomeric state of Rh-6G corresponding to $S_0 \rightarrow S_1$ transitions, with a vibronic shoulder around 490 nm arising due to the mobility of the amino groups attached to the dye molecule [21]. The absorption intensity first increases with the dye concentration from 2.5×10^{-6} M to 1×10^{-4} M and then shows saturation. With further increase in dye concentration, the shape of absorption band also changes along with the appearance of a prominent absorption peak around 465 nm in addition to the 530 nm peak. The initial increase in intensity upto the concentration of 1×10^{-4} M is attributed to the increase in the number of monomeric species in the solution. Upto that concentration, the spectral line shapes of the samples are similar to monomeric solution which indicates that no dimers or very small amount of dimers are formed. The observed spectral broadening for the samples with higher dye concentration clearly indicates the formation of molecular aggregates. Also, the absorption maxima for Rh-6G doped in methanolic medium suffer a blue shift with the increase in the Rh-6G concentrations. This blue shift in the absorption spectra may arise due to the formation of non-emissive H-dimers or oblique J-dimers in the studied solution.

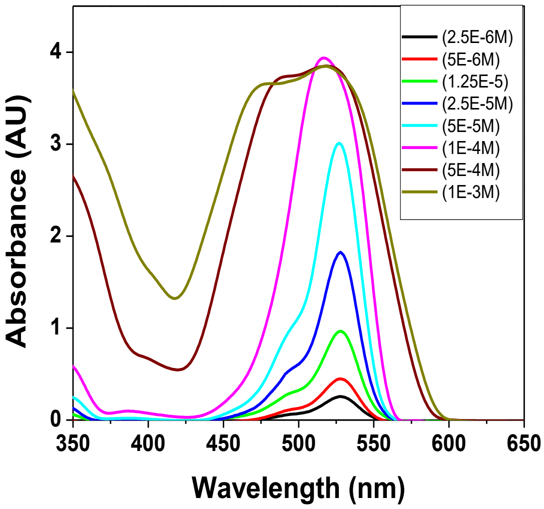

Fig. 1. Absorption spectra for varying concentrations of Rh-6G in methanol

In case of the absorption spectra for Rh-6G doped $Al(NO_3)_3$-SiO_2 sol-gel glasses with varying the dye concentrations (Fig. 2), it is observed that the absorption intensities of the glass samples are lower in comparison to that of methanolic samples. This decrease in absorption intensity is due to the formation of dimers as well as the decrease in amino group vibrations in the solid glass matrix. The absorption band maxima for the glass samples arising due to $S_0 \rightarrow S_1$ transitions occur in the range 490 to 570 nm compared to that of the methanolic samples which lie in the range of 517 to 528 nm. These red and blue shifted absorption bands for glass samples in comparison to the methanol medium can be explained on the basis of single exciton theory [21-24]. According to this theory, these red and blue shifting of absorption bands signify the formation of oblique J-dimers when the dyes are incorporated into the glass matrix [25], since in an amorphous solid, monomers and both types of dimer viz. J-dimers and oblique J-dimers are expected [26]. Similar to the dye doped samples in methanol, the absorption intensities increased on increasing the concentration of dye molecules in glasses as well, indicating the enhancement of dimer concentration (active species) with the concentration of dye. It is also observed from the absorption spectra of the Rh-6G doped glass samples that the absorption edge undergoes both blue and red shift with increase in the dye concentration which is also attributed to the presence of oblique J-dimers [26].

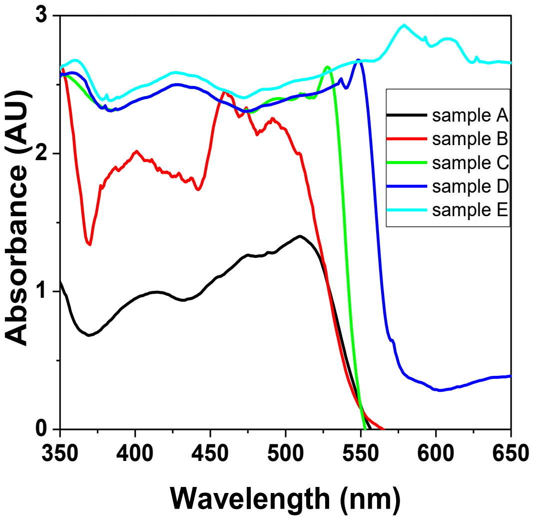

Fig. 2. Absorption spectra for varying concentrations of Rh-6G in $Al(NO_3)_3$-SiO_2 sol-gel glasses

3.2. Photoluminescence study

Fig. 3 depicts the variation of emission intensity with the simultaneous variation in excitation and emission wavelengths for the Rh-6G doped $Al(NO_3)_3$-SiO_2 sol-gel glasses. The figure depicts the intensity maxima around 558 to 576 nm emission wavelengths for the excitation wavelengths ranging between 464 and 472 nm. The photoluminescence excitation (PLE) spectra (shown in Fig. 4), recorded for the peak emission wavelength at 565 nm shows two prominent intensity maxima around 398 nm and 468 nm excitation wavelength. These excitation maxima indicates the presence of oblique J- dimers in the Rh-6G: $Al(NO_3)_3$-SiO_2 glass matrix.

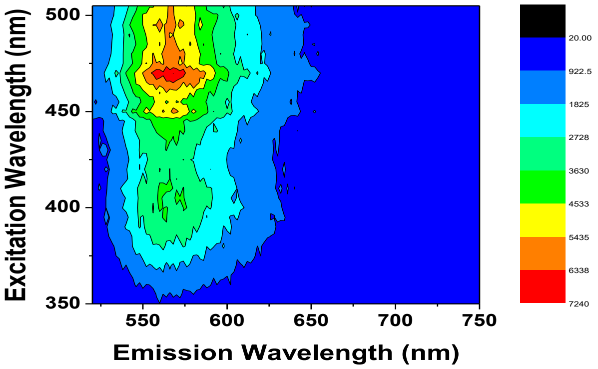

Fig. 3. 3D plot depicting the emission intensity variation with simultaneous variation of emission (520 to 750 nm) and excitation wavelengths (350 to 505 nm) for Rh-6G: $Al(NO_3)_3$-SiO_2 sol-gel glass

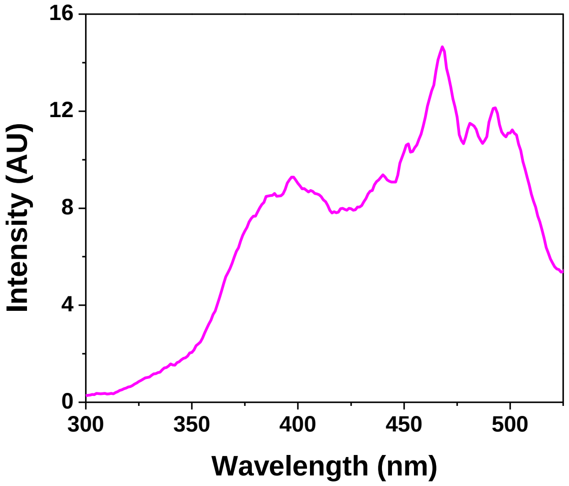

Fig. 4. PLE spectra for Rh-6G doped $Al(NO_3)_3$-SiO_2 sol-gel glass

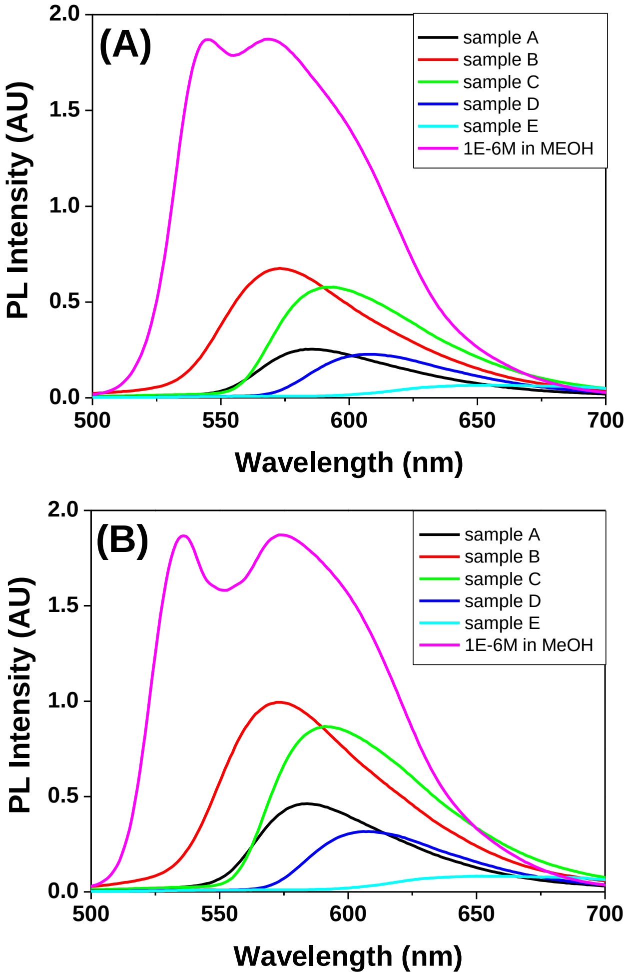

Fig. 5. PL spectra for varying concentrations of Rh-6G doped $Al(NO_3)_3$-SiO_2 glasses respectively under (A) 398nm and (B) 468 nm excitations (PL spectra for Rh-6G (10^{-6}M) doped in methanol is also shown for comparison)

Table 1. PL characteristic parameters of Rh-6G doped $Al(NO_3)_3$-SiO_2 sol-gel glasses under 398nm and 468nm excitation wavelengths

Conc. of Rh-6G (M)	**PL Peak Wavelength (λ_{PL})(nm)**		**FWHM (nm)**		**Peak Intensity (I_{PL})($x10^5$)(AU)**		**Quantum Yield**	
Exc (nm) →	**398**	**468**	**398**	**468**	**398**	**468**	**398**	**468**
5×10^{-5}	585	584	66	65	25.41	46.22	0.114	0.180
1×10^{-4}	573	572	70	74	67.59	99.37	0.318	0.427
5×10^{-4}	594	591	69	71	57.81	86.81	0.262	0.349
1×10^{-3}	607	608	67	66	22.74	31.62	0.101	0.123
5×10^{-3}	654	652	101	104	6.61	8.28	0.043	0.046

Based on the 3D plot and PLE spectra, PL spectra for the Rh-6G doped glasses were recorded for two excitation wavelengths viz. 398nm and 468nm respectively. The respective PL spectra are shown in Figs. 5(A) and (B). The spectra show single bands for each excitation wavelengths with the emission peaks in the range between 572 and 608 nm, ascribed to the cationic Rh-6G species [27]. The emission intensities increase initially with increase in the dye concentration from 5×10^{-5} M to 1×10^{-4}M along with blue shifting of peak emission wavelength. While increasing dye concentration beyond 1×10^{-4} M, a decrease in PL intensity is observed accompanied by gradual red shifting of the peak emission wavelength. As the variation in emission intensity with concentration is accompanied by both blue and red shifting of the peak emission wavelength, the results can be attributed to the formation of oblique J-dimer which is also evident in the absorption spectra. The decrease in intensity with the red shifting at higher dye concentrations may also occur due to the formation of J-dimers in addition to the oblique J-dimers in the glass samples.

To enumerate the Rh-6G PL intensities as well as yield, their emission spectra are compared with that of the emission spectra for Rh-6G in methanolic solution. It is justified, since the quantum yield of Rh-6G in methanol was reported as 0.96 [28]. For methanolic medium the highest quantum yield is observed for Rh-6G concentration of 1×10^{-6} M and hence the sample with 1×10^{-6}M Rh-6G concentration is used as reference for the determination of relative quantum yield of the dye doped glasses. The areas under the PL spectra are used for the determination of quantum yields [29]. The PL peak wavelengths (λ_{PL}), their full widths at half maximum (FWHM), PL peak intensities (I_{PL}) and the quantum yields of the Rh-6G doped glasses are summarized in Table 1.

As can be observed from Table 1 that the dye concentration of 1×10^{-4} M is the optimum concentration for Rh-6G doped $Al(NO_3)_3$-SiO_2 sol-gel glasses. Glass sample with that concentration possesses the lowest peak wavelength, highest peak intensity as well as maximum quantum yield along with comparable FWHM with the other PL peaks. Moreover, 468 nm excitation wavelength shows better quantum efficiency. The results indicate that dye concentration of 1×10^{-4}M and excitation wavelength of 468 nm are the optimum values for Rh-6G in $Al(NO_3)_3$-SiO_2 sol-gel glasses.

In case of Rh-6G dye in different hosts, the mechanism of aggregation is attributed to π–π interaction of the aromatic ring orbitals of the molecules, and its extent is related to the polarity of the media [22]. The degree of aggregation directly influences the spectroscopic properties of the dye. The aggregation and the resultant effect of these aggregations on the spectroscopic behavior can be well explained with the help of Single Exciton Theory [21–24]. The theory assumes two types of dimers called “H-dimers” which are non-emissive and “J-dimers” which are emissive. These dimers are differentiated by the angle between the monomer’s dipoles as illustrated in Fig. 6.

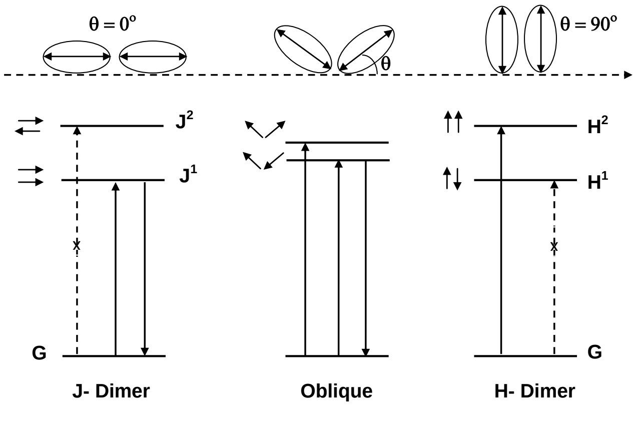

Fig. 6. Single Exciton Theory model and Schematic Energy level Diagram for Rhodamine 6G J- and H-Dimers. θ indicates the relative angle between the monomer transition dipole moments while arrow indicates their orientation [26]

The H-dimers are at the limit of plane-to-plane aggregates ($\theta = 90^o$) while J-dimers are at the limit of end-to-end aggregates ($\theta = 0^o$). Their spectral features can be understood based on the coupling of the molecular transition moments of two monomers, leading to an excited state with a lower energy component (H^1 or J^1) and a higher energy component (H^2 or J^2) in relation to the ground state (G). Because the component H^1 corresponds to antiparallel dipoles, the $G \rightarrow H^1$transition is forbidden, and only $G \rightarrow H^2$is observed, imposing a blue-shift to the excitation/absorption spectrum as compared to the monomer. The excited state component H^2 rapidly relaxes to H^1, which decays non-radiatively; therefore, H-dimers are non-emissive. On the contrary, for the case of J-dimers, the lowest energy component J^1 corresponds to aligned dipoles, thus $J^1 \rightarrow G$ is allowed. This fact implies a red shift to the excitation/absorption and emission spectra as compared to those of the monomers. An intermediate case is that of oblique dipoles, which present partially allowed transitions from ground state to both upper and lower energy components. These aggregates result in spectral changes such as the splitting of excitation band and blue shifted emission as compared to the monomer. Even though in an amorphous solid a distribution of Rh-6G monomers and different types of aggregates may be expected, in most cases, a certain population dominates the luminescent properties of the solid [26]. The present study reveals the dominance of oblique J-dimers in determination of the spectroscopic behavior for Rh-6G in $Al(NO_3)_3$-SiO_2sol-gel glasses.

4. Conclusions

In this communication, the spectroscopic behavior of Rh-6G doped $Al(NO_3)_3$-SiO_2 sol-gel glasses have been studied. The analysis of the PL and absorption spectra of sol-gel prepared Rh6G-$Al(NO_3)_3$-SiO_2 sol-gel glass samples indicated the presence of fluorescent aggregates. The emission peak first blue shifts and then red shifts as the dye concentration increases. The investigation confirms that 1×10^{-4}M is the optimum concentration for the Rh-6G dye in $Al(NO_3)_3$-SiO_2 sol-gel glasses for maximum efficiencies in terms of quantum yields and emission intensities. The experimental quantum yield and other radiative parameters clearly suggest that $Al(NO_3)_3$-SiO_2 sol-gel glasses can be a prospective alternative in the search for solid state host for dye lasers and other optical devices. Moreover, since the spectroscopic features of the hybrid samples can be varied by increasing the dye concentration over a large range of emission wavelengths the samples represent good candidates for the preparation of optical devices, and in particular for the development of solid state dye lasers.

Acknowledgements

The author acknowledges the financial support by Govt. of Assam in the procurement of Fluoromax 4P Spectrofluorimeter.

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