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Molecular Forms of Coumarin-307 in Sol-Gel Glasses

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Abstract Coumarin-307(C-307) impregnated sol-gel glass samples were prepared by two methods - (I) predoping using HNO_3 as catalyst, and (II) postdoping using HNO_3 as catalyst and formamide as drying control chemical additive (DCCA). The absorption/fluorescence properties including fluorescence lifetime of the dye in these sol-gel host matrices were studied and results were compared with dye in methanol (MeOH). In addition to usual non-polar form of C-307 that exists in MeOH, amino-protonated form and dimer of dye have also been found to co-exist in the dried state of samples prepared by predoping method. This behaviour of dye was uncommon to sol and gel states of materials. The fluorescence quantum yield (Q_f) of C-307 doped solid was found to be 0.77 and it was almost constant in the concentration range 5×10^{16} to 8.8×10^{17} cm^{-3}. On the other hand, only non-polar form of C-307 has been observed in the samples prepared by postdoping method. The Q_f value of dye was 0.96 in the postdoped samples. To explain such behaviour of C-307 in the two types of sol-gel matrices: dye concentration, role of HNO_3, water, formamide and matrix effect have been taken into account.

Keywords Absorption · Fluorescence · Laser-dye · Coumarin · Spectroscopic · Sol-gel

Introduction

Dye doped solid host materials have technical advantages over solution counterpart for use in various applications like solid-state dye laser, sensor, solar concentrator etc. Since last two decades, researchers have shown inherently increasing interest in sol-gel materials for its use as host matrix for variety of dopant species [1–15]. This has happened because of low temperature production process in desire geometrical form (thin film, rectangular block, cylinder, coating) and excellent properties like high purity, controlled porosity, and high transparency.

Coumarin laser dyes with an amino group at 7-position are very efficient laser dyes for the spectral response in the blue–green region of the electromagnetic spectrum [16–19]. Several laser dyes of this class have been widely studied in various solvents and solid hosts [1–3, 5–8, 16–24]. Depending on solvent environment, 7-aminocoumarin (a dye like coumarin-2 (C-2)) exits in various molecular forms [16] as shown in Fig. 1. A variety of possible interactions between 7-aminocoumarin and solvent molecules have been reported [25, 26] and spectral shifts and internal conversion process have been discussed using twisted intramolecular charge transfer state (TICT-state) and the umbrella-like motion model [25–27]. Furthermore, acidification of dye solution causes protonation in ground state as well as in the excited state of aminocoumarin resulting in a large change in photophysical properties [16]. The photophysical properties of laser dyes provide basic information for their use in different applications that in turn depend on the molecular structure of the dye. Therefore, the understanding of basic spectroscopic properties of these dyes is very important for their use in various applications.

Many laser dyes (coumarin or Rhodamine) incorporated in silica gels, usually show deviations from the characteristic spectroscopic behaviour observed in the solution phase, which is typically considered as standard. There are numerous experimental reports on the difficulties involved in retaining the optimum spectroscopic properties of organic

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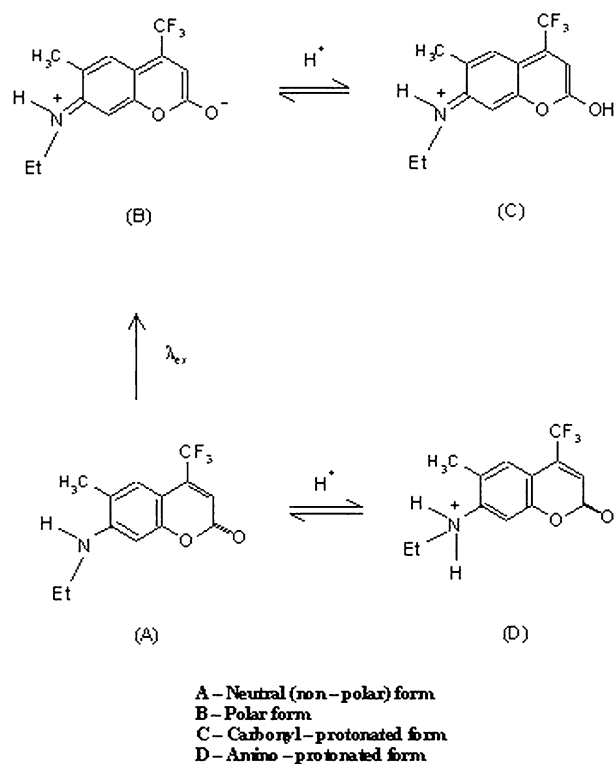e-mail: vcdeshp@vsnl.com, daparna@udct.org

A – Neutral (non–polar) form
B – Polar form
C – Carbonyl–protonated form
D – Amino–protonated form

Fig. 1 Various molecular forms of C-307

dyes when incorporated in sol-gel silica [24, 28–32]. These changes affect the photophysical properties of dye in sol-gel solids.

Previously, we have studied the photophysical performance of C-2 in (HNO₃ and HCl) catalysed sol-gel glasses and it has been pointed out that performance of C-2 taking into account the photophysical properties required for good lasing action is better in HNO₃ catalysed than that in HCl catalysed sol-gel glasses [31].

In the present paper, in continuation with our study of laser dyes [20, 21, 23, 31], we are reporting molecular forms and spectroscopic properties of C-307 in two types of HNO₃ catalyzed SiO₂ sol-gel matrices prepared by predoping and postdoping methods. In predoping method, dye was added with starting sol-gel precursor, whereas in postdoping method, the glass samples were first synthesized and then dye molecules were trapped in gel materials by immersing them in MeOH solution of the dye. All the samples prepared by these two methods were in the form of block. The absorption/fluorescence properties and fluorescence lifetime of dye-impregnated solids were studied and results were compared with the dye in MeOH. Co-existence of protonated form and dimer of C-307 (in addition to monomer species) in predoped sol-gel sample is remarkable, whereas dye molecules do not show any deviation in spectroscopic properties in postdoped sol-gel samples.

Experimental

Sample preparation

C-307 was obtained from Lambda Physik (Laser grade). Tetraethylorthosilicate (TEOS) (Merck), MeOH (GR grade, Merck), HNO₃ (Analar, BDH) and formamide (Merck) were used without further purification.

Predoping method

The solid samples were prepared by hydrolysis of TEOS followed by polycondensation in the presence of HNO₃. TEOS– 11.15 ml, distilled water–9 ml, MeOH–6 ml and HNO₃–1 ml (0.035 M) were used for sol preparation. Glass sol and MeOH solution of C-307 of known concentration were mixed in appropriate proportion and then this homogeneous solution was used for the sample preparation. The samples are cast by pouring sol in polystyrene cuvettes and the dried samples are in the form of blocks of size $1.5 \times 0.5 \times 0.5$ cm³. The concentration of dye solution or volumetric ratio of dye solution and glass sol was adjusted to obtain the desired dopant concentration. Drying and aging were carried out at room temperature under controlled environment.

Postdoping method

The molar ratios of TEOS : water : HNO₃ : MeOH : formamide were 1 : 10 : 0.45 : 3 : 3. Formamide was added after 6 hours of stirring and the sol was used for the sample preparation. Twenty days after preparation, samples were used to immerse in MeOH solution of C-307 of known concentration for different intervals of time. The number density of dye molecules in the solid host was calculated by difference method from the knowledge of absorption spectrum of the C-307 solution before and after the dipping of glass sample. The number density is calculated by measuring absorbance value (-three times) of the solution of dye at absorption maximum before dipping and after dipping which involves error of the order of 0.002 in optical density measurement. Also the dimensions of the samples are measured using traveling microscope with accuracy of the order of 0.001 cm. Hence the number density determination is quite accurate having errors less than 0.5%. The dipped samples were rinsed with MeOH and drying of samples was carried out at room temperature. The leaching test was carried out which involves dipping of dried sample (after one year of preparation) in water for an hour and checking the absorption of water before and after dipping the sample and of the sample. It was found that there was no leaching of the dye. The concentration of dye in MeOH and time interval of dipping were adjusted to obtain desired number density in solid host.

Measurement of absorption, fluorescence and lifetime

The absorption spectra of dye-doped samples were recorded by taking atleast three scans (scan speed 100 nm per minute) with respect to undoped glass sample using Milton Roy Spectrophotometer. The fluorescence spectra were recorded using an assembled fluorimeter with front surface excitation emission geometry with penetration depth approximately 2–3 mm [20, 21, 23, 31, 33]. Fluorescence spectra of C-307 impregnated solid samples and C-307 in MeOH were scanned at the same excitation wavelength, 380 nm with excitation and emission bandwidths of 5 nm. Atleast three scans (scan speed 50 nm per minute) are used to determine fluorescence spectrum. All the recorded spectra were corrected for the photomultiplier and monochromator sensitivities.

Fluorescence lifetime of C-307 in dried sol-gel samples and MeOH was measured at Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Mumbai by using single photon counting technique. The experimental set-up consists of a flashlamp(hydrogen filled) with 100 kHz frequency, FWHM < 2 ns, rise time <1 ns as excitation source, excitation/emission monochromators (excitation at 380 nm), start and stop photomultipliers, time to amplitude converter, multichanel analyzer and a computer. The deconvolution technique with single exponential decay curve fitting (chi square value between 1.0 and 1.03) was used to find the lifetime values.

Results

Predoping method

Depending on solvent environment, the various mesomeric forms of C-307 are shown in Fig. 1. The transmission of undoped dried sample was 90% from 800–350 nm and 65% at 300 nm. The absorption/fluorescence characteristics of C-307 were studied in starting sol, gel and dried solid xerogel and results were compared with absorption/fluorescence properties in MeOH (Table 1). The absorption/fluorescence peaks of C-307 in sol state were observed at 399 nm and 503 nm respectively, which were the same in the gel state.

After complete drying, multiple absorption peaks were observed in the absorption spectra of dye doped solid samples (Fig. 2). For lower concentrated (5.6×10^{15}–1.36×10^{16} molecules cm^{-3}) dye doped samples, the absorption peaks were observed at 398 nm and 325 nm while samples with intermediate concentrations showed three absorption peaks at 398 nm, 370 nm, and 325 nm. In the absorption spectra of dye doped samples with increasing concentration of dye (more than 4.76×10^{16} molecules cm^{-3}), the multiple peaks were found to be overlapping and no separate peak

Table 1 Spectroscopic properties of C-307 in MeOH, sol, gel and dried state of sol-gel

S. N.	Method	Host	λ_a (nm)*	λ_f (nm)*	Q_f #	τ (ns)
01	—	MeOH	397	502	0.92	4.85
02	Predoping	Sol-state	399	503	—	—
		Gel-state	399	503	—	—
		Dried solid	398	491–502	0.77	4.83
			370	555		
			325			
03	Postdoping	Dried solid	403	504	0.96	5.04

*Uncertainty in λ_a and λ_f = ± 2 nm.

#Uncertainty in Q_f = 0.1.

#Uncertainty in τ = 0.25 ns.

was seen except peak at 398 nm. On the other hand, the fluorescence spectra of all the dye-doped samples have single emission peak in the wavelength region 491–502 nm except for higher concentration (Fig. 3). The higher concentrated samples (more than 8.7×10^{16} molecules cm^{-3}) showed two fluorescence peaks at 502 nm and 555 nm, shown in Fig. 3. The FWHM of emission spectrum was found to be increasing with increasing dye concentration. The concentration dependent absorption/fluorescence properties of the dye in dried sol-gel solids are shown in Table 2. The lifetime of C-307 in MeOH and dried sol-gel solid host were 4.85 ns and 4.83 ns respectively.

Postdoping method

The transmission of clear glass sample was 90% in the wavelength region 800–400 nm and 60% at 330 nm. The spectral profile of absorption/fluorescence of C-307 in dried solid is shown in Fig. 4. The absorption/fluorescence peak positions 403/504 nm respectively remain unchanged with drying time and no change in optical density as well as fluorescence intensity at peak were observed with lapse of time (minimum up to two years). The fluorescence quantum yield and lifetime of dye in sol-gel solid prepared by this method were 0.96 and 5.04 ns respectively (Table 1).

Discussion

Predoping method

To understand the spectroscopic behaviour of C-307 in sol-gel host prepared by predoping method, it is necessary to understand the drying process which runs from sol stage upto dried stage. During initial stage of drying, MeOH and water get evaporated and expelled out from the pores of the sample, whereas HNO_3 does not do so [34]. Because of large volume shrinkage in the sample, the acid concentration increases and therefore, the first possibility is

Fig. 2 Absorption spectral profile of C-307 in dried predoped sol-gel solids with various dye concentrations in units molecules cm^{-3} (uncertainty in concentration <0.5%)
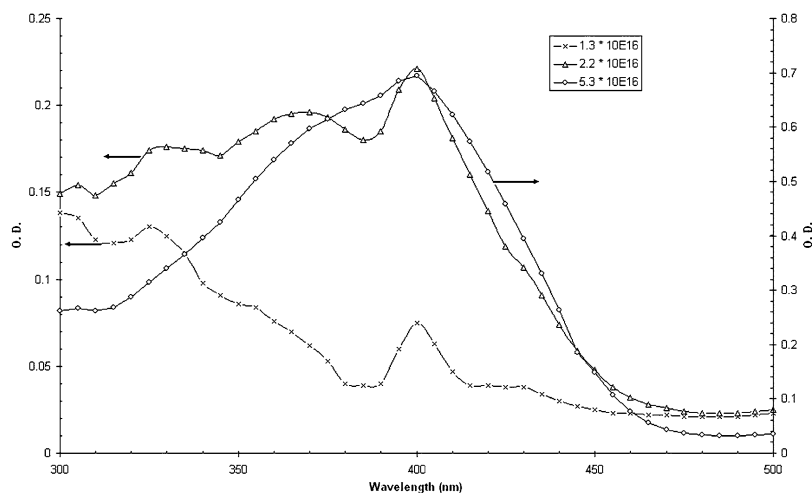
the protonation of C-307 at amino/carbonyl groups as earlier reported with other 7-aminocoumarins in acidic solution phase [16]. Secondly, the high concentration of dye as well as the proximity of dye molecules on drying also causes dimerization [16, 37–39]. Both these possibilities have been investigated in detail in the present study.

Generally, 7-aminocoumarin exists in two mesomeric forms – non-polar (in ground state) and polar (in excited state) (Fig. 1) [16]. Therefore, on optical excitation the electric dipole moment increases, and a major rearrangement of the surrounding solvent molecules takes place immediately after excitation resulting lowering of the excited state energy before light emission occurs. This causes large stokes shift in the coumarin derivatives [16]. The similar trend is followed by C-307 in MeOH with absorption and fluorescence peaks 398 and 502 nm respectively giving rise to stokes shift about 100 nm. A comparison of absorption/fluorescence peaks of C-307 in starting sol precursor, gel state, and dried solids [Table 1] with those in MeOH shows that species with $\lambda_a = 398$ nm and $\lambda_f = 502$ nm are associated with unprotonated monomeric form of C-307 that exists in MeOH. The

number density of HNO$_3$ molecules in dried sol-gel solids is of the order of 10^{18} cm^{-3}. These acid molecules may create protonated form of C-307 in dried solids.

This possibility was checked by studying the effect of increasing acid (HNO$_3$) concentration on absorption/fluorescence properties of C-307 in MeOH keeping the dye concentration 2.98×10^{16} cm^{-3} constant throughout. In contrast to the absorption and fluorescence spectra of C-307 in dried sol-gel samples (multiple absorption and fluorescence peaks), the acidified MeOH solution of C-307 show single absorption and fluorescence peaks at $\lambda_a = 397$ nm and $\lambda_f = 502$ nm respectively (not shown here). The optical density as well as fluorescence intensity were found to be decreasing with increasing acid concentration and increase in absorbance was appearing at shorter wavelength side (below 350 nm). In 7-aminocoumarins, two types of protonation have been reported – one at amino group and other at carbonyl group [16]. The amino protonated form causes reduction in optical density at main absorption peak (398 nm in the present case) of the dye because it does not absorb at this wavelength and it appears at shorter

Fig. 3 Fluorescence spectral profile of C-307 in dried predoped sol-gel solids with various dye concentrations in units molecules cm^{-3} (uncertainty in concentration <0.5%), excitation wavelength is 380 nm and excitation/emission bandwidths = 5 nm
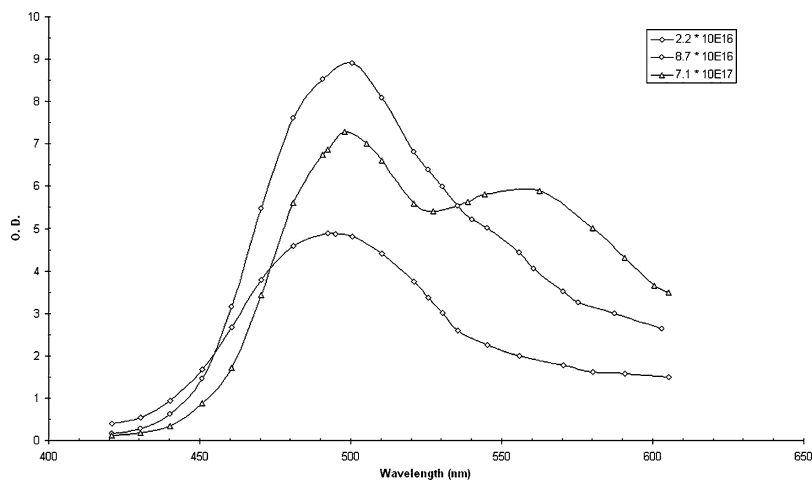
Table 2 Concentration dependent absorption/fluorescence properties of C-307 in predoped dried sol-gel solids

S.N.	No. Density per cm^3	λ_a (nm)	O.D.	λ_f (nm)	If (A.U.)	FWHM (cm^{-1})
01	2.8×10^{16}	398	0.248	496	640	2160
		370	0.248			
		325	0.207			
02	4.7×10^{16}	398	0.696	500	520	2178
		370	0.598			
03	5.3×10^{16}	398	1.280	502	840	2156
04	8.7×10^{16}	398	1.564	502	880	2207
05	2.4×10^{17}	398	2.539	502	870	2321
				555	500	
06	4.7×10^{17}	Broad	Very high	502	710	3009
				555	520	
07	7.1×10^{17}	Broad	Very high	502	720	3574
				555	580	
08	8.8×10^{17}	Broad	Very high	502	660	3454
				555	540	

wavelength side [16]. Further amino protonated form is the most favoured form in ground state in acidic medium which absorbs at shorter wavelength than the unprotonated nonpolar form [31]. The absorption spectrum of MeOH was quite clear upto 220 nm but acidified MeOH was found to be absorbing strongly below 350 nm (spectra are not shown here) leading to the conclusion that it is not possible to judge the absorption of dye below 350 nm in acidified MeOH. When acidified MeOH solution of C-307 was excited at shorter wavelengths (below 350 nm), there was no fluorescence observed. Hence species of C-307 which absorb below 350 nm in acidic MeOH can be concluded to be nonemitting. The same behaviour (non-emitting and exists at shorter wavelength side of the main band) of the species appearing at 325 nm absorption peak in dried sol-gel solids was seen. Therefore, it seems to be judicious to claim that absorption peak 325 nm of C-307 in dried sol-gel sample can be due to amino-protonated form. The protonation at carbonyl group occurs in excited state of dye molecule and is diffusion controlled. This form emits at longer wavelength compared to

unprotonated monomer form [16]. These excited molecules come back to the ground state in non-polar form (by deprotonation process) by emitting radiation. Thus, appearance of carbonyl protonated form cannot be seen in absorption spectrum. To understand the correlation of the absorption and fluorescence peaks, the dye doped solid samples were excited with $\lambda_{ex} = 320$ nm, 370 nm and 398 nm and only two fluorescence peaks nearly 502 nm and 555 nm were observed. The ratio of fluorescence intensities at 555 nm and 502 nm were calculated from fluorescence spectra corresponding to each excitation wavelength and the ratio was found to be maximum corresponding to 370 nm excitation. This confirms that $\lambda_f = 555$ nm emission peak is because of the absorption at 370 nm. Therefore, the absorption and emission wavelengths 370 nm and 555 nm respectively of C-307 in dried sol-gel host can not be associated with carbonyl protonated form.

The second possibility is of dimer formation due to proximity of dye molecules during drying. A dye like C-2 does show some basicity in the ground state, but it is

Fig. 4 Absorption/fluorescence profile of C-307 in dried postdoped sol-gel sample. Concentration of dye is 1.52×10^{17} cm^{-3} (uncertainty in concentration <0.5%), excitation wavelength is 380 nm and excitation/emission bandwidths $= 5$ nm
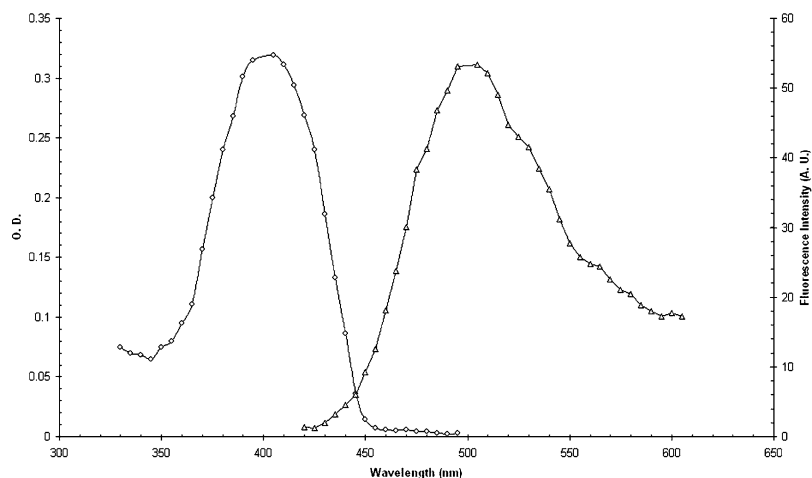
associated with the amino group rather than with the carbonyl group [16]. Due to this reason, water molecules take part in hydrogen bond formation with amino group of C-307. During drying period of C-307 impregnated sample, large volume shrinkage occurs and two neighbouring dye molecules come closer to each other than in sol or gel state. In this condition, the two dye molecules give rise to dimer formation which is further enhanced because of presence of water [32].

To confirm the dimerization of C-307 in sol-gel solid as mentioned above, the absorption /fluorescence spectra of C-307 in water were studied with various dye concentrations lying in the range of 10^{15}–10^{17} cm^{-3}. The absorption spectra of C-307 in water (not shown here) showed two new absorption bands at 370 nm and 440 nm in addition to normal monomer peak 398 nm. As the dye concentration increases, the sharpness of secondary absorption peak at 370 nm decreases because of increasing overlapping region between dimer and monomer absorption spectra governed by increase in the dimer concentration. These are in agreement with the observations in dried sol-gel samples. In the process of dimerization, the degenerate energy levels of monomers split into two energy levels of dimers which give rise to possibility of two-absorption bands of dimer. Schafer et al. have reported that the long wavelength transition has almost practically vanishing transition moment and therefore, only one absorption band of the dimer is observed, lying to the short wavelength side of the monomer band [16]. This explains well the existence of only one absorption band at 370 nm of C-307 dimer in sol-gel solids. The fluorescence spectra of C-307 in water show only emission from monomer species at 502 nm. It does not mean that dimer of C-307 is non-fluorescent. The upper energy level from which the fluorescence starts is always the lowest-lying excited electronic level and in dimers a small transition moment of the lowest level is coupled to a long lifetime of the excited state. Therefore, these dimers show very slow decay of their fluorescence

making them (dimers) susceptible to competing quenching processes such as intramolecular torsion, which are diffusion controlled and very fast in liquid solution. Consequently, in most of the cases the fluorescence of the dimers is completely quenched and cannot be observed in liquid phase [16]. But this is not the case in sol-gel solids.

On the basis of above discussion, the absorption peak 370 nm of C-307 in sol-gel glass has been associated with dimer species. As we have discussed earlier that longer wavelength emission peak 555 nm is associated with absorption at 370 nm, and therefore, it is concluded that the dimer of C-307 in dried state of sol-gel sample is fluorescent in nature and characterized by $\lambda_a = 370$ nm and $\lambda_f = 555$ nm. However, the existence of monomer-monomer closely spaced pair (behaves like dimer) cannot also be denied at higher dye concentration, which is not a stable dimer [32]. The optical density at 370 nm peak increases with increasing dye concentration in sol-gel host because of increase in the dimer concentration. This increase in dimer concentration causes increase in the overlapping region between monomer and dimer absorption spectra. And consequently, the dimer peak cannot be seen clearly with high dopant concentration. The fluorescence quenching of C-307 dimer in water is very fast, which is restricted in dried sol-gel host because of being hard and rigid host medium and therefore, it could be possible to observe the dimer fluorescence from C-307 impregnated sol-gel sample.

A change in fluorescence intensity at 555 nm (fluorescence intensity at dimer peak – I_{fd}) and 491–502 nm (fluorescence intensity at monomer peak – I_{fm}) and ratio I_{fd}/I_{fm} with dopant concentration are shown in Fig. 5. The decrease in fluorescence intensity at monomer emission peak (491–502 nm) with increasing concentration is because the concentration of the monomer species emitting at this wavelength is getting reduced and there is increase in concentration of the dimer species emitting at longer wavelength at 555 nm. The continuous increase in the fluorescence intensity at 555 nm shows

Fig. 5 Fluorescence intensity of C-307 in dried sol-gel solids at monomer peak (491–503 nm) (I_{fm}), dimer peak (555 nm) (I_{fd}) and I_{fd}/I_{fm} with dye concentration
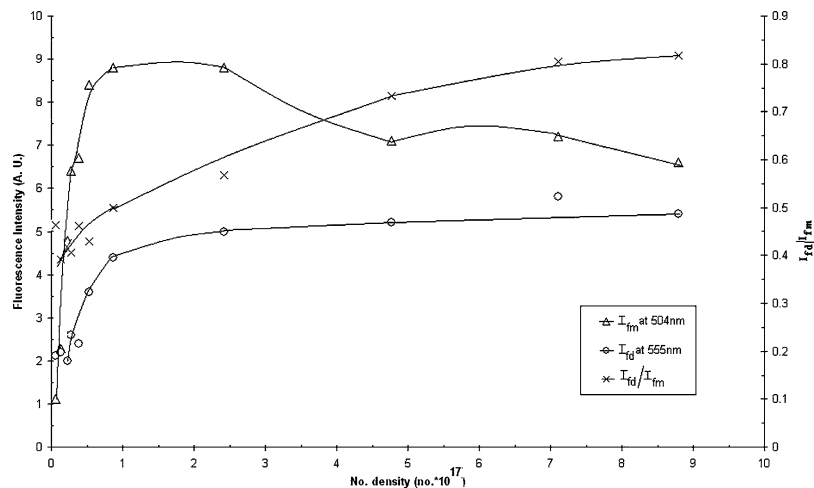
that no conversion of fluorescent dimer has taken place to some other nonfluorescent species with increasing dye concentration, which is in contrast to the observations in many rhodamine dyes in sol-gel glasses [27–29]. The dimer emission peak at 555 nm was not seen clearly in the fluorescence spectra of lower no. density samples (Fig. 3). It is because of two reasons- (i) dimer is less fluorescent than usual monomer form of C-307 and (ii) its (dimer) concentration is not enough to get detected. The total number of dye molecules trapped in the solid silica cage is utilized into three ways: a part of it gets converted into amino-protonated form which appears on shorter wavelength side at 325 nm in absorption spectrum and non-fluorescent in nature; another part of it undergo dimerization appearing at 370 nm in the absorption spectrum with emission at 555 nm, and remaining molecules are unprotonated monomer appearing at 398 nm (non-polar form in ground state) in the absorption spectrum with emission at 491–502 nm (polar form in excited state). Quantum yield of dye in dried sol-gel solid is equal to 0.77 and is almost constant in the concentration range 5.3×10^{16}–8.8×10^{17} cm^{-3}. The lifetime of C-307 in MeOH and dried sol-gel matrix are the same. This shows that major emitting species of C-307 in both that is in MeOH and sol-gel are the same. The change in fluorescence peak wavelength (491–502 nm = 11 nm) of C-307 in sol-gel samples is the dye concentration effect.

Thus, we can summarise as - the absorption (398 nm, non-polar form) and emission (502 nm, polar form) properties of C-307 in sol and gel state of matrix prepared by predoping method are similar to those of dye in MeOH. In addition to usual molecular form of C-307 that exists in MeOH, sol, and gel state of matrix; the dye has been found to exist in two new and distinct molecular forms mentioned as amino-protonated form and dimer in the dried state of samples. The amino-protonated form is generated as a result of protonation at amino group due to acidic environment created by HNO$_3$ used as catalyst in the preparation of sol-gel materials. This species is characterized by absorption peak at 325 nm and non-fluorescent in nature. The dimers of C-307 are produced due to proximity of dye molecules and presence of some water molecules in the solid host. Comparing spectroscopic properties of C-307 in sol state, gel state, MeOH, acidified MeOH, water and dried solid, it is clear that not only acid (HNO$_3$) and water are responsible for molecular changes but solidification (matrix effect) also plays an important role.

Postdoping method

The sol-gel material, prepared using formamide, has large pore volume [40] making it suitable for the impregnation of dye molecules in the solid cage by postdopng method.

The absorption/fluorescence peak wavelengths, fluorescence quantum yield and fluorescence lifetime of these samples are shown in Table 1. The absorption/fluorescence peaks and fluorescence quantum yield value of dye in dried solid sample are comparable to those of dye in MeOH. A slight red shift in absorption peak position (nearly 5 nm) of C-307 in solid sample compared to those of dye in MeOH have been associated with the refractive index and rigidity of the sol-gel materials. These observations show that major emitting species of C-307 in postdoped dried solid sample and MeOH are the same. Based on earlier discussion, we conclude that C-307 exists in usual monomer form in postdoped dye impregnated samples. No trace of the existence of protonated and dimer species was seen in the absorption/fluorescence spectra of these postdoped samples (Fig. 4). During dipping of gel samples in MeOH solution of dye, HNO$_3$ molecules were coming out of the cage resulting in lowering down the pH of the dye solution after dipping. And consequently, the insufficient acidic level in the pores was the reason for non-existence of protonated species [34]. It has also been reported that pores of the sol-gel solids contain some portion of formamide even after dipping [34, 41]. The presence of formamide is helpful in reducing the tendency to form dye aggregate in the sol-gel solids as earlier suggested by Arvan and Zaitseva during the study on effect of various solvents and their mixtures on the aggregation of dye molecules [42]. Therefore, it is reasonable to say that formamide present in the pores even in the dried state of postdoped sol-gel solids is responsible for reduced tendency of dimerization of C-307.

Thus, in contrast to the structural changes in dye in sol-gel host prepared by predoping method, no change in molecular structure of C-307 is observed with samples prepared by postdoping method. Also photophysical properties of these samples are comparable to those in MeOH. These solid samples do not show any degradation in photophysical properties up to period of 2 years from the date of preparation. This shows that the shelf-life of these samples is minimum two years, which is very promising from point of applications of these samples.

Comparison of spectroscopic properties

1. C-307 exists in three molecular forms - amino-protonated species, monomer and dimers in dried sol-gel host prepared by predoping method. On the other hand, the dye has been found to exist in only monomer form in sol-gel samples prepared by postdoping method.
2. The amino-protonated species are non-fluorescent in nature, whereas monomer and dimer species are fluorescent with emission peaks at 491–502 nm wavelength region and 555 nm respectively. Monomer is common in both types of sol-gel samples.

3. The fluorescence quantum yield of C-307 in the samples prepared by predoping method is 0.77 and it is nearly constant in the concentration range 5.3×10^{16}–8.8×10^{17} cm^{-3}, whereas quantum yield value of the dye is 0.96 for the samples prepared by postdoping method.

4. The behaviour of C-307 in postdoped sol-gel samples is similar to the dye in MeOH, while there is a large deviation in the absorption/fluorescence properties of dye in sol-gel samples prepared by predoping method from those of dye in MeOH.

Conclusion

C-307 is embedded in HNO$_3$ catalyzed sol-gel glasses using two different methods mentioned as predoping and postdoping. The spectroscopic properties of the dye have been found to be highly dependent on method of dye trapping.

In addition to usual molecular form of C-307 (with $\lambda_a = 398$ nm, $\lambda_f = 502$ nm) that exists in MeOH, sol, and gel state of matrix; the dye has been found to co-exist in two new and distinct molecular forms mentioned as amino-protonated form (with $\lambda_a = 325$ nm, non-fluorescent) and dimer ($\lambda_a = 370$ nm, $\lambda_f = 555$ nm) in the dried state of samples prepared by predoping method. Acidic environment of the cage, created by HNO$_3$ used as catalyst, and water molecules, produced even in the late stage of drying as a result of polycondensation, are responsible for the protonation at amino group and dimerization of C-307 in sol-gel samples prepared by predoping method respectively. However, the presence of monomer-monomer closely spaced dimer cannot be denied in higher dye concentrated sol-gel samples.

On the other hand, the spectroscopic behaviour of C-307 in postdoping sol-gel samples is similar to that of MeOH dye solution. The less acidic environment and presence of formamide molecules in the pores are responsible factors for non-existence of protonated and dimer species respectively. The absence of any degradation in absorption/fluorescence properties of C-307 in these samples with drying time for two years confirms that the dye molecules are very stable in these solids.

The comparative study of C-307 in sol-gel matrices prepared by predoping and postdoping methods shows that the performance of dye by taking into account photophysical properties of the dye in postdoping sol-gel samples is better than the performance in predoping samples. From enhanced stability of dye molecules, high quantum yield and good longevity of these dye impregnated postdoped solids, it can be inferred that these solids can be used as active materials in solid state dye-lasers emitting in blue-green region of spectrum.

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