

Research Article

Parametric Characterization of Spectroscopic Properties of Malachite Green in Sol-Gel Derived Silica Matrices with a Prospective Analysis of Optical Usage

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Abstract

Spectroscopic properties of Malachite green (MG) confined in porous matrix of sol gel silica glasses is studied extensively. Variation of absorbance and fluorescence intensities, radiative and non-radiative transition probabilities with dye concentration in the glasses is reported. Observed fluorescence quantum yield of MG is increased in the matrices by an order of $\sim 10^3$ compared to that in solution. Decay time of fluorescence in the matrix is in the range of 2.90 ns to 3.58 ns.

Keywords: Malachite Green dye, Sol-gel silica glass, Quantum yield, Lifetime, rigid cage effect

1. Introduction

Thermal instability of organic molecules impeded incorporation of organic molecules into inorganic solid matrices like conventional glasses or crystals which limited the use of organic molecules in the development of optical systems. Development of low temperature oxideglass preparation method by sol-gel process paved the way for inclusion of organic dyes into porous inorganic solid matrices for the first time in 1983(Reisfeld,R 1990). And with further improvement in the low temperature technique over the years sol-gel derived glasses, zeolites etc. emerged as an excellent porous medium for synthesis of composites (Gelb, L D et al 1999). The rigid pores of these medium, having dimension of few molecular diameter, can change the optical and physical properties of fluorescent dyes and organic chromophores confined in them, more often than not the changes are beneficial. It results in enhanced radiative efficiency, improved long term photo stability and reduced molecular dimerization that are attributed to physical and/or chemical interaction of confined molecules with rigid pores of the medium. The size and rigidity of the pores can also constrain the rotational modes in the molecules that determine intra molecular relaxation between excited states (Joshi, M P et al 2001, Casalboni, M et al 1997). These rotational relaxations constitute the chief routes of non-radiative deactivation of excited molecules.

These effects of confinement on optical properties of trapped organic chromophores are extensively exploited in synthesis of materials for optoelectronic devices such as solid state dye laser (Costela, A et al 2003). Most of the studies in this context are restricted to the use of fluorescent dyes with reasonably high fluorescence quantum yield and life time and are aimed at improving dye photo stability, thermal conductivity of the materials, etc. (Nikogogian,D N 1997). As such, reported works on optical properties of dyes with relatively low quantum yield, lifetime in confinement(i.e. trapped in solid matrices), enhancement or otherwise achieved in their properties and their utility in optical applications are very few (Chernyak,V et al 1991).

In view of the considerations, the present work investigates the optical behaviour of Malachite green (MG) —a non-fluorescent dye (Weichen,X et al 2010) of the triarylmethane group — trapped in the pores of sol-gel derived SiO₂ glass with emphasis on its radiative properties. A structural analysis of the silica matrix is also undertaken.

2. Experimental

2.1. Material Synthesis

Reagents grade chemicals from Merck are used for Tetraethylorthosilicate (TEOS), methanol, doubly distilled water, nitric acid and Malachite Green (oxalate) in preparation of Malachite Green (MG) doped SiO₂ glasses by sol-gel technique, where TEOS solution in methanol – the metal alkoxide – is polymerized under the catalyst action of doubly distilled water and dilute nitric acid. The sol-gel process being a low temperature synthesizer of glasses, ceramics enables doping of volatile elements like organic chromophore and fluorescent dyes without destruction of its characteristics (Reisfeld, R et al 1990; Brinker, CJ et al 1990). Four batches of glasses viz.; M1,

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M2, M3 and M4 were prepared for the study by varying the concentration of dopant MG in the range 1×10^{-5} M to 5×10^{-4} M. The concentrations of MG in the glasses are as: M1: $(1 \times 10^{-5}$ M), M2: $(5 \times 10^{-5}$ M), M3: $(1 \times 10^{-4}$ M) and M4: $(5 \times 10^{-4}$ M).

At first MG was dissolved in 10.5 ml mixture of methanol (8.75 ml), distilled water(1.25 ml) and dilute nitric acid(0.5 ml) taken in proportion of 70 (Methanol): 10 (H₂O): 4 (HNO₃) parts out of a total mixture of 12.5ml solvent where TEOS (2ml) forms 16 parts, and was continuously stirring for 15 minutes in a magnetic stirrer with Teflon coated stirrer bar. Then 2ml of TEOS was added to it and was further stirred for 1h till the gel formation began. At this stage the contents from the magnetic stirrer was transferred into plastic moulds and left to dry and solidify at room temperature (25-27°C). progress of hydrolysis the gel got solidified and With formed a colored stiff hard mass in 72 - 96 h, which is the xerogel or sol-gel glass. The colour to the glass is imparted by the dye molecules trapped in the pores of the xerogel /sol-gel glass. It is observed that with ageing of the sol-gel glass, during which the matrix of the glass shrinks, the colour of the glass changes to deep orange. It indicates of a change in the 'complementary' colour of MG from green to deep orange. The contrast in colours is evident from Fig.1.



Fig.1: (A) Malachite Green (Oxalate) dye (B) Molecular structure of Malachite Green (Oxalate) (C) p-quinoid and o-quinoid structures (D) M1, M2, M3&M4classes of MG doped SiO2 glasses

2.2. Experimental Methods and Instruments

High resolution surface morphology imaging (SEM micrograph) of MG doped SiO₂ glass matrix and energy dispersive X-ray analysis (EDAX) of element present in the matrix were performed in a Quanta 200 FEG Scanning Electron Microscope(SEM) in environment scanning (EM) mode. X-Ray Diffraction spectra to study the structure of the matrix was recorded in a PDX-11P3A, JEOL (Japan) diffractometer using CuKa radiation,

operated at 30 kV and 10 mA, while to investigate into the structure- composition relation of the matrix network. IR spectra in the range 4000–400 cm^{-1} was recorded using KBr technique with а Jasco FT/IR 300E spectrophotometer. VIS absorption spectra of the glasses in the range of 400-700 nm were recorded in UV-VIS-NIR spectrophotometer (CARY-5E) and the corresponding fluorescence spectra were taken in a JY Fluorolog-3-11 spectrofluorometer, excited by 445 nm wavelength of a 450W Xenon lamp, keeping slit widths at 5nm, with integration time 0.1s and step size 1nm. Decay time measurements at λ_{em} = 585 nm were Fluorocube - a life time measurement performed in system from JOBIN-YVON with Instrument Response Function (IRF) of 1.263ns on using LUDOX SM-30 colloidal suspension in water. The excitation source for decay time measurement is a 460nm LED. All measurements and recordings were done in room temperature $(25-27^{\circ}C)$.

3. Results and Discussion

3.1. Structural Analysis

3.1.1. SEM and EDAX

The SEM micrograph of Glass M1 in Fig. 2 reveals an inhomogeneous surface morphology of the matrix with particles of size ~ 17 μ m. The EDAX spectra alongside it indicate of a large presence of Si and O in the matrix which forms Si-O-Si and Si-O groups. The various network vibrational modes identified in the IR spectra confirm these groups formation. Apart from Si and O, C (18.14 wt %) and N (4.95wt %) are also traced. C forms the unstable ethoxy group, seen as a sharp band at 1384 cm⁻¹ in the IR spectra while the small amount N in the matrix do not contribute to the network formation of the glass.



Fig.2: (A) HR-SEM photograph of M1 glass (B) EDAX of M1 glass

3.1.2 XRD and IR spectra: Structure - composition relation of matrix:

The X-ray diffraction and IR-absorption spectra of SiO_2 sol-gel glass M1 are shown in Fig.3 (A) and Fig.3 (B), respectively. The X-Ray diffraction pattern is without any features to indicate crystallinity and confirms the amorphous nature of SiO_2 sol-gel matrix. The use of X-

ray diffraction in determination of glass structure is limited because of the absence of long-range order in glasses. Techniques such as the one that determines the radial distribution function of electron densities about specific atoms too has its limitations, as the symmetry and extent of short range order cannot be resolved adequately. IR absorption spectroscopy using KBr technique is, however, successful in the study of structure -composition relation in glasses and ceramics (El Batal,HA et al 2004). Moreover, it can be used to identify low concentration impurities, such as water, hydroxyl ions; etc. in glasses (Dunken, H et al 1987) The finger print region of the IR spectra in Fig. -3(B) are predominated by bands associated with network vibrational modes of Si-O-Si and Si-O Strong and intense band due to Si-O-Si groups. asymmetric stretching appears around 1088 cm⁻¹ and due to its bending mode at around 464 cm⁻¹ (with a shoulder at around 549 cm⁻¹). The weak band at around 797 cm⁻¹ may be assigned to Si-O-Si symmetric stretching of the bridging oxygen. The band around 969 cm⁻¹ be assigned to Si-O stretching with one or two non-bridging oxygen (Brinker,CJ et al 1986). Besides, at around 1384 cm⁻¹ a strong and intense band is attributed to vibration of TEOS, ethoxy group (due to CH₃ symmetric bending) (Chul,J R et al 1991). This band is very unstable and disappears on application of heat. The very strong and broad band on the higher wave number side of the spectra i.e. around 3461 cm^{-1} corresponds to the fundamental vibrations of -OHgroups and indicates strong presence of hydroxyl groups in the air dried glass. Similarly, the band around 1634 cm⁻ ¹ assigned to bending modes of water molecules indicates strong presence of adsorbed water.



Fig.3: (A) XRD spectra (B) IR spectra of MG doped SiO2 glasses

3.2 Absorption Spectra

The visible absorption spectra of glasses M1, M2, M3 and M4 together with the spectrum of MG in ethanol with MG concentration of 5×10^{-4} M is presented in Fig.4(A). The absorption maxima of MG in SiO₂ glasses are blue shifted by ~176 nm compared to its maxima in ethanol with a corresponding increase in absorbance by ~1.06. Observed shift in the absorbance maxima is consistent to a "complementary" colour change of the glass (dye) and may be attributed to rearrangement of p-quinoid structure of MG molecules to o- quinoid in the SiO₂ glass matrices. In the final phase of xerogel formation pores of diameter 2-200 nm are formed in the matrix by expulsion of solvent from the gel via hydrolysis (Reisfeld,R et al 1990;Brinker,CJ et al 1990). The dopant molecules i.e., MG within the SiO₂ matrices are trapped in these pores. With ageing, when the matrix further shrinks and becomes dense, the pore dimensions are reduced and the trapped molecules get squeezed. This can cause a rearrangement of quinoid structure from para- to ortho- . Rearrangement of quinoid structure from para- to ortho- raises the energy difference between ground and excited singlet states and results in absorption of comparatively larger energy accompanied by a change in "complementary' color of glass(dye) as observed. It may be recalled that colors of triarylmethane dyes are attributed to the p-quinoid group that along with two benzene rings attached to the central carbon forms the molecular structure and that o - quinoid is known to impart orange and red colours (Finer,I L 1996).

The absorbance of MG in SiO₂ matrices exhibits linear increase with concentration up to 1×10^{-4} M, which is indicative of absorbance in accordance to Beer-Lambert law and at concentration higher than 1×10^{-4} M absorbance decreases non-linearly. The variation of absorbance with MG concentration is presented in Fig.4 (B). Observed deviation of absorption from Beer-Lambert law at higher concentration here is primarily due to shadow effect of the absorbing dye molecules, which effectively is screening of molecules from the incident light by another molecule in its path. If this deviation was caused by refractive index changes of absorbing medium, seen at high concentration of dopants, absorbance would increase since with correction due to refractive index absorbance is:



Fig.4: (A) Absorption spectra of MG glasses & MG in solution of EtOH (B) Variation of absorbance with Molar concentration of MG

$$A = \varepsilon c l (n^2 + 2)^2 \tag{1}$$

In Eqn.1 *A* is absorbance, ε is the molar absorption coefficient, *c* is the dopant concentration, *l* is the path length and *n* is the refractive index of the medium. Furthermore, deviation from Beer-Lambert law caused by electrostatic interaction between dyes is seen at concentration >0.01M (Skoog,DA et al 2003). The oscillator strength of absorption bands are measured from integrated absorption coefficients using the formu $f = 4.32 \times 10^{-9} \int \varepsilon(\upsilon) d\upsilon$,

Where

$$\int \varepsilon(\upsilon) d\upsilon \approx \varepsilon(\upsilon) \times \Delta \upsilon \tag{2}$$

In Eqn. 2 $\varepsilon(v)$ is the molar absorption co-efficient at

frequency $\mathcal{U}(\text{cm}^{-1})$ and $\Delta \mathcal{U}$ is the band width at $\frac{1}{2} \mathcal{E}(\mathcal{U})$ measured directly from absorption spectra. Molar absorption co-efficient of MG is calculated directly from the slope of the absorbance - concentration curve in the region where Beer –Lambert law is obeyed. The absorbance values in the Fig. 4(B) are for identical path lengths of 0.1 cm.

Table 1: Optical Parameters of MG

Glass	MG Conc.	^a Abs. Max	^b Os cillator	°FW HM	^d Abs.Co-eff	
	(x 10 ⁻⁵) M	(λ_{abs}) nm	$\operatorname{Strength}(f)$	(Δ) n m	$(\epsilon x 10^4) M^{-1} cm^{-1}$	
M1	1	441	3.93	11377.46	8	
M2	5	439	3.06	8857.36	8	
M3	10	442	5.26	15230.54	8	
M 4	50	447	1.78	10819.33	3.82	

^aPeak Absorption wavelength (λ_{abs}), ^bAbsorption oscillator strength(*f*) of absorption bands at different concentation of MG in SiO₂ sol-gel glass,^c FWHM ($\Delta \nu$), and its molar ^dAbsorption coefficient (\mathcal{E})

The absorption maxima wavelength (λ_{abs}), oscillator strength (f) and FWHM ($\Delta\lambda$) of absorption bands in the four MG doped SiO₂ glasses together with the molar absorption coefficient (ε) of MG are compiled in Table 1.It is seen that molar absorption coefficient, oscillator strength is very much reduced for M4 glass.

3.3 Fluorescence Spectra; Lifetime and Quantum Yield:

MG in solution by itself non-fluorescent with a low fluorescence quantum yield of 7.9×10^{-5} for absorbance maximum of 618 nm (Weichen,X et al 2010; Babendure,J R et al 2003). But when the environment around the dye molecules is altered, say, embedded in solid matrices as in SiO₂ sol-gel glasses, dye exhibits fluorescence with relatively strong intensity. Fluorescence quantum yield is adversely affected by non-radiative losses due to internal rotation and diffusion quenching of emitting dye molecules. These processes are reduced in solid matrix as each dye molecule impregnated into porous solids is caged in a single pore (Meneses-Nava, MA et al 2001).

The fluorescence spectra of MG in SiO₂ sol gel glasses at concentrations for which absorption were recorded and in ethanol (flat line) with MG concentration of 5×10^{-4} M under excitation of 445 nm are presented in Fig. 5(A). It may be noted that no fluorescence was observed from MG in ethanol even when excited by 621 nm, the wavelength at which absorbance maxima is recorded for MG in ethanol. The broad fluorescence bands in the glasses have peaks centred in the range 567-587 nm. Its relative fluorescence intensity is marked by sharp linear increase up to a MG concentration of 5x10⁻⁵ M .Above 5x10⁻⁵ M concentration the variation becomes non-linear and the intensity gradually decreases non-linearly with concentration after reaching a maximum at around 12x10⁻⁵ M concentration[Fig.5 (B)]. The non-linear variation and loss in fluorescence intensity is because of the possible effects of non-radiative de-excitation discussed earlier becoming enhanced at higher concentration.



Fig.5: (A) Emission spectra of MG glasses & MG solution in EtOH (B) Variation of fluorescence intensity with Molar concentration of MG

The radiative (K_r) and non-radiative (K_{nr}) transition probabilities are calculated using the following relations (Costela, A et al 2008):

$$K_r = \frac{\phi}{\tau} \tag{3}$$

and
$$K_{nr} = \frac{(1-\phi)}{\tau} \tag{4}$$

where ϕ and τ are measured fluorescence quantum yield (QY) and decay time, respectively, of MG in SiO₂ matrix. Fluorescence Quantum Yield (ϕ) is measured by comparison to a reference fluorophore of known QY using the single point method by using the following equation (Lakowicz,J R 1999).

$$\phi = \phi_r \frac{I}{I_r} \times \frac{OD_r}{OD} \times \frac{n^2}{n_r^2}$$
(5)

In Eqn. 5, ϕ_r is the quantum yield of the reference fluorophore. In these measurement Riboflavin with $\phi_r = 0.3$ is taken as the reference. *I* is the integrated fluorescence intensity, *OD* is the optical density and *n* is the refractive index of solvent. Subscript _r refers to the reference fluorophore. Decay time (τ) of MG in SiO₂ glasses is estimated by double exponent iteration of the recorded curves. The decay curves for Glasses M1 and M4 are presented in Fig. 6.



Fig. 6: Fluorescence decay of MG in M1 & M4 glasses

The radiative parameters of MG determined using Eqn. 2 - 5 along with peak emission wavelength (λ_p), effective band width ($\Delta \lambda_{eff}$) and decay time (τ) in Glasses M1, M2, M3 and M4 are compiled in Table-2 for 445nm excitation.

Table 2: The radiative parameters of MG

Glass	MG Conc. (x 10 ⁻⁵) M	⁸ Peak Em. Wavelength (λ_p) nm	^b Effective Bandwidth (Δλ _{eff}) nm	°QY (9)	^d Life Time (7) ns	*Radiative Trans. prob. (K,)(x 10 ⁸)s ⁻¹	Non-radiative Trans. prob. (K m) (x 10 ⁸)s ⁻¹
M1	1	573	133.36	0.06	3.58	0.17	2.62
M2	5	587	150.86	0.07	2.90	0.25	3.19
M3	10	567	151.27	0.06	3.41	0.17	2.76
M4	50	585	132.69	0.07	3.01	0.21	3.09

^aPeak emission wavelength (*j*_p), ^bEffective band width (*d*_{*i*,q}), ^cFluorescence Quantum Yield(φ), ^dadiative decay time (*t*), ^dRadiative rate constant (*K*₀), ^bNon-radiative transition probability (*K*_w)

The measured radiative decay time (τ) and fluorescence quantum yield (ϕ) values of ~ 3.58 ns and ~ 0.06, respectively, for MG in the SiO₂ matrix is enhanced ~ 10³ times compared to their values in low viscous solvents . In low viscous solvents excited state lifetime of MG is ~ 2 ps, $\lambda_{abs} = 620$ nm (Ippen,E P et al 1976). The measured decay time (τ) and hence radiative and non-radiative parameters varied on the concentration of MG in the matrices. Furthermore, the variation in radiative properties of M4 glass compared to the other glasses is not as large as its corresponding variation in absorption properties.

Conclusion:

Several absorption and radiative properties of MG trapped in SiO₂ sol gel glass are determined by varying the concentration of MG between 1×10^{-5} and 5×10^{-4} M. Considering emission at 585 nm under excitation of 445nm fluorescence quantum yield (ϕ), radiative decay time (τ) , radiative (K) and non-radiaive transition probability (K_{m}) are investigated to understand the optical behavior of MG confined in the solid matrix. In the confinement SiO₂ matrix MG exhibits relatively strong fluorescence with a quantum yield and decay time enhanced by an order of $\sim 10^3$ compared to its value in low viscous solvents .However, the non-radiative transition probability is still on the larger side. The physical interaction between confined MG molecules and pores of the SiO₂ sol-gel glasses forced a rearrangement of the quinoid structure from para - to ortho- resulting in a blue shift of absorbance maxima (λ_{abs}) in SiO₂ sol-gel glasses. It may be concluded that the results obtained are encouraging for further investigation to be carried out on MG in confinement of different solid matrices and in presence of co-dopants in order to enhance further of its radiative properties.

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