

# Time-resolved fluorescence spectroscopy of cationic dyes incorporated in silica matrix by high pressure compaction

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## Abstract

The cationic dyes 9-amino acridine (9AA) and auramine were incorporated into silica matrix by sol–gel method, producing transparent monoliths. These fluorochromic materials were converted into powder and compacted at room temperature at 6 GPa to form optical crack-free compact glasses. The dyes incorporated in these three forms (monolith, powder and compact glass) were studied by time-resolved fluorescence spectroscopy in order to obtain information of the excited state dynamics under soft and compressed silica environment. Both dyes have multi-exponential decays in these solid phases. 9AA in monolith and in silica powder shows biexponential decay with components of 8.4–9.0 and 23–24 ns. In compact glass, a fast component of 2.4 ns is detected in addition to the two cited slow components, and it has been ascribed to electronic energy migration among dyes and exciton trapping by dark dimers. For auramine, a dye that fluoresces in rigid matrix by precluding its fast intramolecular twisting and subsequent non-radiative deactivation, the three types of solids enhance the fluorescence signal and give rise to decay processes from picoseconds to nanoseconds in the time scale. In monolith and silica powder, the behavior is practically the same, with three decay components of 0.3, 1.3 and 4.3 ns. However, in compact glass, the two first decay components are shifted to larger values of 0.63 and 2.3 ns, while the third component remains practically constant with a value of 4.1 ns. These results are analyzed with the model of emissive and non-emissive states of auramine under restricted torsional molecular motion.

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## 1. Introduction

The fluorescence of organic dyes has been so far well studied in homogeneous and in micro-heterogeneous media like polymers, nanoparticles, micelles and biomolecules in solution [1–3]. Fluorescence probe methods have been developed for many applications in chemistry and biology as practical results of these studies. Fluorophores and their properties have also been investigated in solids, porous materials and nanotubes, and organic modified surfaces [4–6]. Fluorescent dyes incorporated in solid media have been used in optics as filters, active gratings, waveguides, laser media and LEDs [7–11].

In most of the cases, dyes are adsorbed onto the solid phase or surface from a solution or they are deposited by casting or spin coating to form thin films. On the other hand, the entrapment of organic dyes in silica matrix has been achieved by sol–gel method, which by drying process produces porous material [5,6]. However, porosity facilitates the leaching of the dye when the material is in contact with liquid solvents, a problem that also appears in thin films, unless the dye is chemically bound to the matrix. To overcome this problem and to produce more stable silica-doped materials, a high pressure compaction at room temperature, which causes a cold sintering of the silica powder, has been recently developed [12–15].

From the point of view of fluorescence properties, a dye in a surface has in many cases tremendous differences from behavior in liquid solution. Specific interactions of the dye with the surface, restricted molecular motion, self-aggregation and strong

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exciton coupling, are some of the effects responsible for the unique properties found in solids. In this contribution, two dyes of known fluorescence properties in water and liquid organic solvents (9-aminoacridine and auramine) are studied in three types of silica matrices by time-resolved fluorescence spectroscopy. The dyes are incorporated in silica by sol–gel method, and the solvent drying gives rise to low-density transparent monoliths. These materials are converted into silica powder, and then to optical crack-free compact glass by using high pressure technique at room temperature.

## 2. Experimental

The silica powders doped with 9AA and auramine (from Aldrich Co. and recrystallized from methanol/acetone), were obtained by the sol–gel technique based on the hydrolysis and polycondensation of the precursor tetraethyl orthosilicate (5 ml, TEOS, Merck, Schuchardt, for synthesis) in water (1.6 ml) and ethanol (5 ml, EtOH, Merck, grade for analysis) solutions under acidic conditions (0.1 ml, HF, 40%, w/w, grade for analysis) [12–15]. The dyes (1 mg) were previously dissolved in ethanol and this solution was added to TEOS. Both samples were prepared with water-to-TEOS molar ratio 4:1 and the analytical concentration ratio for 9AA and auramine was, respectively,  $1.8 \times 10^{-4}$  and  $1.5 \times 10^{-4}$  mol dye/mol TEOS. The sol–gel solution was distributed in three small plastic dishes, which were inside a large Petri dish and just covered, without sealing. Drying and aging were carried out in air, at room temperature for about 15 days. The slow solvent evaporation at room temperature of these sol–gel solutions rendered the monolith samples, which are comminuted in an agate mortar, during 7 min, to obtain the best quality powder to be compacted. This control makes the process quite reproducible. The powder was initially pre-compacted to approximately 0.2 GPa in a piston–cylinder type apparatus. This sample was placed inside a lead container of 8 mm diameter, which operated as a quasi-hydrostatic pressure-transmitting medium, and the full compaction at 6 GPa was performed in a toroidal-type high pressure chamber during 10 min to promote the cold sintering process of the silica sample. Detailed description of the high pressure method as well as of the characterization of silica matrices with incorporated dyes are given elsewhere [12–17]. The density of the cylindrical compact of about 3 mm diameter was estimated by using a picnometer. The dye concentration in the samples was determined from UV–vis absorption measurement of the dye extracted with methanol from a given amount of silica powder.

Fluorescence spectra and decays of the solid samples were measured by time-correlated single photon counting technique using a CD-900 Edinburgh spectrometer equipped with Glan–Thompson polarizers, and a Peltier cooled PMT (Hamamatsu R955) or a Hamamatsu R3809U-50 MCP as photon detectors. The light pulse was provided by frequency doubling the 200 fs laser pulse of Mira 900 Ti–sapphire laser pumped by a Verdi 5W coherent. The laser pulsed frequency was reduced by using a Conoptics pulse picker system [18]. The solid samples were placed in front-face irradiation compartment. The fluorescence decays were analyzed by reconvolu-

tion procedure with multi-exponential models and using global methods [3].

## 3. Results and discussion

The solid samples (monolith, powder and compact) of the dyes are highly fluorescent materials when incorporating 9AA but only moderate emission occurs with auramine. The concentrations of the dye in the investigated samples are 0.6 mg/g of silica for 9AA and 0.90 mg/g of silica for auramine. In general, the monoliths are soft materials with low density of the order of  $0.5 \text{ g/cm}^3$ , while the compact glasses are hard solids that are approximately four times denser ( $2.0 \text{ g/cm}^3$ , approaching to 90% of the full density of silica). In a compact glass, the dye is entrapped in closed nanopores, but a monolith is an open porous material that does not prevent the leaching of the dye when immersed in polar organic solvents [12,15].

The emission spectra of 9AA in the three solid samples are reported in Fig. 1. In powder and in monolith, the emission maximum occurs at 454 nm, but in compact glass there is a small redshift of about 3 nm. Although the structured emission of 9AA in these samples is in the same spectral region of that of the monoprotonated dye in methanol or water solution [19], the vibronic band shape is different. In methanol, the two first vibronic peaks have similar intensity [21], while in these solid samples the second vibronic peak dominates the emission. This would indicate that silica surface is disturbing excited-state coupling with ground state, due to specific interaction with the dye.

In the case of solid samples with auramine, the emission occurs at the same maximum (485 nm) for the three solids, however the fluorescence intensity of the compact is higher, and its emission spectrum shows a clear shoulder at about 602 nm (see Fig. 2). This shoulder in auramine emission spectrum appears as long as the dye is in a restricted medium. It may be ascribed to the partial charge transfer in excited state competing with the fast deactivation by internal torsion relaxation of the dye. In water or methanol, auramine has a very low fluorescence with maximum at about 460 nm. It is well known that for auramine, fluorescence

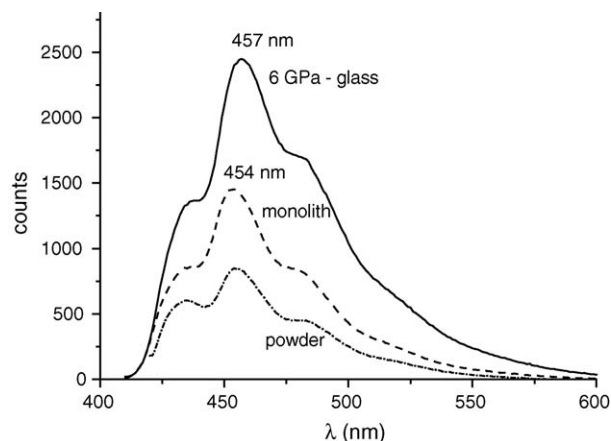


Fig. 1. Emission spectra of 9-aminoacridine in silica matrices ( $\lambda_{\text{exc}} = 400 \text{ nm}$ ).

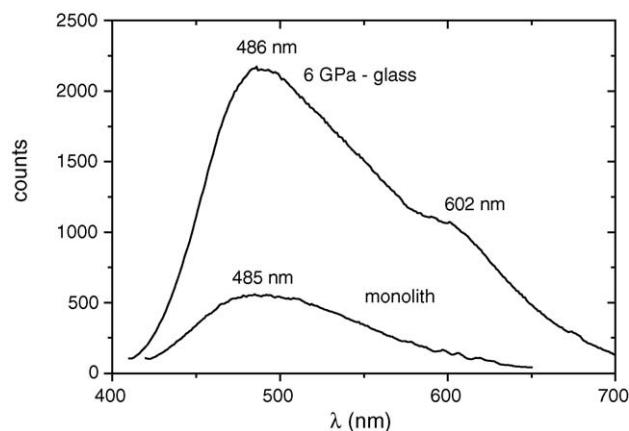


Fig. 2. Emission spectra of auramine in silica matrices ( $\lambda_{\text{exc}} = 400$  nm).

emission increases and shifts to red when this dye is in a high viscous or solid media, and bound to polymers [20–26].

The perceptible changes in emission spectrum with silica samples would indicate slightly different arrangement, distribution and binding of the dyes with the type of solid support. This fact will become evident from the time-resolved behavior of the dyes. 9AA in monolith and in silica powder shows bi-exponential decay with components of 8.4–9.0 and 23–24 ns. In compact glass, a fast component of 2.4 ns is also detected in addition to the two slow components. The decay times of the two dyes in the solid samples are reported in Table 1. In the case of 9AA samples, the global analysis of the decay surface with linked components was applied.

A decay trace of 9AA in a compact glass is shown in Fig. 3, and it illustrates the multi-exponential character of the fluorescence deactivation of this dye in this material.

For auramine in the silica samples, the decay process occurs from picoseconds to nanoseconds in time scale. In monolith and in silica powder, the decays are similar, with three components of 0.3, 1.3 and 4.3 ns. However, in compact glass, the two first decay components are shifted to larger values of 0.63 and 2.3 ns, while the third one remains practically constant with a value of 4.1 ns. The increase of the average lifetime of auramine is only fairly small and it changes from 2.1, 2.2 and 2.7 ns for monolith, powder and compact glass, respectively. The wavelength-dependent fluorescence decay of auramine does not allow a global analysis

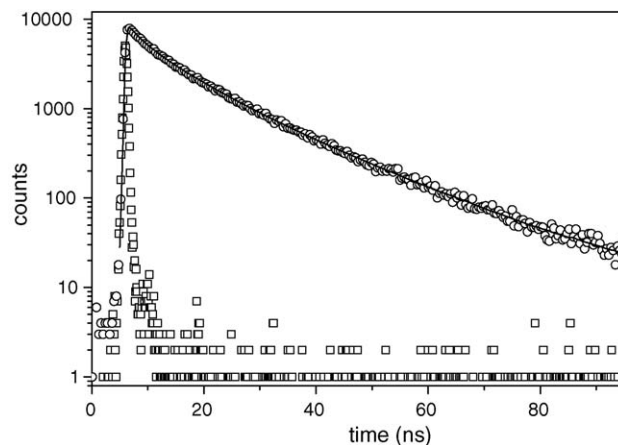


Fig. 3. Fluorescence decay of 9AA in a compact silica glass obtained with high pressure of 6 GPa.

with linked decay times as performed with the 9AA samples. The fluorescence decay of auramine in silica powder is given in Fig. 4.

The non-radiative deactivation of the excited state of auramine occurs by intramolecular twisting of the phenyl groups and possible charge delocalization from the electron-donating  $\text{N}(\text{CH}_3)_2$  group [20–22] (dye molecular structure is given in Fig. 5). Thus, the silica is providing a high friction environ-

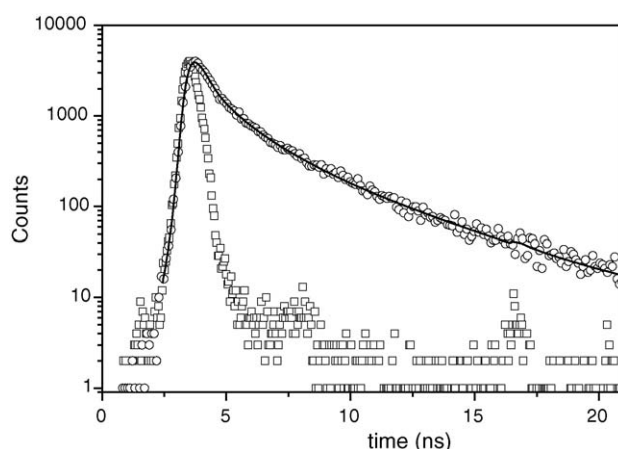


Fig. 4. Fluorescence decay of auramine incorporated in silica powder.

Table 1  
Fluorescence decay times of 9-aminoacridine and auramine in silica matrices

	Silica sample	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)	$\chi$	
9-Aminoacridine	$\lambda_{\text{exc}} = 389$ nm	–	$8.4 \pm 1.9$	$23.3 \pm 2.1$	1.152	
	$\lambda_{\text{em}} = 420\text{--}530$ nm	–	$9.0 \pm 2.2$	$23.9 \pm 2.3$	1.078	
	Global analysis <sup>a</sup>	Glass 6 GPa	$2.4 \pm 0.6$	$11.1 \pm 1.4$	$23.7 \pm 2.2$	1.023
Auramine	$\lambda_{\text{exc}} = 385$ nm	Powder	$0.30 \pm 0.02$	$1.32 \pm 0.06$	$4.18 \pm 0.11$	1.110
	$\lambda_{\text{em}} = 490$ nm	Monolith	$0.31 \pm 0.02$	$1.25 \pm 0.07$	$4.42 \pm 0.11$	1.142
	Single-curve	Glass 6 GPa	$0.63 \pm 0.02$	$2.30 \pm 0.20$	$4.10 \pm 0.26$	1.106

<sup>a</sup> Analysis of 11 decay traces.  $\chi$  is the chi-square value in the multi-exponential fit.

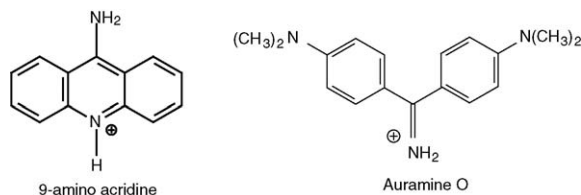


Fig. 5. Dye molecules incorporated in silica matrices in monoprotonated form.

ment that precludes partially this deactivation pathway, and on the other hand, the binding of the dye to the surface is decreasing the electron donating capacity of the amine groups. These two effects are responsible for the long-lived fluorescence of auramine adsorbed in silica. In a non-viscous solvent, the two decay times of auramine are about 1–5 ps in ethanol, but a third long-lived component in the range of 60 ps appears when auramine is in a high viscous medium like *n*-decanol [22]. When adsorbed in solids or bound to polymers and biopolymers, its average fluorescence lifetime may increase up to hundreds of picoseconds. Thus, in compact glass the restriction to the torsional molecular motion of the dye may be enhanced compared to silica powder and monolith surfaces, which explains the shift of two first decay times to larger values. Another interesting result is the long-lived component of about 4.2 ns appearing in all three samples. It is larger than the long fluorescence lifetime of 2.3 ns found for auramine adsorbed on microcrystalline cellulose [23,24], or the values measured with this dye in poly(acrylic acid) matrix under different pressures [25].

In contrast, sample with 9AA decreases its average decay time when in a more restricted and dense medium such as the compact glass. The presence of the fast decay component of 9AA in compact glasses indicates a quenching process. Acridinic dyes are fluorescent probes with emission quantum yield and lifetime that are dependent on solvent, pH and solubilization site, as reported for their photophysical properties in complex liquid like micelle solutions [27]. The two slow decay components could be ascribed to different interactions of the dye through hydrogen bonding with specific silica sites. The interaction of the exocyclic  $\text{NH}_2$  and endocyclic  $\text{N-H}$  group of 9AA with  $\text{SiO}_2$  or with residual silanol ( $\text{Si-OH}$ ) group by hydrogen bonding is predicted to be very specific in ground and excited states (9AA molecular structure is given in Fig. 5). For instance,  $\text{SiO}_2$  would form a H-bond with the dye through a six-member ring involving the exocyclic  $\text{NH}_2$ . On the other hand,  $\text{SiO-H}$  group could interact more specifically with the nitrogen atom.

The fluorescence lifetime of 9AA in acidic and basic methanol is 15 and 9.5 ns, and its fluorescence quantum yields are 0.54 and 0.45, respectively [19]. Its radiative decay rate constant is of the order of  $3.6$  and  $4.7 \times 10^7 \text{ s}^{-1}$  for the monoprotonated and neutral species, respectively. It follows that the long-lived decay time of 9AA of about 24 ns seems to originate from the monoprotonated species but with a higher quantum yield. This effect could be obtained by hindering some non-radiative deactivation pathway of 9AA when in silica. The H-bonding of the exocyclic  $\text{NH}_2$  with  $\text{SiO}_2$  may restrict the rotational motion of amine group reducing then the non-radiative decay rate constant. This long-lived component of about 23–24 ns could be

related to the diprotonated 9AA in aqueous sulfuric acid solution, for which the value of 25 ns is reported in literature [28]. However, the diprotonated species has an emission spectrum strongly redshifted by about 40 nm, and a bandshape with only two emission maxima at 471 and 496 nm, when compared with the monoprotonated species. Such spectral properties are not found in the emission spectra of 9AA in silica matrices (see Fig. 1). The % of the long-lived component indicated by the pre-exponential factor (vide infra) is high enough to modulate the emission bandshape, but this effect does not occur as would be expected if the diprotonated species were present in a large percent. The decay time observed in the range of 8.4–11 ns ( $\tau_2$ ) is ascribed to the presence of a fraction of neutral species. The relative % of the components is practically independent of the emission wavelength and are 16 and 84% for  $b_2$  and  $b_3$  in both 9AA in powder and in monolith. In the compact glass with triexponential decay, the short component contributes with only 5% while the two long-lived components give 43 and 52%. Thus, the similar weight between the two long-lived components in the glass points out that the quenching seems to occur mainly from the long-lived fraction with about 24 ns decay time.

The presence of the short-lived component of about 2.4 ns indicates a fast fluorescence quenching process without molecular diffusion of the species. Acridinic dyes exhibit self-aggregation [29,30]. It has been recently reported that self-aggregation of 9AA in pre-micellar solution of anionic surfactant generates H-type of dimers in which the parallel transition dipoles are out-of-phase [30] (a forbidden transition in the exciton model). These dimers are active quenchers because they have no transition dipole moment to the ground state, and for the same reason they cannot transfer or migrate the electronic energy to another chromophore by means of a Förster type transfer mechanism. They work as exciton trapping or quenching centers (dark dimers). As the compact glass is four times more concentrated in 9AA than the monolith and powder, 9AA could form in this dense medium statistical dimers with nearly close geometry of the dark H-dimer, and therefore they will act as fluorescence quenching centers during energy migration by multipole interaction. The trial fitting of the decay of 9AA in compact glass using Förster dipole–dipole decay function plus an extra exponential term did not result in acceptable fitting parameters, which indicates that simple dipole–dipole mechanism do not explain properly the quenching process in this system.

The presence of statistical dimer acting as quenchers is predicted when planar dyes are dispersed in disordered solids or films, because a more parallel configuration is favored by steric hindrance [31,32]. In addition to this effect, the dye in silica powder has a solubilization toward the surface of the particles. When these particles are cold sintered by applying a high pressure, the particle surface contact is enhanced, porous average size is reduced and those effects could provide a close approaching of a fraction of the dye molecules. It is worthwhile to mention that the analytical concentration of 9AA in the compact glass used is of the order of  $6 \times 10^{-3} \text{ M}$ , much higher than the threshold of dimerization in aqueous solution ( $10^{-5}$  to  $10^{-4} \text{ M}$ ). Dimerization of basic dyes in clays is well recognized as an important process in solute–matrix interaction [4,33,34]. Pyrene

pi-stacking and excimer formation has also been observed on the porous surface of silica gels [35].

#### 4. Conclusions

The dye-doped silica matrices studied are fluorescent materials in which the spectral and time-resolved fluorescence properties are function of the degree of compactness of the solid. Monoliths and powder obtained by sol-gel method are similar in photophysical properties of the dyes, but dye-doped compact glasses obtained by high pressure are dense optical materials with different behavior. In compact glasses, the concentration of the incorporated dye increases as a result of the area and volume reduction, and therefore bimolecular interactions causing energy migration and trapping may occur, as observed in 9AA-silica system. On the other hand, the dye squeezed in silica matrix may change its excited state dynamics due to restriction of some intramolecular relaxation motions as in the case of the auramine photophysics.

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