Plasma exposure to the solid sample of viologen was performed in a 25-mL Erlenmeyer flask. The sample was then mixed with degassed DMF and the spectra measured.

ESR spectra were measured on a quartz probe at room temperature using JES-FEIX spectrometer (Nippon Denshi Ltd.).

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Registry No. BV^{2+}, 1102-19-8; BV–Br, 27768-49-6; MV–I, 1983-60-4; MV, 1910-42-5; BuV–Br, 32449-18-6; PXV, 31586-24-0; MB, 61-73-4; BG, 633-03-4; DPPH, 1898-66-4; 4,4′-bipyridine·1,4-bis(chloromethyl)benzene copolymer, 31533-65-0.

The Nature of the Silica Cage As Reflected by Spectral Changes and Enhanced Photostability of Trapped Rhodamine 6G

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Rhodamine 6G was embedded in a matrix of silica gel glass by the sol to gel technique. The special features of an inorganic oxide glass as a carrier of an organic dye are discussed in comparison with other solid environments, such as adsorption on powders and within porous glasses, thin films, and doping of plastic matrices. Among the advantages mentioned are photostability of the glass matrix, trapping of the dye molecule, and its total isolation from undesired interactions with its neighboring dye molecules, impurities, and photodecomposition products; nonleachability of the dye; the ability to reach stable very high dye concentrations; reduction of translational, rotational, and vibrational degrees of freedom of the trapped dye; good transparency down to the UV. Embedding R6G in the silica glass enables one to reach high concentrations without undesirable dye aggregation. Stokes shift is larger in the glass than in water. Photostability of the dye is higher in the glass than in water. A remarkable front-face fluorescence stability is observed. These observations, and a critical review of the literature, are used to elucidate the nature of the silica glass cage: it is suggested that it is a hydroxylic polar environment, though somewhat less polar than water. The rigidity of the cage is discussed in terms of required reorientation of the environment around an excited state.

Introduction

Organic laser dyes have found in the past two decades an increasing variety of applications in spectroscopy, in optics, and in lasers. Rhodamine 6G (R6G) has been one of the most frequently used probes in these studies, due to its high quantum yield of fluorescence, absorption and emission in the visible 500–600-nm range, and good laser properties.[1]

One of the key problems in the investigation and application of organic laser dyes is the matrix which hosts the dye. This is not surprising, since the nature of the matrix affects virtually all characteristics of the dye, e.g., it causes spectral shifts of both absorption and emission, it affects photostability, and it alters the distribution between processes the excited state may undergo, such as intersystem crossing, collisional energy loss, and consequently also fluorescence lifetime.[1]

Special attention has been given to solid matrices, including solid solutions, in contradistinction to fluid environments. The solid environments used to carry R6G as well as other fluorescent organic dyes may be grouped into four categories: (a) high surface area powdered materials in slurries or as colloids,[2] such as our recent study of R6G adsorbed on clays,[3] (b) high surface area porous glasses,[4,5] such as our study of fluorescent organometallic compounds adsorbed on Vycor porous glass and on disks of compressed fumed silica,[6] (c) polymeric blocks and thin films in which the dye is homogeneously distributed,[7,8] (d) monolayers and submonolayers of low surface area supports.[9] Here we wish to describe yet another solid matrix offering several unique features, namely, an *inorganic oxide glass* within which the dye is embedded. Recent developments in the low-temperature sol–gel process of oxide-glass preparations[10,11] opened the possibility to use these superior materials instead of organic carriers. Specifically we report here some preliminary observations made on the system $R6G^+Cl^-$/silica gel glass. Of special interest are the increase in fluorescence stability, the lack of aggregation at concentration of 10^{-4} M and higher, the increase in Stokes shift, and the UV transparency of the matrix. Unexpectedly, the rate of decrease in front-face fluorescence intensity of the doped glass was lower than the rate of absorption fading.

Advantages of the New Solid Dye Carrier

We list now a number of advantages in using an inorganic glass as a carrier for organic dyes, in comparison to fluid media and

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to the other solid matrices described above:

1. There is no translational freedom for the dye. Intermolecular collisional deactivation is thus avoided. Each molecule is trapped in its own cage.

2. Initial impurities in the dye are isolated and do not interfere by destructive (photo)processes. Embedding the dye in the glass amounts to effective purification of the dye.

3. Similarly, photodecomposition products do not migrate and thus cannot facilitate further photodecomposition.

4. Unlike permeable organic plastics, and unlike adsorbed dyes, the molecule of interest is totally isolated from surrounding gas, liquid, or polymeric environments.

5. A severe limitation of plastic carriers[7] and organic solvents[12] is their low photostability and low thermal stability. Silica glass is inert photochemically and can tolerate heat well above organic decomposition temperatures.

6. The doped glass is nonleachable (see below). Leachability is a problem in films or in porous supports which carry the dye at the surface.

7. The solid cage reduces internal rotational modes in the dye, probably to a greater extent than the relatively flexible organic polymer molecules. Rotational relaxation of the excited state of laser dyes is one of the main modes of nonradiative energy loss.[13]

8. Isolation of the dye molecules from each other enables one to reach unconventional high dye concentration, without changing the local environment, from the points of view of chemical character and probability of deactivation processes (e.g., aggregation and translational collision). In other words, optical considerations, such as reabsorption processes, become isolated from many other high-concentration interferences.

9. Many plastics absorb in the near-UV; the above-mentioned powders, Rayleigh scatter in this range. Our silica glass is devoid of these optical obstacles (Figure 1) well beyond the visible range.

10. The desired geometry is easily obtainable either at the sol–gel transition stage or by manipulation on the final glass.

Experimental Section

Solidified monolithic silica gel glasses were prepared by basic hydrolysis of $Si(OMe)_4$, followed by slow (1 week) condensation polymerization at room temperature following the procedure of Yamane et al.[11] $R6G^+Cl^-$ was added prior to gellation. The resulting shrunken glass in the form of a disk, 2 cm in diameter, 1.3 mm thick, was further dried for 24 h at 65 °C to remove physisorbed water and methanol. Front-phase fluorescence (λ_{ex} = 523 nm) was measured on an Aminco-SLM spectrofluorimeter. Absorption spectra were recorded on a Cary-219 spectrometer. Photodecomposition was carried out by placing the samples in front (60 cm) of a 1.6-kW halogen–quartz lamp, with proper cooling and filtering of <300 nm. Radiation dosage as measured by a radiometer was 65.2 mW/cm^2.

Results and Discussion

1. Transparency due to the Small Size of the Cages. The glass formed in the sol–gel process is porous. However, the pore radii are much smaller (1.5–10 nm)[11] than the near-UV or visible radiation wavelength. The cages are probably even smaller than 1.5 nm (see section 3 below). Consequently, the glass is transparent (Figure 1). In comparison, the commonly used dye carrier, poly(methylmethacrylate), filters light <330 nm.

2. Nonleachability from the Cage. It was important to establish that the dye molecules are indeed incorporated within the bulk of the glass and not adsorbed at the exposed walls of the pores. For comparison purposes, an undoped porous gel glass was prepared, and R6G then adsorbed onto its surface, as previously described.[6] A doped gel glass and an adsorbed glass were then immersed in two leaching solvents: water and methanol. Equilibrium between adsorbed and solvated R6G was reached (quickly for methanol, slower with water) in the case of the adsorbed glass, and the solvents were strongly colored. No detectable (by eye or by instrument) leakage of R6G was observed from the doped glass. It is thus estabished that R6G is either completely trapped in a surrounding rigid case or that R6G molecules are trapped in bottleneck pores,[14] with rigid pore entrances of diameter smaller than the effective diameters of methanol or water (~4 Å).[15]

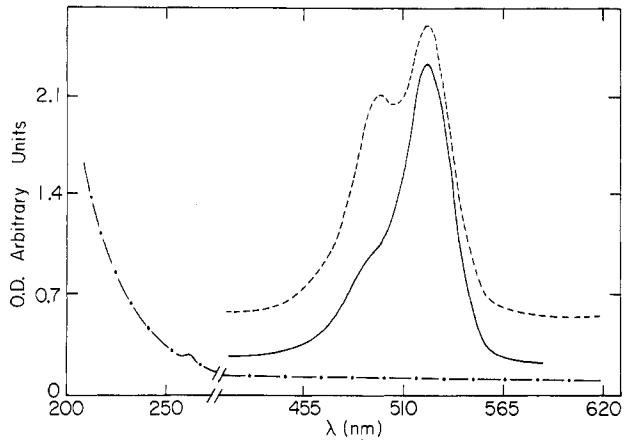

Figure 1. Absorption spectra of rhodamine 6G: (---) 1.4×10^{-4} M in water. The dimer is clearly visible at 496 nm. (—) 1.6×10^{-4} M in gel glass; (-·-·) undoped glass.

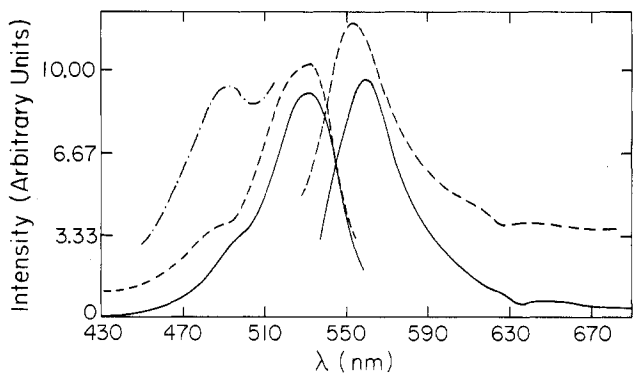

Figure 2. Emission and excitation (λ_{ex} = 523 nm) spectra of rhodamine 6G(----) in solution (1.4×10^{-4} M) and (—) in gel glass (1.6×10^{-4} M). The dimer (-·-·) is reproduced from Figure 1 for comparison purpose.

3. Lack of Dimerization as Reflecting Some Properties of the Cage. The dimerizations and aggregations of laser dyes have gained an intensive and on-going study because of the strong effects of these processes on spectral and lasing properties. At 10^{-4} M, in water, R6G is not lasing due to dimerization.[16] Much controvery exists on the question of whether R6G dimers fluoresce[17-19] or not.[16,20] It seems to us that the bulk of evidence agrees with Levshin's old conclusion (1927[21]) that dye aggregation is the basic cause for concentration quenching of dye luminescence. Drexhage pointed out[16] that not only do these aggregates not fluoresce but they also reabsorb fluorescence from the monomer. Chibisov and Slarnova have shown[18] that fluorescence quenching in R6G aggregates is mainly due to efficient intersystem crossing.

In view of all this, we found it of advantage that, when embedded in our glasses, R6G does not aggregate much beyond the limit of 10^{-4} M (moles of dye per liter glass) (e.g., Figure 1). A

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similar deaggregation effect was observed when R6G was adsorbed on the surface of the porous glass, at least up to 10^{-3} M (or when adsorbed on smectite clays[3]). Lack of aggregation is also evident from the excitation spectrum of the doped glass (Figure 2). In solution, deaggregation of R6G may be achieved by using organic solvents,[20,22] mixtures of water and organic solvents,[20] and various water-soluble organic additives.[16] However, unlike silica glass, all these organic media are photolabile and actively participate in photodegradation processes.[12]

The fact that in the glass R6G does not aggregate may shed some light on the nature of the local environment of the dye, although, as was the case with the question of aggregate fluorescence, controversy still exists on the role of water in causing aggregation.[16] Special attention was given to solvent dielectric constants as a stabilizing force, reducing Coulombic repulsion.[23] However, as pointed out correctly by Rohatgi and Singhal,[24] the (unknown) microscopic dielectric constant around the dye and not the bulk constant should be of interest. Arvan and Zaitseva[25] clearly demonstrated this point. Following Drexhage and Reynold's argumentation,[26] it seems to us that much of the published experimental data points to a picture in which the higher the hydrophobicity of the dye, the greater its tendency to form aggregates. Consequently, a polycationic organic species, such as the R6G dimer dication, is more easily watersoluble than a monocationic organic species.

Two types of silicon groups probably form the walls of the silica glass cage: silanols (Si–OH) and siloxanes (Si–O–Si).[14] Both groups are indeed of lower polarity and higher hydrophobicity than water. Leermakers has measured[27] the Kossower Z value[28] of silica gel and found $Z = 88$, which is in between the values for methanol and water. The hydrophobicity of siloxane surfaces is well established.[29] For R6G attached to siloxane planes in clays we found an effective polarity resembling the lower-chain alkanols as reflected in absorption maxima red shifts.[3] The silica cage is, however, probably rich in silanols (and perhaps few residual physisorbed water molecules) as judged from the fact that no such red shift in λ_{max} compared to water (525 nm) is observed. Taking into account Leermaker's measurement[27] and Chou et al.[22] measurements in which water and methanol gave the same λ_{max}, we felt that, if a comparison to solvents is desired, the cage may be regarded as a hydroxylic, relatively polar environment, less polar than water.

The fact that no dimers are observed may serve as an indication to the size of the cage: roughly that of a single molecule, i.e., 10 Å; otherwise, sufficient water would be trapped (a) to form dimers at the high dye concentration employed and (b) to remove the dye from the cage wall as indicated by the experiment of leaching the adsorbed dye, so that the fluorescence would not have been red shifted compared to water (next section).

4. Cage Rigidity and Fluorescence Red Shift. Red shifts (5–10 nm) have been observed for the emission maximum (Figure 2). This desirable increase in Stokes shift (from 30 to 40 nm) may shed more light on the nature of the silica cage. In most cases spectral shifts in fluorescence maxima are associated with the effects of solvent molecules having sufficient time to reorient themselves around an equilibrium excited state. This new orientation is different from the solvent cage of the ground state and the corresponding Franck–Condon excited state.[30] A silica glass cage is unique in that the only possible reorientation of the cage walls are rotations around the Si–O–H bonds, i.e., relocation of hydrogen bonding to the dye. Under this restricted cage freedom, the rotational movements of the *molecule*, rather than its surroundings, become important in excited-state stabilization by interactions with the cage. As discussed above, the glass walls are less polar than water; this was further corroborated by the fluorescence red shift, such as observed also in nonaqueous solvents.[1] These red shifts may be interpreted as reflecting a decrease in the dipole moment of the excited molecule.[30] Apparently, the restricted motions of the silica walls and of the dye are sufficient for the desired stabilizing mutual reorientation.

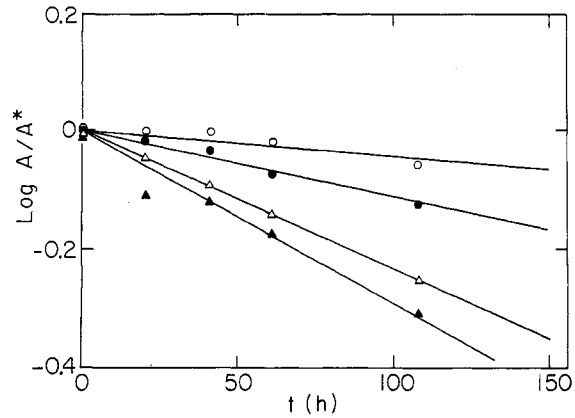

Figure 3. Photodecomposition of rhodamine 6G. A/A^* is the relative decrease in intensity of either absorption (△ in water, ● in glass) or emission (▲ in water, ○ in glass). Concentration in water: 10^{-4} M; in glass: 1.5×10^{-4} M. All fluorescence measurements, including water, were by front-face geometry, and comparison to $t = 0$ (A^*) carried out repeatedly for each point. See also Table I.

TABLE I: Rhodamine 6G Absorption and Fluorescence Photostability

	$t_{1/2}$, h	k, 10^{-3} h^{-1}
fluorescence in water	86	8.11 ± 0.16
absorption in water	111	6.25 ± 0.02
fluorescence in glass	622	0.11 ± 0.04
absorption in glass	235	2.95 ± 0.03

5. Absorption and Fluorescence Photostability. It is perhaps expected, in view of the material presented so far, to find an increase in photostability: trapping of the dye molecule, their photodecomposition products, and other impurities; deaggregation; and reduction of both vibrational and rotational modes of energy dissipation all contribute to the enhanced stability. Comparative first-order decomposition[8,31] analysis, under the conditions described in the Experimental Section, revealed the data collected in Table I and in Figure 3. In water, the fluorescence intensity falls faster than absorption intensity. This is due to the great sensitivity of fluorescence to a steady increase of photodecomposition products. In glass, however, this order is reversed: the fluorescence intensity decrease is much slower than absorption intensity decrease. This interesting phenomenon may perhaps be understood by noticing that, in the bleaching process, R6G is transformed into colorless products.[31] Therefore, in measuring the glass fluorescence by a front-face geometry, new deeper layers of undestroyed R6G molecules are constantly exposed, and their emission is not blocked by the transparent photodecomposition products which are trapped in the upper layers. This constant renewability of doped glass layers, which amounts to an increase in the apparent fluorescence stability, seems to us of important practical consequences such as for dye blocks for dye lasers. Absorption spectroscopy, on the other hand, reveals the gradual decrease in number of dye molecules along the measurement path length and hence the difference in apparent decrease in photostability, compared to fluorescent measurements.

Comparative measurements by transmission fluorescence, either at 180° or at 90°, are impossible at this preliminary stage due

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to the high dye concentrations employed and due to scattering from the edges. Optical improvements are in progress.

The potential uses of fluorescent gel glasses in photoprocesses and optics are numerous. Examples are light guides for lasers and for luminescent solar concentrators and filters for linear and nonlinear optics. These and other uses as well as the material described in this paper are patent pending.

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Registry No. Rhodamine 6G, 989-38-8; silica, 7631-86-9.

Vibrational Spectroscopic Study of the Interlamellar Kaolinite–Dimethyl Sulfoxide Complex

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The intercalation complex involving the layer silicate kaolinite and dimethyl sulfoxide (Me_2SO) is studied through the combined application of Raman and infrared absorption spectroscopy. The spectral data indicated that the Me_2SO molecules were in a restricted, highly ordered interlamellar conformation, with the oxygen of the sulfonyl group hydrogen bonded to OH groups in the gibbsite-sheet surface of kaolinite and the sulfur atom of the group keyed into the ditrigonal cavity on the opposing siloxane surface of the mineral. The methyl group in the intercalated molecule appeared to be influenced by both of the opposing mineral surfaces to the extent that vibrational degeneracy in the CH stretching modes was lifted.

Introduction

The ability of interlamellar layer aluminosilicate surfaces to accommodate organic molecules and modify the structure and reactivity has prompted renewed interest in clay minerals as selective catalysts.[1-3] Of importance equal to the chemical conversions catalyzed by interlamellar surfaces are the structural perturbations that they induce in intercalated organic species. These perturbations provide a means of investigating the structure and reactivity of clay mineral surfaces themselves, similar to the use of adsorbed inorganic species as probes in electron spin resonance studies of interlamellar layer silicate surfaces.[4,5]

Infrared (IR) absorption spectroscopy has been the only vibrational spectroscopic method used previously to study intercalation complexes formed between clay minerals and organic compounds. Although the IR technique is characterized by a high sensitivity to low concentrations of adsorbed species,[6] it is limited severely by the opacity of the adsorbent.[7,8] This restriction is especially evident in studies of adsorbed species on clay minerals and oxides, where strong IR absorption bands below 1300 cm^{-1}, associated with framework vibrational modes, can obscure a considerable portion of the IR spectrum of an adsorbed species.[9] By contrast, the framework vibrational modes of clay minerals and oxides are only weakly Raman active.[10,11] Thus, Raman spectroscopy may be useful for studying the vibrational spectra of clay mineral intercalation complexes. The objective of the present paper is to exploit this possibility by investigating both the vibrational Raman and IR spectra of the kaolinite–dimethyl sulfoxide (Me_2SO) intercalation complex, with emphasis placed on the unique ability of the Raman technique to probe vibrational modes below 1300 cm^{-1}.

Kaolinite, a 1:1 layer aluminosilicate,[11] has been observed to intercalate a relatively large number of polar organic compounds including dimethyl sulfoxide,[12-15] formamide, *N*-methylformamide, dimethylformamide, and acetamide,[16-19] and pyridine *N*-oxide.[20] The kaolinite–Me_2SO complex should provide an especially good example for a comparativie Raman–IR study because of the high stability of the complex relative to other kaolinite intercalation complexes,[13] the appearance of well-defined, discrete bands in the hydroxyl stretching region of the IR spectrum of the complex,[14] and the high Raman activity of many of the vibrational modes of Me_2SO.[21]

True intercalation of Me_2SO into kaolinite, as opposed to multilayer adsorption on external surfaces, has been confirmed

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