DODCI molecules incorporated in sol–gel glasses: the interaction with the silica matrix

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Abstract

The optical properties of the dye DODCI (3,3'-diethyloxadicarbocyanine iodide) incorporated in sol–gel silica-glass matrices have been investigated with regard to interaction with the surrounding silica cage. The absorption and emission spectra have been measured in silica-glass samples with different pore sizes and compared with the spectra obtained in liquid solutions that simulate different environments for the dye molecule. Measurements of a DODCI-derivative molecular structure have been performed by NMR spectroscopy in dimethyl sulfoxide. The results suggest that new electronic states are produced in the trapped molecule, for glass-pore sizes in the range of 2.5–3.5 nm, as a result of the attack of Si–O groups on the conjugate chain and the protonation to the dicationic form. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Silica-based glasses obtained through the sol–gel low-temperature synthesis have recently received considerable attention for application in integrated optics [1–3]. Funzionalized transparent monoliths as well as good-quality films for optical waveguides can be prepared using this simple and low-cost procedure. Moreover, the incorporation of organic molecules, thanks to the low temperature of preparation, opens promising avenues for new optical materials. Guided-wave optical amplification [4], lasing [5], electrooptical modulation [6] and third-order optical non-linearity [7] have already been demonstrated in several research laboratories and the field is mature for the transfer to the industrial framework.

An important issue addressed by these studies is the role played by the interaction between the trapped organic molecule and the host silica matrix. This interaction governs the radiative efficiency, the long-term photostability, the amount of Stokes shift...
and the decrease of the molecular dimerization rate, leading to potential great improvements. Avnir et al. [8], in a pioneering study on sol–gel glasses doped with Rhodamine 6G, first discussed the features of the absorption and emission spectra of the incorporated dye in terms of the chemical interaction with the Si–OH groups (silanols) that form the walls of the silica cage and produce a hydrophobic, relatively polar environment for the trapped molecule. In addition, the small size and the rigidity of the silica cage were assumed to hinder the rotational movements required for the intramolecular relaxation dynamics of the excited state. The same two mechanisms accounted for the change from direct photochromism to reversed photochromism in trapped spiropyrane [9], as the evaporation of the residual solvent and the gradual shrinkage of the pore size proceed with aging.

In recent studies on cyanine dyes, tetraarylporphyrins and spirooxazines [10,11] the specific effect of silanols was suggested to originate from the Lewis alkalinity of these dyes and the consequent protonation of the dye molecule to the dicationic form. The efficiency of this process, which requires the contact of the dye molecule with the cage walls, was related to the pore size indirectly through measurements of the fluorescence lifetime [11]. The direct correlation of time-resolved fluorescence measurements with the pore-size distribution, derived by adsorption-isotherm measurements, was carried out by our group [12] in trapped 3,3′-diethyloxadicarbocyanine iodide (DODCI), a cyanine dye which has long been studied for its use in laser media and saturable-absorbers [13–15]. With respect to liquid solutions, we found a rigid blue-shift of both the absorption and the emission spectra, the increase of the lifetime with the decrease of the silica pore size and the quenching of the molecular photoisomerization. These effects were attributed to the physical constraints caused by the rigidity of the silica cage for the pore size in the range of 1.8–2.8 nm, nearly the same size as the DODCI molecule.

In this Letter we extend the previous study on trapped DODCI to the chemical aspects of the interaction with the silica matrix in a different range of the pore size and report on new absorption and emission bands we attribute to the attack of the Si–OH groups to the dye–molecule conjugate chain.

2. Experimental

Bulk sol–gel glasses were prepared using tetramethyloctasilicate (TMOS) hydrolysis, with formamide as the drying-control chemical additive (DCCA), the molar ratio of the constituents being: TMOS/H₂O/formamide = 1:7:1.3. Two series of samples were prepared by the addition of different amounts of HCl to catalyze the reaction with values of pH 3.5 and < 1, respectively, as measured in the sol–gel phase after the hydrolysis (see below). In both cases the required amount of DODCI was previously dissolved in methanol and then added to the starting solution up to a molar concentration of about 5 × 10⁻³ M. After a 2-week aging at a temperature of 40°C, the xerogels were reduced in size to about 2 × 5 × 5 mm³ for the purpose of the optical measurements. For the comparison of spectroscopic properties, liquid solutions were studied in 1-mm-thick optical cells. For the measurements of the molecular structure, the reaction of DODCI with Si–O⁻ groups was performed in dimethyl sulfoxide (DMSO), monitored by means of thin layer chromatography (TLC) and characterized by NMR and IR spectroscopy using an H²O 200 MHz and C 50 MHz nuclear magnetic resonance spectrometer and an FT–IR double-beam double monochromator. All the spectra were recorded at room temperature in deuterated DMSO.

The absorption spectra of DODCI in liquid solutions and in silica-gel samples were recorded at RT by using a conventional spectrophotometer. The emission spectra were obtained by means of a standard apparatus for photoluminescence studies using either the monochromatized light of a 100 W tungsten lamp or the 488 nm line of a cw argon-ion laser. The sample fluorescence was dispersed and detected by using an optical multichannel analyzer (for the lamp excitation) or a 40 cm grating monochromator with a 1P28 photomultiplier (laser excitation).

3. Results and discussion

In Fig. 1 we report the typical absorption spectrum of a DODCI-doped silica-gel sample prepared at pH < 1, after a 2-week aging and without any heat-densification procedure. As reported in a previ-
ous study [12], the spectrum of DODCI incorporated in non-densified xerogel exhibits a broad band peaked at 580 nm, which is also observed in methanol solutions (see Fig. 2, curve A) and attributed to transitions to the N-isomer excited state. This similarity can be due to the relatively large sizes of the pores of the xerogels, distributed in the range of 2.5–3.5 nm as determined by nitrogen desorption measurements (see the inset in Fig. 1) and to the presence of residual solvent. The trapped molecules thus experience a methanol-like environment with little modification of the excited state. Differently, in the case of pore sizes of approximately 2.0 nm, obtained in the heat-densified samples, the physical constraints imposed by the rigidity of the silica cage give rise to a blue-shift of the absorption band and the increase of the luminescence decay time [12].

It should be noted, however, that even in the non-densified samples under consideration, the absorption spectrum differs from that of methanol solutions (Fig. 2, curve A) because of a new absorption band at approximately 490 nm. We attribute this new structure to the interaction between the silanol groups of the silica cage and a fraction of the dye molecules that are trapped in the pores of the glass matrix. In order to verify this hypothesis, we have performed a series of test absorption measurements, reported in Fig. 2, on DODCI in liquid solvents which simulate a number of different environments for the dye molecules. As noted above, the structure at 490 nm is not observed in the absorption spectrum of the dye in a solution in methanol (Fig. 2, curve A). Instead, a band peaked at the same wavelength is observed in DODCI dissolved in a water solution of trimethylchlorosilane (volume ratio 1:1) with the addition of NaOH up to pH 2 (Fig. 2, curve B). According to the reaction:

$$(\text{CH}_3)_3\text{SiCl} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{SiO}^- + \text{HCl}$$

this solution contains molecules with Si–O$^-$ groups and free protons H$^+$ originating from the dissociation of hydrochloric acid. The presence of both species can simulate the environment that the dye molecules experience inside the pores of the xerogel soon after gelation has occurred. Indeed, the silanols dangling from the cage walls of the silica matrix can provide both high-acid protons [11,16] and Si–O$^-$ groups according to the Lewis-acidity behavior:

$\text{Si–OH} \rightarrow \text{SiO}^- \ldots \text{H}^+.$

We suggest that Si–O$^-$ groups can attack the trapped DODCI molecules so as to interrupt the conjugate chain and give rise to new electronic states responsible for the absorption band at 490 nm. How-
ever, by dissolving the dye in a water solution trimethyl silyloxy sodium salt (TMSOS) at pH 7, we have verified that the presence of Si–O groups alone gives rise to an absorption band at 430 nm (Fig. 2, curve C) and thus cannot account for the band observed in solid samples. Moreover, also the bare protonation of the dye molecule seems not to be responsible for the band at 490 nm, along the mechanism suggested in Ref. [11] for the case of other cyanine dyes, since in solutions of hydrochloric acid DODCI shows a peak at 350 nm (Fig. 2, curve D). Finally DODCI in alkaline water solution shows a band at 420 nm (Fig. 2, curve E). From these findings we infer that the contemporary presence of both Si–O groups and H$^+$ ions is required for the onset of the band at 490 nm. Specifically the Si–O groups attack those dye molecules that are in the dicaticionic form because of protonation at a nitrogen site. As discussed above, these conditions are fulfilled when the dye molecule interacts with the pore walls in non-densified silica gel. Consistently with this hypothesis, it was verified that the new band disappears completely when the sample undergoes densification by heating at 95°C (Fig. 1 in Ref. [12]) due to partial de-hydroxylation [17]:

$$\text{Si–OH} + \text{Si–OH} \rightarrow \text{Si–O–Si} + \text{H}_2\text{O}$$

One more indication that new electronic states originate in some of the trapped dye molecules is provided by photoluminescence data. In Fig. 3 we report the luminescence spectra of the non-densified silica gel samples excited with the monochromatized light from the tungsten lamp. The well-known luminescence band peaked at 600 nm, observed when DODCI is excited in the N-isomer absorption band at 540 nm (Fig. 3, curve A), gradually decreases for excitation at shorter wavelengths (510 nm, Fig. 3, curve B) and is eventually substituted with a new emission structure peaked at 500 nm for excitation at 470 nm, in the tail of the absorption band at 490 nm (Fig. 3, curve C).

In a different approach, nuclear magnetic resonance (NMR) measurements were performed to verify the possibility and determine the site of Si–O$^-$ attack on the DODC molecule. The samples were prepared by dissolving DODCI and TMSOS at a molar ratio 1:1 in dimethyl sulfoxide (DMSO). Due to the high polarity of this solvent, DODCI shows a solubility up to $2 \times 10^{-1}$ mol and the reaction with TMSOS occurs instantaneously and in 100% yield as confirmed by TLC chromatography.

In the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra the DODC derivative appears to be completely unsymmetric because of the loss of conjugation and the changed substitution in C$_2$ in the chain which is now linked to an oxysylil group (see Fig. 4). The electrophilic

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{H$^1$ NMR spectra of DODCI in DMSO (a), and after the reaction with TMSOS (b). Chemical shift $\delta$ relative to TMS.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Emission spectra of DODCI-doped sample excited at different wavelengths: $\lambda_{\text{exc}} = 540$ nm (curve A), $\lambda_{\text{exc}} = 510$ nm (curve B) and $\lambda_{\text{exc}} = 470$ nm (curve C).}
\end{figure}
center in C$_2$ is also foreseen from resonance structures of pentamethine oxadicarbocyanine. The assignment is further confirmed by decoupling experiments in $^1$H NMR and by $^{13}$C NMR.

We note that the optical absorption spectra of such samples show the same band at 430 nm as that observed in water solutions (Fig. 2, curve C) where, however, the reaction occurs in 60% yield, with longer reaction time and only by using a big excess of salt. In spite of the trend of DMSO to prevent protonation, by treating this sample in water solution at pH $< 1$, the arising of a shoulder around 490 nm was observed, supporting the attribution of the corresponding band of curve B in Fig. 2.

Finally, to investigate the role of the cage dimension in the dye–matrix interaction, some silica samples with larger pores (average size of $\approx 4.0$ nm as shown in the insert of Fig. 5) were prepared by using starting solutions at pH 3.5, as described in Section 2. In Fig. 5 we report the absorption and the emission spectra of DODCI incorporated in these samples (continuous curves). The absorption spectrum shows no appreciable difference from that obtained from DODCI in methanol solutions (not reported in the figure) and, in particular, no absorption band is observed at 490 nm. This effect confirms that the approach of the dye molecule to the pore walls is necessary in order to achieve the attack by the dangling silanol groups [11]. When almost all the silica pores are much larger than the dye molecule the interaction is hindered through the solvation of DODCI by the residual solvent molecules and the behavior of the excited state is not modified with respect to the methanol solution.

However, at high-power excitation, the emission spectrum in the solid matrix (continuous curve, Fig. 5) differs from that observed in methanol solution at the same power (dashed curve, Fig. 5) where the P-isomer emission band at 635 nm appears superimposed to the vibrational shoulder at approximately 645 nm.

This indicates that the intramolecular rearrangement involved in the photoisomerization process [18,19] is more affected by the physical constraints than the steady-state structure of the N-isomer excited state. The formation of the P-isomer, in fact, is achieved through large-amplitude motion of an aromatic group and the further increase of the molecular length that is still prevented in these samples and could require even larger pores.

4. Conclusion

From the comparison of the absorption and emission spectra of DODCI in different matrices it is found that the optical properties of the dye incorporated in sol–gel glass are strongly influenced by the interaction between the trapped molecules and the walls of the surrounding silica pore. The modification of the energy of the excited state and the increase of the luminescence decay time are due to the physical constraints imposed on the dye molecule by the rigidity of the silica cage in xerogels with a pore size of approximately 2.0 nm. Conversely, in non-densified samples with larger pores (2.5–3.5 nm), the chemical interaction seems to be responsible for new absorption and emission bands. This occurs via the attack of silanol groups in the C$_2$ site of the methinic chain and contemporary protonation by the solute H$^+$ ions. For even larger pores ( $\approx 4.0$ nm), the only effect of the matrix is the hindering of the molecular photoisomerization. The knowledge of the behavior of DODCI in different environmental conditions improves the chance of using this dye as a probe species for testing new solid-state matrices.
such as organically modified silicates (ORMOSIL) that seem promising for optoelectronic applications.

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