Probing the chemical environment of 3-HydroxyFlavone doped ormosils by a Spectroscopic Study of excited state intramolecular proton transfer

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I. INTRODUCTION

Increasing interest has been devoted in the past decade to the production of fluorescent dye molecules embedded in sol-gel derived xerogels, owing to the extended range of applications of this type of hybrid materials in the field of optical sensing. Amongst the huge number of dyes, 3-HF is a particularly attractive molecule because of its large Stokes shift ($\Delta\lambda \sim 180$ nm) due to the excited-state intramolecular proton transfer (ESIPT) [1]. The ESIPT mechanism in the 3-HF molecule, as described in figure 1, enables the formation of a tautomeric form (T*), whose emission band lies in the range 500-575 nm, whereas the normal emission band of excited 3-HF (N*) is found in the range 375-475 nm [2, 3].

The tautomeric equilibrium between 3-HF excited structures N* and T* is affected by the protic character and polarity of the surrounding medium, being structure N* most favored in protic/polar environments [1-4]. In this paper we compare the emission and excitation features of encapsulated 3-HF molecules in both monoliths and films obtained from different organically modified silicate systems (Ormosils). The chemical nature of the dye microenvironment has been derived for each hybrid system, by using the 3-HF molecule as an optical probe. The photostability of the sol-gel glass under prolonged UV irradiation has been also tested and the influence of either the sample form and the chemical nature of precursor alkoxides on this property has been studied.

II. EXPERIMENTAL

The precursor solutions were prepared by using tetraethoxysilane (TEOS) and mixtures of TEOS, methyltriethoxysilane (MTES) and phenyltriethoxysilane (PTES), as described elsewhere [3]. Different molar ratios between TEOS and trifunctional silicates were used, as specified by the sample labels. 3-HF was added with a 0.0013:1 dye:alkoxide molar ratio.

Fourier transform infrared spectroscopy (FTIR) was performed at room temperature in transmission mode (spectrometer Jasco 660 plus), with resolution of 4 cm^{-1}.

Fluorescence spectra were recorded at room temperature in front-face geometry (spectrofluorimeter Jasco 770), equipped with a 150 W Xe lamp.

III. RESULTS AND DISCUSSION

In Figure 1 are illustrated the FT-IR spectra, normalized to the amplitude of the highest peak, of T100, TM5050 and M100 film and monolithic samples.
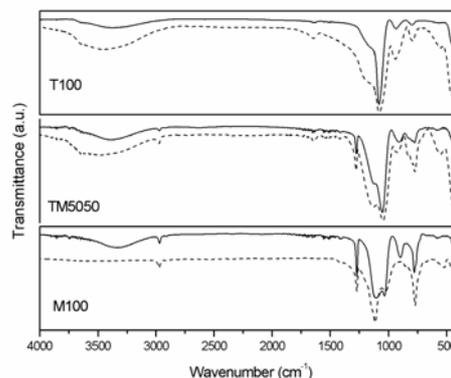

FIG. 1: *FT-IR spectra of samples T100, TM5050 and M100 as films (solid line) and monoliths (dashed line).*

In monolithic samples, the intensity of the components ascribed to O-H groups (3350 cm^{-1}), molecular water (1630 cm^{-1}) and silanols (940 cm^{-1}) decreases as the amount of non-hydrolizable organic groups increases, until it is not detected in the M100 samples, as reported in the literature [5]. On the contrary, in thin films the 1630 cm^{-1} water peak is not visible for all the spectra, while the amplitudes of the bands assigned to O-H and to Si-OH groups slightly increase at increasing MTES content.

The FTIR findings fit with the difference reported in literature between the rates of condensation and evaporation processes in monolithic and thin film xerogel samples. In fact, in monolithic systems the smaller evaporation rate allows the condensation reaction to continue, thus forming a more cross-linked network where water and solvents can be entrapped. Besides, by increasing the amounts of low polarity groups such as Si-CH$_3$ or Si-(C$_6$H$_5$) the network becomes more hydrophobic, so that the hydroxyl groups and water contents decrease [5]. On the other hand, the faster evaporation of solvent during the production of thin films by spin-coating causes a sudden shrinkage of the gel structure, so that the condensation reaction between adjacent Si-OH groups is limited at the early stages of drying.

Quite impressive evidence of the difference between

film and monolithic samples is given by the excitation spectra of TP samples. In Figure 2a, are reported three excitation spectra of TP5050 samples: the thin film T* excitation spectrum, the thin film N* excitation spectrum and the monolith T* excitation spectrum. As can be seen, the first spectrum has a band at 270 nm, whose amplitude increases with the PTES fraction, as shown in Figure 2b. The same band is present as a shoulder in the N* spectrum and is not detected in the spectrum of the monolithic sample (Fig. 2a).
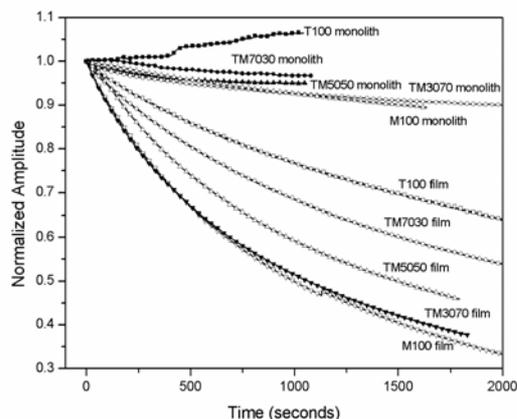

FIG. 2: a) excitation spectra of TP5050 film and monolithic samples; b) excitation spectra of the T band in thin films at increasing PTES concentration; c) emission and excitation spectra for the undoped P100 film.*

The spectral feature peaked at 270 nm shown by TP samples can be found in the absorption spectra of monosubstituted benzene [6], so that it can be assigned to the phenyl group bonded to the silica network. Excitation and emission spectra collected from the P100 undoped thin film (see Fig. 2c) have the same T* excitation peak observed for the doped samples and an emission band at 325 nm. Since the emission band lies in the same wavelength range of the 3-HF molecule excitation band, an efficient energy transfer process between the two chromophore groups is deduced. It can be inferred that 3-HF molecules which display the T* excited state are closer to the network pendant phenyl groups in thin films than in monolithic samples, where the absence of any feature in the UV range indicates that the energy transfer process does not occur. This observation can be related to the difference between thin film and monolithic networks [7]. In thin films the fast evaporation of water and solvent prevents the condensation reaction from continuing. Therefore, the network is able to compact and shrink, thus forming a dried surface with low porosity and low pore volume. On the other hand, in the monolithic samples the formation of new Si-O-Si bonds through condensation gives rise to a more rigid structure which opposes the compaction and shrinkage. In this case a microporous network is expected to form and the 3-HF molecules are

probably located in larger sites with respect to thin films.

Another interesting feature is the T* band amplitude decrease during the UV irradiation. In Figure 3 are shown the T* peak normalized amplitudes for the TM series detected as a function of time (λ_{ex} = 350 nm). The photodegradation rate increases with increasing organic content in the matrix and it is lower in monolithic samples compared to thin films.
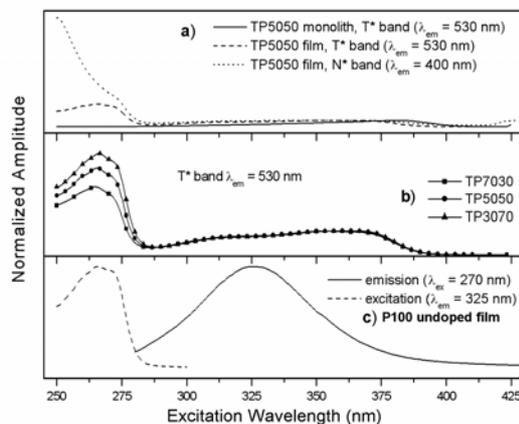

FIG. 3: T band emission amplitude as a function of time for TM monolithic and film samples.*

The photodegradation process can be explained as follows: the cleavage of labile organic bonds under UV irradiation can take place, thus producing reactive free radicals which can react with the 3-HF molecule. The lack of integrity of the dye causes the formation of non-fluorescent species, such as flavone. It turns out that the increase of organic content in the matrix by introducing methyl or phenyl groups causes the formation of a larger amount of free radicals, thus increasing the photodecay rate. On the other hand, in monolithic samples the dye molecules are located in larger sites, thus providing a more efficient screening effect from the network, so as to decrease the degradation rate of the 3-HF molecule.

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