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Effect of PMMA impregnation on the fluorescence quantum yield of sol–gel glasses doped with quinine sulfate

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Abstract

The fluorescence quantum yield of quinine sulfate in sol–gel and PMMA impregnated glasses is measured. The observed quantum yield improvement in the sol–gel matrix, compared to ethanol, is interpreted as a reduction of non-radiative relaxation channels by isolation of the molecules by the cage of the glass. PMMA impregnated sol–gel glasses show an extra improvement of the fluorescence yield, which is interpreted as a reduction of the free space and the rigid fixation of the molecules to the matrix. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Fluorescence quantum yields of organic molecules are affected by polarity, viscosity, hydrogen-bond, pH and temperature of the medium in which they are contained. Non-radiative losses due to internal rotation and diffusional quenching are some of the processes that reduce fluorescence yields. The use of solid matrices, in particular glasses made from the sol–gel technique, can reduce both effects.

The main advantage of porous glasses over fluid solutions, which can provide an insight on the improvement of quantum yields, is the ability of the glass to trap each molecule in its own cage. Thus, elimination of translational freedom of the molecules is achieved and deactivation of excited molecules by intermolecular collisions is avoided. Since each molecule is trapped in a different cage, impurities in the solute and photodecomposition products are isolated. Further, the solid cage that surround the molecule also reduces internal rotational modes in the molecule, these rotational relaxations are one of the main paths of non-radiative deactivation of excited molecules.

On the other hand, concentration effects such as molecular aggregation are known to decrease

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quantum yields. Studies of aggregation of R6G in sol–gel glasses [1,2], and pyrene and naphthalene [3], have shown that in sol–gel glasses dimer formation occurs at higher concentrations than in liquid solutions. Consequently, these studies show that isolation of organic molecules from each other by the sol–gel cage enable the use of high concentrations without changing the molecular aggregation.

An increase in quantum yield has been observed in Ru(bpy) [4], malachite green [5], and $BP(OH)_2$ [6]. All these studies show that sol–gel glasses indeed can improve the quantum yield of organic compounds. They also show that the particular chemical properties of the molecules and the properties of the glass that contain them and their interactions play an important role on the behavior of the radiative characteristics.

In this work, we study the effect of the solid sol–gel matrix on the quantum yield of quinine sulfate before and after PMMA impregnation.

2. Experimental

Sol–gel glasses from Geltech, were used. The sol–gel and PMMA impregnated samples were prepared as described previously [7], and the range of final concentration of the sol–gel glasses were between 1.75×10^{-7} and 3.14×10^{-5} M. The quantum yields were measured using optically diluted samples and side view detection of the fluorescence. A xenon arc lamp and a compact monochromator were used for excitation and an optical multichannel analyzer (OMA) as the detection system. As a quantum yield standard, we employed quinine sulfate in 1 N H_2SO_4 at similar concentrations as in [8]. A test on the reliability of the experimental setup was carried out employing rhodamine 6G. The quantum yield measured for this laser dye in methanol was 0.91, that is 4% different from the values obtained by Olmsted [9] and Drexhage [10]. In ethanol the obtained value was 0.94, that is in close agreement with the results obtained by Butein et al. [11], Arden et al. [12] and Kubin and Fletcher [13]. The reproducibility of the measurements was 2%.

Due to the porous nature of the sol–gel glass, scattering of the pump light was also present. The drawback of the scattered light by the sample is that some of it can reach the detection system and introduces errors in the determination of the quantum yield. For this reason, all the yield measurements have been corrected for the scattered light.

3. Results

The measured values of the quantum yield, for quinine sulfate in ethanol, are almost constant in the range of concentrations used, 2×10^{-7}–6×10^{-5} M. The quantum yield of the sol–gel glasses densified at 600°C, samples S6, show an increase of approximately six to seven times compared to values in ethanol, Fig. 1. This result shows a reduction of the non-radiative channels by

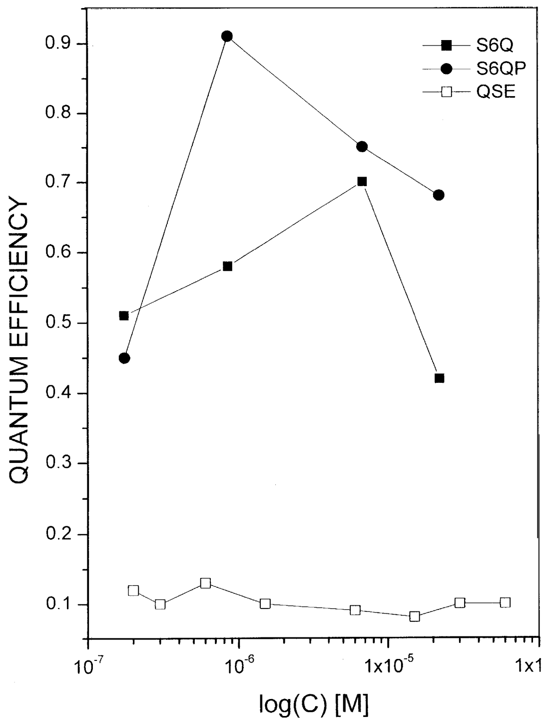

Fig. 1. Quantum efficiency of quinine sulfate in 600°C densified sol–gel glass (S6Q), sol–gel/PMMA composite (S6QP) and ethanol (QSE).

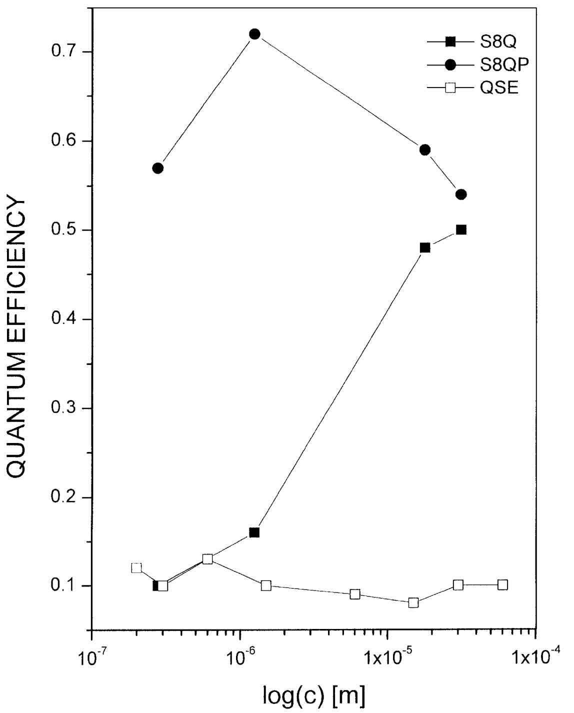

Fig. 2. Quantum efficiency of quinine sulfate in 800°C densified sol–gel glass (S8Q), sol–gel/PMMA composite (S8QP) and ethanol (QSE).

the cage of the glass. After PMMA impregnation there is an extra improvement of the yield by 20%. This is not the case for the sample at lower concentration where a decrease of 10% of the value in plain sol–gel glass was measured. For the glasses densified at 800°C, S8 samples, the quantum yield is approximately 20% higher than in ethanol at similar concentrations, Fig. 2. Notice that at higher concentrations the quantum yield increases by a factor of five. Again, after PMMA impregnation, an extra increase of about 13% is achieved for the samples with higher concentrations. There is an increase by a factor of five for the less concentrated samples.

4. Discussion

The higher values of quantum yields for the sol–gel glasses, compared to those obtained in ethanol, are due to the rigid matrix that restricts the rotational or torsional relaxation of excitation. Since the mechanism of internal conversion often involves the twisting of molecular constituents around a single or double bond in the excited state and under the restricted freedom imposed by the sol–gel glass, excited state stabilization by interaction with the cage becomes important.

It has been reported [14], that after PMMA impregnation of sol–gel glasses, a considerable reduction of scatter light is achieved and that bulk attenuation is reduced from 8.2 to 0.04 dB/cm after PMMA impregnation. Since all the quantum yield measurements were corrected for scattered light, the reduction of the bulk attenuation by impregnation with PMMA, does not explain the higher values obtained for the PMMA/sol–gel composites, but other mechanisms are involved.

When the glasses are impregnated with PMMA the pores are filled, leaving less space and increasing the rigidity of the molecules trapped in the pores. In rigid matrices, where free volume effects are present, structural relaxation are dependent on the degree of rigidity of the matrix that can restrict the relaxational freedom to a limited range along the relaxation coordinate. After PMMA impregnation, the matrix experiences an increase in rigidity. This rigidity reduces the space available for the molecules and restricts their motion, yielding to the further increase in quantum yield.

5. Conclusions

The quantum yields of sol–gel glasses and sol–gel/PMMA composites doped with quinine sulfate were measured. The higher values for the fluorescence quantum yields in the sol–gel glass leads to the conclusion that the molecules are isolated by the glass and non-radiative channels hindered. An extra increase in quantum yield in sol–gel/PMMA composites is measured. This result shows that the isolation of the molecules by the cage of the glass, the increased rigidity of the matrix and reduction of the free volume space reduces the non-radiative channels.

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