



Improvement of the emission properties of sol–gel silica matrices containing Eu^{3+} in the presence of poly(ethylene glycol)-200

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Abstract

Composite organic/inorganic sol–gel matrices have been made with tetramethoxysilane and poly(ethylene glycol)-200, incorporating Eu^{3+} ions. Polyethylene oxide oligomers match well with silica giving solid transparent gels. Europium ions are associated with the organic phase and they are protected from quenching mechanisms usually present in silica matrices. Thus, emission intensity and decay time increased and spectral bandwidth decreased in the presence of the oligomer. Increase of the decay time was also obtained with organic cationic dyes in the presence of the oligomer. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The photolytic properties of rare earth ions are studied with a lot of interest because they are used as visible and near-IR radiation sources, some of them particularly important for lasers and optical communication devices [1]. The popularity of lanthanides stems from their two great advantages: They emit narrow line, almost monochromatic light and they have long emission lifetimes. However, the radiative transitions of rare earth ions incorporated in matrices of sol–gel made silica are quenched, due to coupling with the vibrations of the matrix, in particular, with –OH groups [2]. In addition, aggregation or migra-

tion to the surface also degrade emission properties. Various strategies have been adopted to solve these problems. Doping silica matrices with aluminum has revealed a preferential association of Eu^{3+} with AlO^- bonds, which leads to doubling of fluorescence intensity [3]. Amino groups on alkoxy silanes bind and immobilise lanthanide ions [4]. By using the colloid–polymeric route, it has been found that monophasic silica with large lanthanide content can be prepared [5]. Association of Eu^{3+} ions also with organic molecular species can, however, be successfully obtained and aggregation and migration can be impeded. Thus, in the present work, we show that the presence of poly(ethylene glycol) (PEG, $M_n = 200$) and other PEG oligomers results in decreased spectral width, increased decay time and increased emission intensities of europium ions, especially, those related to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, situated

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around 617 nm. We also show that the increase of the luminescence decay time in association with PEG oligomer is a more general phenomenon and it applies to organic cationic dyes as well as to Eu^{3+} .

2. Experimental

All chemicals employed in the present work have been purchased from Aldrich and were used as received. Millipore water was used in all experiments. Sol–gel matrices containing polymer were made as follows: Tetramethoxysilane (TMOS) was partially hydrolysed by mixing with acidified water (HCl, pH 3.0) at the molar ratio TMOS:water = 1:2. The mixture was continuously stirred for 1 h. At the beginning it was turbid but in the course of proceeding hydrolysis it became clear. Then, to 1 ml of this original sol was added 5 ml of water or a mixture of water and PEG-200, in different concentrations, under stirring. Stirring continued for 1/2 h and then the mixture was poured into plastic PMMA cuvettes, covered with perforated aluminum foil, and put in an oven at 50°C. Gelation was rapid in the presence of PEG and it was faster when the PEG concentration was higher. Thus, the solution was solid gel 2 h after preparation, when the overall proportion of PEG was ≥ 70 wt%. In the absence of the polymer, complete gelation took one week at 50°C. One more week, after gelation, was also necessary to obtain a volume shrinkage and formation of xerogel. PEG-200 and TMOS match well together as they gave transparent xerogel composite matrices which did not break into pieces. They also gave transparent films by dip-coating. They are then good supports for photolytic measurements. Larger molecular weight PEG oligomers have also been tried and compared with the PEG-200 samples.

$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ or organic cationic dyes have been incorporated in these matrices by solubilisation in water or in the original aqueous PEG solution. The overall original concentration for the Eu^{3+} was 20 mM and that of the dyes 20 μM .

Fluorescence spectra as well as Eu^{3+} decay profiles were recorded with a spectrofluorometer (Perkin-Elmer LS50-B). The luminescence decay profiles of the dyes were recorded with the photon-counting technique using a homemade hydrogen flash and

electronics (ORTEC). All measurements were made at ambient conditions.

3. Results

When excited at 396 nm, the matrices containing PEG-200 emitted a bright red radiation whose intensity increased with increasing polymer content. Fig. 1 shows emission spectra for three characteristic samples: aqueous solution, silica xerogel without polymer and composite matrix containing 70 wt.% PEG-200. All peaks seen in the emission spectrum originate from the $^5\text{D}_0$ state of Eu^{3+} [1,6]. Forbidden transitions [1], such as the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, are not resolved in Fig. 1, while the three major peaks correspond, in the order of increasing wavelength, to $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_{3,4}$. In going from pure aqueous solutions to polymer composites, we obtained an impressive increase of band intensity and decrease in the width of the bands, particularly for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 617 nm. Interaction with the host environment is apparently changed in the presence of the polymer. This spectral improvement was accompanied by an increase of the emission decay time. The emission wavelength was set at 617 nm, i.e., the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition was selected.

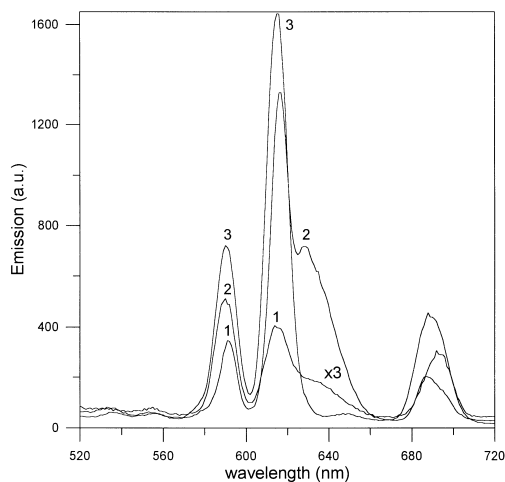


Fig. 1. Emission spectra of Eu^{3+} in various environments: (1) aqueous solutions; (2) silica xerogels made without polymer; and (3) composite xerogels containing 70 wt% PEG-200. The concentration of Eu^{3+} in the sol was 20 mM in all cases. Excitation wavelength = 396 nm.

The decay time of Eu^{3+} emission increased from 0.17 ± 0.002 ms in the absence of the polymer to 0.32 ± 0.001 ms in the presence of the polymer. The decay profiles could be fitted with single-exponentials, indicating that whatever the effect of the matrix on Eu^{3+} emission, all ions have the same environment.

Similar results were obtained with PEG-400 while, for higher-molecular-weight PEG, transparency decreased to completely disappear with $M_n \geq 1000$.

4. Discussion

Increase of Eu^{3+} decay time in poly(ethylene) oxide and poly(propylene) oxide electrolytes has been previously reported [7]. Europium ions are associated with PEG oligomers, a property which is common with other cations [8]. Solvation of ionic salts with PEG involves the formation of both ion/polymer and ion/ion complexes and appears principally to be the result of Lewis acid–base interactions between dissolved cations and ether oxygens of the polymer chain [8,9]. Ionic conductivities studied with various divalent ions have revealed that cations play the role of polymer chain crosslinkers while anions are the charge carriers [10]. Cationic complexation is then expected to be stronger with the trivalent Eu^{3+} cations and, at any rate, strong enough to be preserved in the silica/PEG composite matrix. The preservation of complexes in the matrix is also facilitated by the tendency of PEG to segregate from other co-solubilised water-soluble polymers [11]. Organic cationic dyes dissolved in PEG-200 were also complexed by this oligomer so that their photophysical properties improved with respect to pure aqueous solutions. Indeed, as seen in Table 1, the lumines-

cence decay time was more than doubled in PEG compared with pure water solutions, in the case of some dyes. In some cases, solvation by PEG is also demonstrated by important variations in the fluorescence spectrum (not shown). The luminescence decay time was practically the same in silica/PEG xerogels as it was in pure PEG solutions. This global behaviour of cationic species, both elemental and organic, is a strong indication that when PEG oligomers are introduced in sol–gel silica matrices, they provide an organic subphase complexing cationic luminophores and preserving the improved photophysical properties that they obtain in PEG solutions.

Before closing this section, it is, however, necessary to underline the following finding: complexation of cationic species, such as Eu^{3+} , with PEG does not mean immobilisation. On the contrary, we have previously found [12], by studying luminescence quenching kinetics of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} , in silica matrices containing high PEG percentage, that the probes diffuse in a quasi-three-dimensional viscous medium.

5. Conclusion

The luminescence intensity and decay time of Eu^{3+} as well as of several organic cationic dyes increased when solubilised in PEG oligomers. These properties were also observed in silica/PEG matrices because cations are strongly associated with PEG chains.

Acknowledgements

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Table 1

Luminescence decay times (ns) of various organic luminophores in different environments

Dye	In water	In pure PEG	In silica/PEG matrix (70 wt% PEG)
$\text{Ru}(\text{bpy})_3^{2+}$	480	1080	1010
Cresyl Violet	2.8	6.3	6.3
Thionine	2.2	3.5	3.4
Rhodamine 6G	5.6	7.2	7.3

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