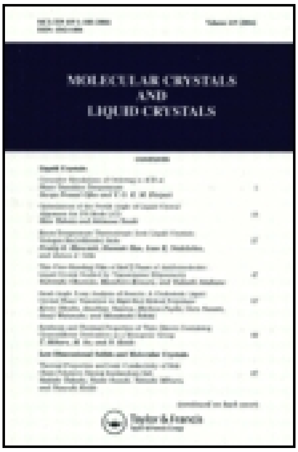

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Lanthanide Cryptates Entrapment in Aluminum Polyphosphate Gels

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In this work, we report for the first time the preparation and spectroscopic investigation of $[\mathrm{Tb} \subset \mathrm{Bipy.Bipy.Py(CO_2Et)_2}]^{3+}$ incorporated in aluminum polyphosphate gels. Gelation occurs under ambient atmosphere at room temperature, which is followed by syneresis, leading to transparent samples after 5-10 days. Transparent auto-standing films were also prepared. The gel samples were characterized by UV-visible absorption spectrophotometry, luminescence spectroscopy and lifetime measurements. The cryptate absorption and emission spectra were not greatly affected by its incorporation within the gel matrix. The lifetime of the Tb^{3+} $^5\mathrm{D}_4$ level increases from 0.7 ms to 1.0 ms after entrapment into the gel. The results imply that these systems are promising for application in fluoroimmunoassays, as well as for the design of new optical materials.

Keywords: lanthanide cryptates; luminescence; photophysical properties; polyphosphates; sol-gel

INTRODUCTION

Sol-gel derived materials are very attractive as supporting media to new optical materials, allowing to produce transparent and mechanically robust matrices with controlled micro- and macrostructure. The low-temperature processing provides a convenient way to synthesize gels doped with temperature sensitive compounds[1,2]. These composites may be processed into fibers, transparent films and monolithic bulks. One can, thus, envisage the incorporation of luminescent compounds on these matrixes, which may lead to new light emitting devices (phosphors[3] and solid state lasers[4,5]), nonlinear optical materials[6] and sensors[7]. Due to the intrinsic and controllable porosity of gels, their application in sensors seems especially attractive.

The properties of luminescent species are strongly dependent upon the chemical environment in which the emitting ion/compound is embedded, thus allowing for the use of such species as labels, probes and/or sensors for a great variety of compounds. Hence, the overall system must be designed to optimize the energy transfer from the absorbing coordinating ligands to the chelated ion in order to maximize the light output and, thus, increase sensitivity. Also, the host matrix must provide a stable network that prevents luminescent quenching and degradation, also allowing for a strong and selective interaction between the luminescent probe and the species to be detected.

The matrixes currently used for this type of application are restricted to silica based host networks, like silica glasses[8], SiO_2-M_xO_y (M = Zr, Ta)[9] and hybrid matrixes (ormosils and ureasils), in which TEOS and TMOS precursors are grafted with silanes[10], polyethyleneglicol[11] and urea/polyoxyethylene[12,13]. Dong et al. developed a sol-gel precursor, which is able to simultaneously originate the silica network and also to coordinate to the lanthanide ion[14]. Chemically selective sensitive silica layers had already been reported [7].

Polyphosphate-based gels are also attractive hosts to new hybrid materials. Sol-gel derived non-crystalline metal polyphosphates can be prepared with a broad range of chemical compositions, with many different morphologies. Rigid foams[15], particles containing closed pores[16], nanoparticles[17], thermoreversible gels and glasses[18] can be synthesized at or near room temperature. This allows envisaging the entrapment of compounds in mild reaction conditions, thus preventing degradation of the active species.

Aluminum polyphosphate (APP) gels are supramolecular ionic (supraionic) networks where the polyphosphate chains are interconnected by aluminum ions. These gels can be processed into fibers, flexible films and monolithic bulk pieces at room temperature [6]. Polyphosphate chains are linear, short ($n < 50$ P atoms) and stiff. They are polyanions, which provide many binding sites to which positively charged species can interact. Further, it is soluble and stable in aqueous solution, but tend to hydrolyze in acidic medium, leading to chain scission. Hence, the gel formation is a consequence of the interaction of the polyanion with Al^{3+}, both high connectivity species.

The room temperature synthesis of APP gels makes them suitable to the incorporation of temperature sensitive compounds, like rare-earth metal complexes to design new Light Conversion Molecular Devices (LCMD).

LCMD's constitute a class of materials with potential applications to a wide range of processes and new technologies[19]. Therefore, the interest in this kind of compounds has increased in the past decade[20], particularly regarding the use of their optical properties, such as in time-resolved microscopy[21], fluorescent lighting[22], luminescent sensors for chemical species (H^+, O_2, halide ions, OH^-)[23], electroluminescent devices[24], UV dosimeters[25-26], antireflection coating for solar cells[27] and luminescent probes in biomedical assays[28-32].

Recently, a research has been performed on lanthanides cryptates doped in gel matrixes[19,33]. In a previous paper, we have studied some spectroscopic properties of the lanthanide cryptates $[Ln\subset bpy.bpy.py(CO_2Et)_2]^{3+}$, giving emphasis to theoretical and experimental studies of photophysical properties in aqueous solution[38]. In the present work, we report on the preparation and spectroscopic study of the $[Ln\subset bpy.bpy.py(CO_2Et)_2]^{3+}$ cryptate incorporated into aluminum polyphosphate gels (cryptate/gels). To the best of our knowledge, this is the first report regarding the use of this kind of material as a matrix to new composite materials.

EXPERIMENTAL

The incorporation of the Terbium cryptate into the polyphosphate gel was carried out starting from sodium polyphosphate (Nuclear), aluminum nitrate (Riedel) and the terbium(III) cryptate, $[Tb\subset Bipy.Bipy.Py(CO_2Et)_2]^{3+}$ aqueous solutions. The cryptate synthesis[34] and the gel preparation[6] methods are described on the literature. The phosphorus to aluminum ratio (P/Al) ranged from 2.0 to 2.8. The $[Tb\subset Bipy.Bipy.Py(CO_2Et)_2]^{3+}$ concentration in the starting solution was $1x10^{-5}$ M. Gelation occurs under ambient atmosphere and is followed by syneresis, leading to transparent samples after 5-10 days at room temperature. Auto-standing films were prepared spreading the gel samples on a flat surface and drying at room temperature in a moisture-controlled environment (~50% relative humidity), for one week.

The absorption spectra of the $[Tb\subset Bipy.Bipy.Py(CO_2Et)_2]^{3+}$ and Tbcryptate/gels was obtained using a UV-visible spectrophotometer Perkin-Elmer LAMBDA 6 model 2688-002.

A 150 W Xe lamp was used to excite the samples. The excitation wavelengths were selected by a 0.25 m monochromator (Jobin Yvon Model H-10). The luminescence was dispersed by a Jobin-Yvon 1m double monochromator (model U-1000) and the signal, detected by a water-cooled RCA C3 1034-02 photomultiplier, was analyzed and processed by a Jobin Yvon Spectralink system. The lifetime measurements were performed at 298K, exciting the sample with the third harmonic of a Nd-YAG laser (λ_{exc} = 355 nm) and detecting the emitted light, after dispersion through a Jobin Yvon model H-10 monochromator, with a P28 photomultiplier tube. The photocurrent was then analysed by Box Car system (EG&G Princeton Applied Research) a Grated Integration model 4402 for data acquisition.

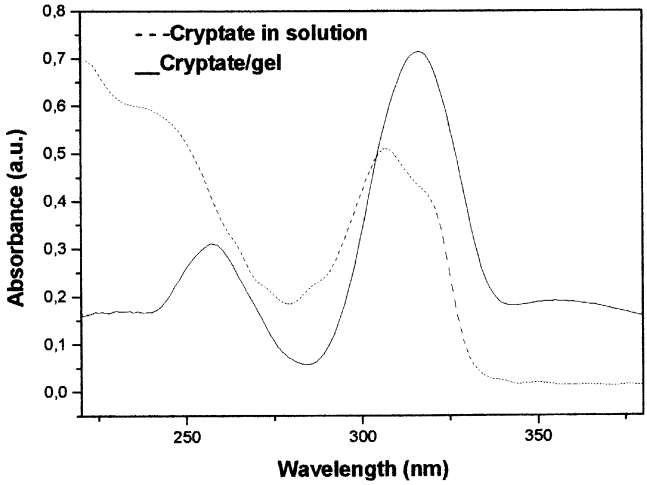

FIGURE 1. Absorption spectra: terbium cryptate in aqueous solution and entraped in polyphosphate gel

RESULTS AND DISCUSSION

The cryptate entrapment on the gel network could be visually confirmed by irradiating the gel with UV light. All samples exhibited the typical green luminescence of the Tb^{3+} ion. The supernatant solution also showed luminescence, but the liquid expelled during the syneresis stage did not. This indicates that the criptate entrapped during the gelation step remains attached to the gel network. Figure 1 presents the absorption spectra of the Tb-cryptate in solution and after entrapment in the APP gel. The band situated near 300 nm presents a slight red shift and a more symmetric shape. Further, the shoulder observed at 370nm for Tb-cryptate in solution is no longer present in the spectra of the Tb-cryptate/APP gel samples.

The emission spectra (Fig. 2) of the $Tb[Bipy.Bipy.Py(CO_2Et)_2]^{3+}$ are not greatly affected by incorporation into the gel matrix, consisting of sharp lines ascribed to the $^5D_4 \rightarrow {}^7F_J$ emission transitions of the Tb^{3+} ion. The position of the observed lines and the branching ratios are essentially the same in both cases, implying that the strength and degree of covalency of the ligand field experienced by the Tb^{3+} ions are not greatly affected by incorporation into the APP gel. No additional lines appeared, and neither quenching was observed. This shows that the integrity of the Tb(cryptate) species is not disturbed upon entrapment into the gel network and that there is a good compatibility between the host and matrix. The route to achieve the composite does not differ significantly to the method used to prepare the APP gel.

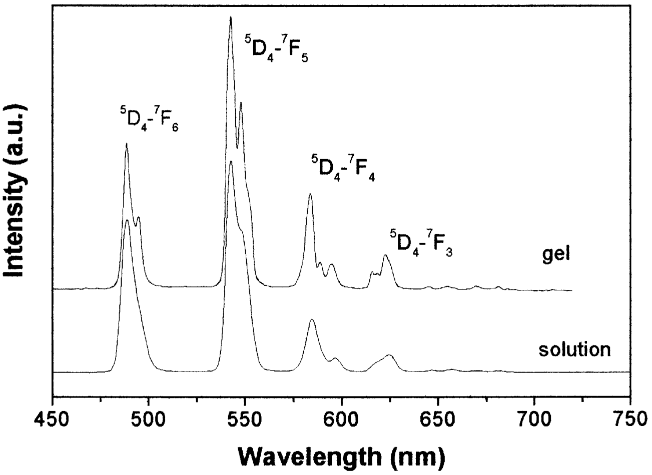

FIGURE 2. Emission spectra: cryptate in aqueous solution and entraped in polyphosphate gel.

The Tb^{3+} emission lines are noticeably narrower on the composite samples, allowing for a better observation of the crystal-field components of the emission transitions. This behavior is similar to the one observed at lower temperatures and points out that, upon encapsulation, the Tb-cryptate is subjected to a more stiff chemical environment, indicating that the gel consists of a rather rigid network and that the interaction between the Tb-cryptate and the polyphosphate groups is rather strong. This is also consistent with the observation that no Tb-cryptate is excluded from the gel during the syneresis step.

A recent work reported luminescence quenching on the encapsulation of Eu(III) cryptates on silica networks and a strong dependence of the emission spectra on the experimental conditions carried out to prepare the samples, mainly the acidity of the reaction medium. Several additional lines were detected and stabillity was also affected[19]. In this work, the matrix and the host cryptate are fully compatible. Our samples are stable for more than six months if properly stored.

The lifetimes of the $^5D_4$ level of Tb^{3+} are observed to increase from 0.7 ms to 1 ms upon incorporation of $[\mathrm{Tb}\subset\mathrm{Bipy.Bipy.Py(CO_2Et)_2}]^{3+}$ into the gel network. A similar behavior has already been reported for other lanthanide complexes incorporated in silica matrixes[19,33]. This increase in the $^5D_4$ lifetime indicates that the non-radiative decay rates decrease after entrapment into the gel network. This decrease in the non-radiative decay rates may be, probably, related to the more restricted environment and to the interaction between the Tb^{3+} ions and the polyphosphate groups.

Finally, APP gel presents two important features which may contribute to its application as a solid support for new hybrid materials: (i) the water amount on the matrix may be controlled in the 40-60% range providing a "solution-like" environment; (ii) samples are also permeable to water vapor. These features may contribute to diffusion processes on the interface and within the material and may be important to the use of polyphosphate based materials as sensors.

CONCLUSIONS

Tb-cryptate was successfully incorporated in polyphosphate gel matrixes with minimal modification on the gel preparation parameters. The absorption and luminescence properties of the Tb-cryptate are not greatly affected by the entrapment showing that the integrity of the Tb-cryptate species is well preserved after the incorporation. The line narrowing and the $^5D_4$ lifetime increasing observed upon entrapment of the Tb-cryptate into the gel network indicates that the incorporated species is subjected to a rather stiff environment and that the non-radiative decay rates are reduced. Polyphosphate gel based supramolecular composite materials were described here for the first time.

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