

Intensely Luminescent Materials Obtained by Combining Lanthanide Ions, 2,2'-Bipyridine, and Poly(ethylene glycol) in Various Fluid or Solid Environments

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Steady-state luminescence spectroscopy and luminescence decay analysis have been employed to study the association of two rare earth ions (i.e., Eu^{3+} and Tb^{3+}) with poly(ethylene glycol) in the absence and in the presence of 2,2'-bipyridine, which acted as an antenna of near-UV radiation. Three different systems have been studied at various polymer concentrations, i.e., aqueous solutions, transparent composite organic/inorganic sol-gel matrixes made by hydrolysis of tetramethoxysilane, and polymer matrixes. The photophysical behavior of the luminescent species has been studied in conjunction with the poly(ethylene glycol) content. In both aqueous solutions and silica matrixes, luminescence intensity and decay time were found to increase by increasing polymer concentration. Addition of 2,2'-bipyridine resulted in complex formation between the ligand and the lanthanide ions. This complex was stabilized by association with the polymer chains. Excitation at the ligand absorption wavelength (337 nm) resulted in ligand-to-metal energy transfer and strong luminescence emission, characterized by the narrow-band emission of the metal. The complex between lanthanide ions and 2,2'-bipyridine possessed its own particular photophysical characteristics and emitted a bright broad blue luminescence with an excitation maximum around 380 nm. Freeze-drying of aqueous solutions of medium size poly(ethylene glycol) containing lanthanide ions and 2,2'-bipyridine produced an intensely luminescent solid material emitting the characteristic luminescence of the metal when excited at the ligand absorption band (337 nm) or the characteristic luminescence of the complex when excited at 380 nm.

Introduction

Several luminescent systems emitting in the visible or near-IR, such as solid-state lasers, screens, optical communication amplifiers, or common lamps contain a lanthanide ion as an active luminescent constituent. The popularity of lanthanide ions stems from their two major advantages, i.e., they emit narrow-band radiation providing high chromatic purity and they are qualified by a long excited-state lifetime. These characteristics of lanthanide ions are due to the fact that the emitting excited state and the ground state have the same f^n electronic configuration and that the f orbitals are shielded from their environment by the outer s and p electrons.^{1,2} Transitions between states of f^n configuration are strictly parity forbidden; therefore, the molar extinction coefficient is extremely low, and the decay time is very long. In reality, experimental decay times are 1 or 2 orders of magnitude lower than the theoretically predicted ones,² indicating an important interfer-

ence of nonradiative decay. Quenching of luminescence is largely influenced by coupling with vibration modes of the host environment. In particular, solvents containing $-\text{OH}$ (e.g., water or oxide matrixes, like SiO_2) extensively reduce luminescence emission intensity and decay time. In addition, clustering, which frequently occurs in sol-gel made matrixes and conventional melt glasses,³ is another main source of luminescence quenching. The design of materials, where vibrational coupling and clustering is reduced and absorption cross section is enhanced, is an important task with obvious merits.

One strategy for reducing quenching processes, in both fluid and solid environments, is to design association of lanthanide ions with organic subphases and coordination with organic ligands.^{4–10} In this respect,

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complex formation between lanthanide ions and certain organic ligands has a double beneficial effect of both protecting metal ions from luminescence quenching processes and increasing light absorption cross section by 'antenna effects'. In this last case, the organic ligand absorbs exciting radiation and transfers excitation energy to the lanthanide emitter. Typical light-harvesting ligands combining with those rare earth ions that absorb in the near-ultraviolet are, for example, 1,10-phenanthroline and 2,2'-bipyridine, which are very promising for several photophysical applications.^{8,11-13}

In the present work, we have studied systems based on poly(ethylene glycol) (PEG) oligomers and medium-size polymers, which simultaneously bind lanthanide ions and their complex with the 2,2'-bipyridine ligand and by this complexation create very efficient luminescent materials. We have previously found⁷ that the presence of PEG-200 in sol-gel made-SiO₂ matrixes¹⁴ resulted in enhancement of luminescence intensity and increase of luminescence decay time of Eu³⁺. Furthermore, enhancement can be obtained by increasing absorption cross-section in the presence of 2,2'-bipyridine^{12,13} through ligand-to-metal energy transfer. In the present work, we have studied two typical rare earth ions, Eu³⁺ and Tb³⁺, that absorb in the near-UV; thus, they can be combined with 2,2'-bipyridine, and they emit in the visible, i.e., they can offer materials scanning the visible spectrum. Organic ligand-lanthanide complexes can, to a certain extent, be protected from moisture and mildly high temperatures when incorporated into inorganic transparent matrixes, such as sol-gel silica.^{8,11} However, a dilution effect has been observed upon incorporation, resulting in decreasing luminescence intensity.⁸ Thus, it is advantageous to use preparation techniques that will enable the original photophysical characteristics of the complex to be preserved up to the final product. We have succeeded to prepare highly efficient quaternary luminescent materials by combining lanthanide ions, 2,2'-bipyridine, PEG oligomers and sol-gel silica. This and other types of materials and their photophysical behavior are described in the present work.

Experimental Section

Tetramethoxysilane (TMOS, Aldrich), poly(ethylene glycol)-200 (PEG-200, Serva), poly(ethylene glycol)-400 (PEG-400, Serva), poly(ethylene glycol)-35000 (PEG-35000, Fluka), Eu(NO₃)₃·5H₂O (Aldrich), Tb(NO₃)₃·5H₂O (Aldrich), and 2,2'-bipyridine (Bpy, Aldrich) were used as received. Millipore water was used in all experiments.

PEG-200 and PEG-400 are both liquids; therefore, solutions of Bpy and metal ions in PEG were easily obtained by direct mixing of the components and a few minutes stirring. Solid PEG, like PEG-35000, was mixed with Bpy and lanthanide ions in an aqueous solution. Solid foamy samples were subsequently obtained by freeze-drying. In a typical procedure, PEG-35000 was dissolved in water at a concentration of 25 wt % (saturated solution). Then 0.04 M lanthanide salt and 0.1 M Bpy were added, strictly in the above order, to avoid

precipitation of Bpy-lanthanide complexes. The liquid mixture was introduced in a vessel, and it was frozen to liquid nitrogen temperature. The vessel was subsequently connected with a freeze-drying apparatus (Labconco), which consists of a vacuum pump and a cold trap. After connection with the freeze-drier, the vessel is exposed to the ambient temperature, but the evaporation of the solvent under vacuum maintains a low temperature and a frozen state for the mixture. Thus the evaporation is slow, leaving the dissolved material undisturbed.

Composite organic/inorganic sol-gel matrixes were made as follows: TMOS was partially hydrolyzed by mixing it with acidified water (pH 3.0) at a molar ratio of TMOS:water = 1:2. The mixture was continuously stirred for 1h. At the beginning it was turbid but in the course of proceeding hydrolysis, it became clear. Then, to 1 mL of this original sol, we added 5 mL of water or a mixture of water with PEG oligomers at various concentrations under stirring. Stirring continued for 30 min, and then we obtained a transparent and homogeneous sol. This sol 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 the oligomer, and it was even faster at elevated oligomer concentration, leading to transparent matrixes. Rare earth salts and Bpy have been incorporated in these matrixes by solubilization in water or in the original aqueous/oligomer solution.

Absorption spectra were made with a Cary 1E spectrophotometer. Fluorescence spectra as well as Eu³⁺ and Tb³⁺ decay profiles were recorded with a (Perkin-Elmer LS50-B) spectrofluorometer. The luminescence decay profiles of the lanthanide-Bpy complexes were recorded with the photon-counting technique using a homemade hydrogen flash and ORTEC electronics.

Results and Discussion

Photophysical Behavior of Eu³⁺ in Different Environments. Eu³⁺ emits red light when excited at 396 nm. Its visible spectrum contains several peaks, three of which are easily measurable. Emission in the visible occurs from the ⁵D₀ state.^{15,16} The three characteristic peaks correspond to the following transitions: ⁵D₀→⁷F₁ (587 nm), ⁵D₀→⁷F₂ (617 nm), and ⁵D₀→⁷F₄ (688 nm). The transition ⁵D₀→⁷F₃ also appears in the same region, close to the ⁵D₀→⁷F₄ transition, but because it is very weak, it is shadowed by the latter transition. The positions of the peaks are shown in Figure 1a, which presents spectra obtained with aqueous PEG-200 solutions, containing Eu³⁺. Corresponding spectra obtained with composite silica/PEG-200 matrixes, also containing Eu³⁺, are shown in Figure 2. In both cases, we note that increasing oligomer content has a dramatic effect on band shape and intensity, particularly, for the ⁵D₀→⁷F₂ transition situated at 617 nm. In the case of silica matrixes, the 617 nm peak was relatively broad at low oligomer concentration or at its absence, indicating an important interaction with the silica environment. However, the peak became narrow and symmetric at sufficiently high oligomer content (≥70 wt %). Similar results have also been obtained with PEG-400. We expect that similar results could be also found with longer chain PEG; however, we did not succeed in making transparent xerogels for PEG size >400. The above spectral improvement was accompanied by an increase in the emission decay time. Decay times for

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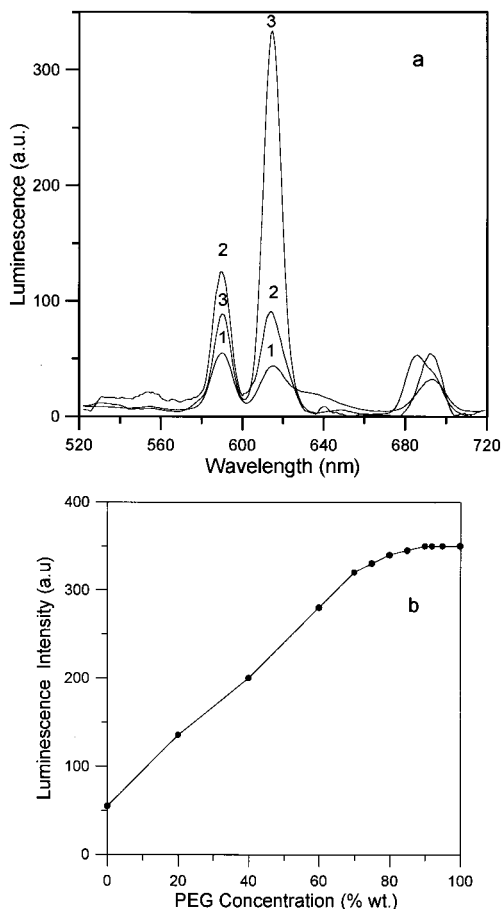


Figure 1. (a) Luminescence spectra of 40 mM Eu^{3+} in aqueous PEG-200 solutions: (1) aqueous solution without polymer; (2) aqueous solution containing 20 wt % PEG-200; and (3) pure PEG-200 solution. Excitation wavelength = 396 nm. (b) Luminescence intensity at 617 nm vs PEG content in aqueous solutions.

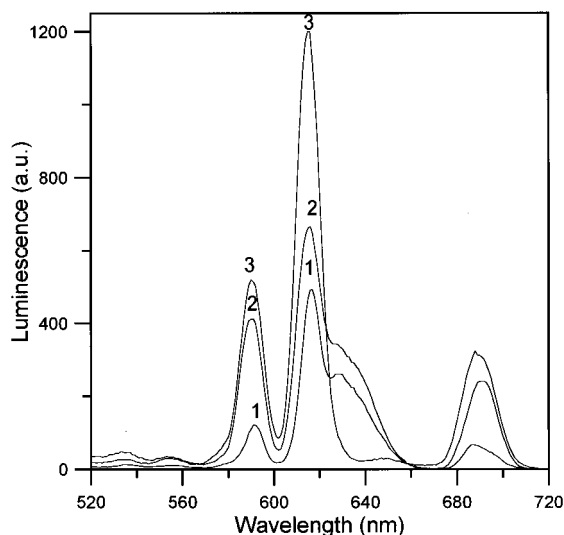


Figure 2. Luminescence spectra of Eu^{3+} in various sol-gel silica matrixes containing PEG-200: (1) silica xerogels made without polymer; (2) composite xerogels containing 15 wt % PEG-200; and (3) composite xerogels containing 90 wt % PEG-200. The concentration of Eu^{3+} in the sol was 40 mM in all cases. Excitation wavelength = 396 nm.

various aqueous solutions and silica xerogel matrixes are listed in Tables 1 and 2. The decay profiles could be fitted with single exponentials, indicating that all Eu^{3+}

Table 1. Luminescence Decay Times (ms) of 40 mM Eu^{3+} in Various Aqueous PEG-200 or PEG-400 Solutions

wt % PEG-200	τ (ms)	wt % PEG-400	τ (ms)
0	0.123	0	0.123
20	0.141	20	0.138
40	0.147	40	0.142
60	0.151	60	0.149
80	0.169	80	0.171
100	0.568	100	0.580

Table 2. Luminescence Decay Times (ms) of Eu^{3+} in Various Sol-Gel Silica Matrixes Containing PEG-200 or PEG-400^a

wt % PEG-200	τ (ms)	wt % PEG-400	τ (ms)
0	0.147	0	0.147
17	0.179	17	0.166
35	0.233	35	0.174
53	0.234	53	0.191
70	0.329	70	0.313
90	0.343	90	0.333

^a The Eu^{3+} concentration was 40 mM and was measured in the original solution before drying.

ions detect the same environment. PEG-200 and PEG-400 practically gave the same results, suggesting a similar behavior of both these oligomers. Thus, the decay time increased from 0.123 ms in the absence of the oligomer (i.e., in pure water) to above 0.560 ms in pure PEG. In the case of aqueous solutions, we have detected a critical oligomer concentration, i.e., 80 wt %, above which an abrupt increase of decay time was observed. Apparently, for a given europium concentration, there exists a critical concentration of aqueous PEG that can produce an important effect on emission characteristics. Indeed, as seen in Figure 1b, where the luminescence intensity for the 617 nm emission is plotted against polymer concentration, there exists a quasi-linear increase up to about 70% polymer, while a plateau was obtained above 80%. The existence of such a critical value indicates a cluster formation with critical aggregation concentration. 80wt % PEG-200 corresponds to about 100 chains per lanthanide ion. However, this a rough calculation simply based on molarity considerations. Most probably, not all of polymer chains take direct part in the formation of the complex, but it takes a substantial amount of PEG-200 to shield Eu^{3+} ions from the effect of water. No critical behavior was however detected in composite silica/PEG matrixes where the increase of Eu^{3+} decay time smoothly evolved with PEG content, particularly for PEG-200. The same was true for the luminescence intensity. This phenomenon is apparently related with Eu^{3+} solubility in water, which is expected to be larger than that in silica, and with the complexing capacity of the oligomer, possibly in coordination with more than one complexing sites on the same or on different molecules. The strong indication of clustering, as deduced by the above data as well as by the different behavior of water and of composite SiO_2/PEG matrixes, is consistent with the formation of organic subphases in the silica matrix. Europium ions preferentially solubilized in such subphases could be fully protected from quenching processes and could thus be unable to detect any critical behavior.

Extension to Tb^{3+} . The behavior of Eu^{3+} has its special characteristics but is not unique. Similar behavior was also registered with Tb^{3+} . Four lines of Tb^{3+} emission can be detected in the visible spectrum (Figure

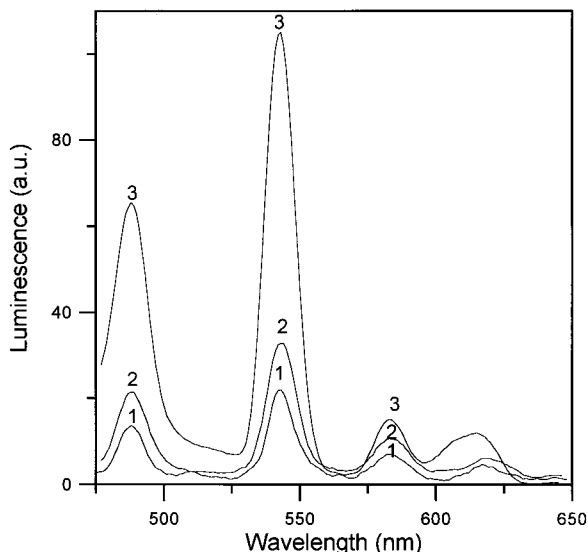


Figure 3. Luminescence spectra of 40 mM Tb^{3+} in aqueous PEG-200 solutions: (1) aqueous solution without polymer; (2) aqueous solution containing 20 wt % PEG-200; and (3) pure PEG-200 solution. Excitation wavelength = 370 nm.

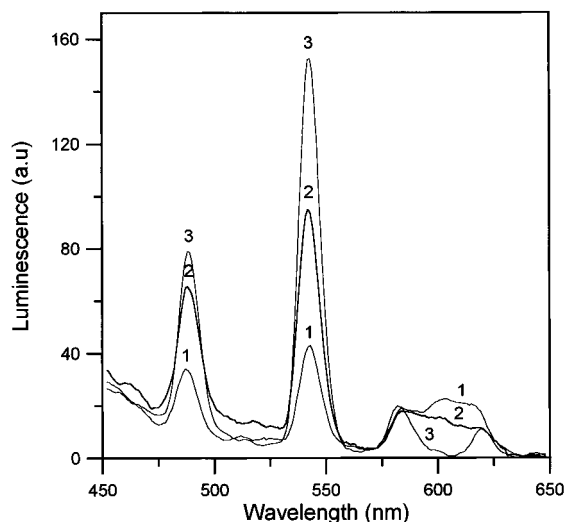


Figure 4. Luminescence spectra of Tb^{3+} in various sol-gel silica matrixes containing PEG-200: (1) silica xerogels made without polymer; (2) composite xerogels containing 15 wt % PEG-200; and (3) composite xerogels containing 90 wt % PEG-200. The concentration of Tb^{3+} in the sol was 40 mM in all cases. Excitation wavelength = 370 nm.

3), corresponding to transitions from the 5D_4 state:¹⁷ $^5D_4 \rightarrow ^7F_6$ (489 nm), $^5D_4 \rightarrow ^7F_5$ (545 nm), $^5D_4 \rightarrow ^7F_4$ (586 nm), and $^5D_4 \rightarrow ^7F_3$ (622 nm). The most prominent line is observed at about 545 nm. As the polymer content increased, we observed a marked increase in the emission intensity, both in aqueous solutions (Figure 3) and silica matrixes (Figure 4) and in the decay times, as seen in Tables 3 and 4. Terbium then demonstrated a similar behavior as europium.

Lanthanide-2,2'-Bipyridine Complexes Stabilized by PEG. PEG-200 is a liquid that can solubilize large quantities of both 2,2'-bipyridine (Bpy) and lanthanide salts. Figure 5 shows the photophysical behavior of Bpy in such a solution. The ligand absorbs in the near-UV, and its fluorescence emission is recorded with

Table 3. Luminescence Decay Times (ms) of 40 mM Tb^{3+} in Various Aqueous PEG-200 Solutions

wt % PEG-200	τ (ms)
0	0.47
20	0.66
80	0.88
100	1.37

Table 4. Luminescence Decay Times (ms) of Tb^{3+} in Various Sol-Gel Silica Matrixes Containing PEG-200^a

wt % PEG-200	τ (ms)
0	0.48
17	0.62
90	1.20

^a The Tb^{3+} concentration was 40 mM and was measured in the original solution before drying.

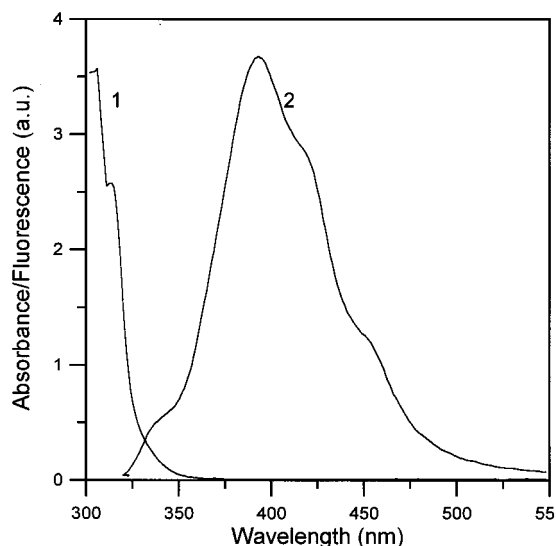


Figure 5. Absorption (1) and fluorescence (2) spectra of a solution of 0.1 M 2,2'-bipyridine in PEG-200.

maximum excitation efficiency at 337 nm and maximum emission intensity at 396 nm. Europium(III) and terbium(III) ions are associated with PEG, a property that is common with other cations.¹⁸ Solvation of ionic salts with PEG involves the formation of both ion/polymer and ion/ion complexes and appears to be principally the result of Lewis acid-base interaction between dissolved cations and ether oxygens of the polymer chain.^{18,19} Ionic conductivities studied with various divalent cations have revealed that cations play the role of polymer chain cross-linkers while anions are the charge carriers.²⁰ Cationic complexation is then expected to be even stronger with trivalent lanthanides. As a result of this complexation, we got an enhancement of luminescence intensity and excited-state lifetime, as seen in the previous two paragraphs. Europium luminescence has been tested in several different environments. Only by direct excitation at its absorption peak at 396 nm is it possible to obtain detectable luminescence (cf. data of Figure 6). The absorption peak at 396 nm corresponds to excitation by transition to the 5L_6 energy state- ($^7F_0 \rightarrow ^5L_6$),²¹ which is the only state that leads to

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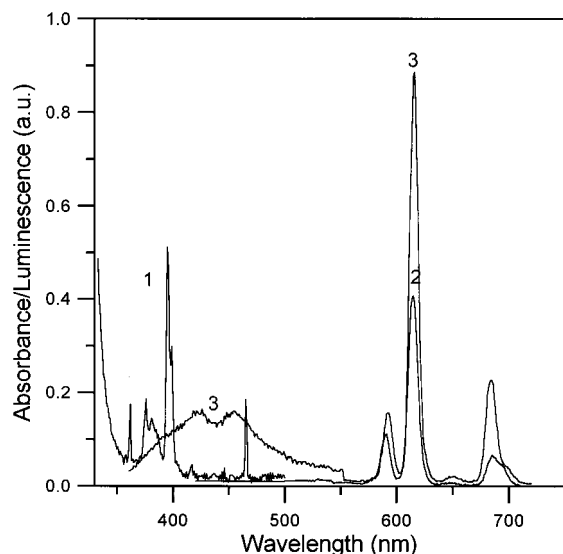


Figure 6. (1) Absorption spectrum of a solution of 0.02 M Eu^{3+} in PEG-200. (2) Luminescence spectrum of the same solution by excitation at 396 nm. (3) Luminescence spectrum of a solution of 0.02 M Eu^{3+} and 0.1 M 2,2'-bipyridine in PEG-200 by excitation at 337 nm.

detectable luminescence. This is verified by the excitation spectrum (not shown). In reality, as indicated by the narrowness of the absorption peak (Figure 6), Eu^{3+} strictly luminesces by excitation around this limited area, a fact that creates practical inconveniences. However, the situation was radically changed when Bpy was added to the solution. In the presence of the ligand, Eu^{3+} red luminescence intensity largely increased, while an additional wide-band luminescence also appeared in the blue (curve 3, Figure 6). Curve 3 shows that the typical red luminescence of Eu^{3+} is enhanced in the presence of Bpy, while excitation is now done at the absorption maximum of the ligand, i.e., 337 nm. Obviously, Eu^{3+} and Bpy readily form a coordination complex assisted and stabilized by PEG molecules.¹² This further increase of the luminescence intensity of Eu^{3+} is a result of the increase of absorption cross-section by excitation of the ligand and energy transfer to the metal ion.² The obtained material gives strong and bright luminescence by near-UV excitation. It is hard to measure the luminescence quantum yield of the above PEG-Bpy- Eu^{3+} complex due to the lack of appropriate standard. Instead, the efficiency of the material is seen in Figure 7a, where a picture of the emitted luminescence was taken by pulsed N_2 -laser excitation at 337 nm. No light can be seen or detected even with sensitive detectors under the same excitation conditions in the absence of Bpy.

Similar data were also obtained with Tb^{3+} in the place of europium ions. The corresponding luminescence spectrum of PEG-200- Tb^{3+} -Bpy complex is shown in Figure 8. Intense green luminescence was observed by excitation at 337 nm, i.e., at the ligand absorption maximum. A picture of Tb^{3+} luminescence under pulsed N_2 -laser excitation at 337 nm can be seen in Figure 7b. The bright green radiation is a result of the increase of absorption cross-section by absorption of Bpy and energy transfer to terbium.

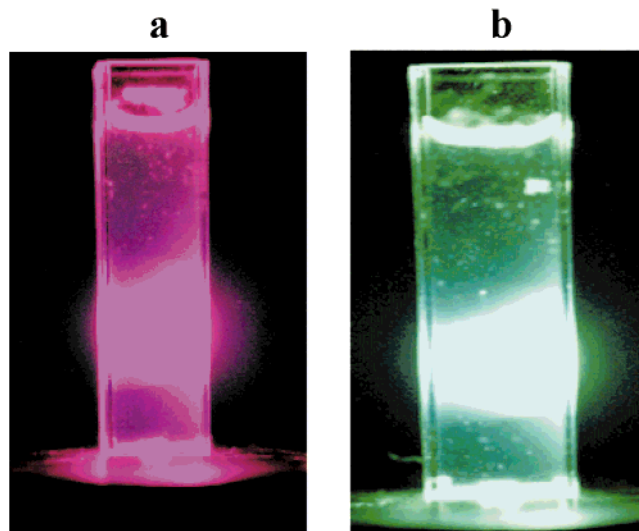


Figure 7. Snapshots of luminescence emission by solutions of 0.1 M 2,2'-bipyridine and 0.04 M Eu^{3+} (a) and 0.04 M Tb^{3+} (b) in PEG-200. Excitation by a pulsed N_2 laser at 337 nm.

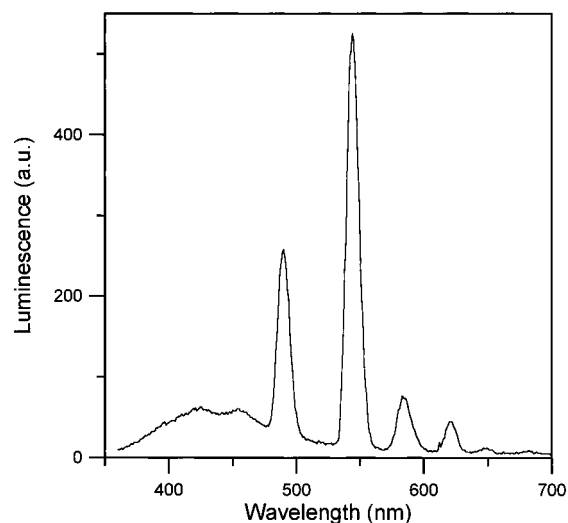


Figure 8. Luminescence spectrum of a solution of 0.02 M Tb^{3+} and 0.1 M 2,2'-bipyridine in PEG-200 by excitation at 337 nm.

If both Tb^{3+} and Eu^{3+} are introduced in the solution, their spectra are superposed and blue (complex), green (Tb^{3+}), and red (Eu^{3+}) luminescence are simultaneously obtained. Thus, the whole visible spectrum can be scanned with a rather simple system by single near-UV excitation.

PEG-400 has also been tried and gave similar results. The choice of oligomers is made for the following two reasons, even though any PEG chain is expected to have a similar complexing capacity: (1) the fluid phase is a convenient form for practical studies; and (2) PEG oligomers match well with silica network^{7,12} producing soft solid matrixes by the sol-gel process. Indeed, a mixture of PEG-200 with prehydrolyzed tetramethoxysilane produces transparent matrixes without any effect on the photophysics of the PEG-lanthanide ion-Bpy complex. Gelling is, of course, obtained by inorganic polymerization and creation of a -O-Si-O- network, as it is known from the rich literature on the sol-gel process by alkoxide hydrolysis and polymerization. The obtained materials gave strong and bright luminescence even by excitation by conventional sources, while all

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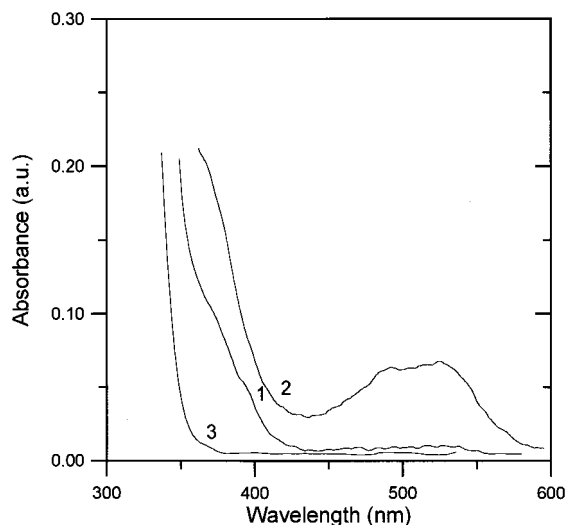


Figure 9. Absorption spectra of solutions of 0.1 M 2,2'-bipyridine and 0.02 M Eu^{3+} (1) or 0.02 M Tb^{3+} (2) in PEG-200. The absorption spectrum of free 2,2'-bipyridine (i.e., without any lanthanide ions) is also shown for comparison (3).

spectral characteristics presented in Figures 5–8 were reproduced in the presence of silica.

Larger chain PEG cannot be combined with alkoxides to give transparent composite silica/organic gels, as already said. However, equally efficient luminescent solid samples can be obtained by freeze-drying aqueous solutions, containing medium (or large)-size polymer chains. The obtained foamy solid was colored due to absorption from the Bpy–lanthanide ion complex (see next paragraph). The material was intensively luminescent as in the previous cases. By Bpy excitation (337 nm), it emitted green or red light when it contained Tb^{3+} or Eu^{3+} , respectively. Obviously, the binding capacity of PEG chains for lanthanide ions and for their complexes with Bpy is not limited to PEG oligomers but, as expected, is a common property of all PEG chains.

Photophysical Characterization of the Bpy–Lanthanide Ion Complexes. In the previous paragraph, we have shown that a complex is formed between Bpy and lanthanide ions. Its presence is clearly demonstrated by the appearance of a new emission band in the blue (maximum at 456 nm), i.e., at longer wavelength than the free Bpy emission (cf. Figure 5) and, as it will be seen below, by the structure of its absorption spectra. The photophysical characteristics of this complex are analyzed here. Figure 9 shows the absorption spectra of the complex (in PEG-200 solutions), which are different from the absorption spectrum of either Bpy or the metal ions (see also Figures 5 and 6). Thus, the complex absorbs at longer wavelengths than Bpy while an important absorption band also occurs in the visible, particularly in the case of Tb^{3+} . This band is at the origin of the coloration of the samples containing such complexes. The luminescence spectra of the complex (also in PEG-200 solutions) are seen in Figure 10. These spectra have been recorded by excitation at the maximum of the excitation spectra (380 nm), which do not much differ from one lanthanide ion to the other. The two curves contain several narrow bands that are due to excitation of noncomplexed lanthanide ions, which apparently exist in solution. If we take out the free lanthanide emission, the luminescence spectra are

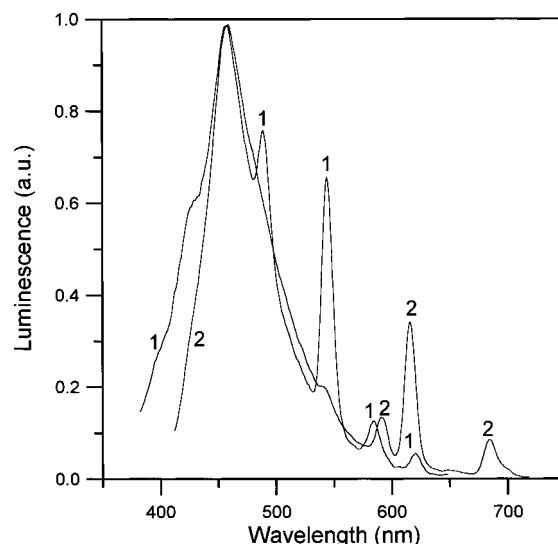


Figure 10. Luminescence spectra of solutions of 0.1 M 2,2'-bipyridine and 0.02 M Tb^{3+} (1) or 0.02 M Eu^{3+} (2) in PEG-200 by excitation at 380 nm.

practically the same for both complexes, and they peak at longer wavelength than that of free Bpy. No emission has been detected by excitation at the visible absorption band of the complexes. The fact that the blue luminescence of the complex originates from the excitation at 380 nm, i.e., from a spectral region where the lanthanide ions have their major absorption peaks (cf. Figure 6, curve 1) and where the free ligand does not absorb light, suggests that the blue luminescence most probably comes from a metal-to-ligand intracomplex charge transfer. The decay time of the blue luminescence was very short (about 6 ns, for both complexes). The decay time of free Bpy is also of about the same value. Thus, a highly probable mechanism of luminescence emission by the complex is the following: complexed lanthanide ions are excited by absorption between 350 and 400 nm, the excited electron is rapidly transferred to an empty state of the ligand, and luminescence is subsequently emitted from a singlet state. The probability of emission from a singlet state is high, hence the short decay time. An alternative mechanism of luminescence emission would have been by excitation and emission between states of the ligand itself, which have suffered an extensive bathochromic shift in the presence of the complex. Such a suggestion might be dictated by the similar appearances of both emission and near-UV absorption spectra of the ligand and the complex. On the other hand, such a large red shift in the spectra is unjustified by comparison to previously published data² on the free ligand's excitation wavelength (337 nm). We then believe that a metal-to-ligand charge transfer is a more plausible mechanism, but this subject is being further studied in our laboratory.

Conclusions

We have shown that association of lanthanide ions with PEG chains results in increasing their luminescence intensity and luminescence decay time in several fluid or solid environments. Complexation is achieved by interaction with the ether oxygen of the ethylene glycol group. The presence of the Bpy ligand results in efficient complex formation between the ligand and the

lanthanide ion with impressive effect on the luminescence emission intensity. Strong green or red light is emitted by excitation of Bpy in the presence of terbium or europium ions, respectively. The broad blue emission band that also appeared in the presence of Bpy is most probably due to metal-to-ligand charge transfer. Transparent organic/inorganic matrixes can be made by the sol-gel method using tetramethoxysilane and PEG oligomers where the above complexes are successfully

incorporated. Solid luminescent materials can be also made with larger PEG chains by means of a freeze-drying method.

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