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The luminescence, molecular and electronic structure, and excited state energetics of tris complexes of 4-phenylethynyl-2,6-pyridinedicarboxylic acid with Eu(III) and Tb(III) prepared in sol–gel

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Abstract

The incorporation of high symmetry racemic lanthanide complexes into sol–gels has recently been demonstrated to be a useful technique to eliminate racemization, and thus allow one the ability to probe individual enantiomers by circularly polarized excitation (CPE) followed by circularly polarized luminescence (CPL). Reduced CPL from sol–gels containing high concentrations of lanthanide complexes has also led to an interpretation of the results in terms of racemization due to excited state energy transfer. This paper is a continuation of our previous studies on the diminished differential excited states concentration of a photoenriched racemic mixture of Eu(dipicolinate = DPA)₃^{3−} incorporated in a sol–gel. The high resolution emission, emission excitation spectra, decay times and CPL of the Eu(III) and Tb(III) complexes of the 4-phenyl-ethynyl-dipicolinic acid at 300 and 77 K in solution and incorporated into silica sol–gel are reported. The kind of experiments mentioned above are inherently sensitive to the nature of the local environment of the complexes in the sol–gel, and this is the focus of the results presented here. This information is critical in the continued development of sol–gel based sensors. Comparison of the CPL, total luminescence, and excitation results with spectra obtained from aqueous solution are interpreted in terms of local and bulk structural properties of the sol–gel system. The mechanism of intra- and intermolecular energy transfer in Eu(III) and Tb(III) systems is also analyzed.

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1. Introduction

Luminescent lanthanide complexes having strong absorption chromophores have attracted considerable attention in recent efforts to produce effective lanthanide-based luminescent sensors. This is due to the remarkably strengthened luminescence intensity of the rare earth ions that is possible through indirect excitation of the emitting state as compared to the weak parity-forbidden intraconfigurational $f \rightarrow f$ absorption.

This phenomenon is often referred to as the “antenna effect” [1–14]. The increased luminescence efficiency and sensitivity that may be obtained is especially important in the design of lanthanide-based luminescence probes of biological structure [2,6–11], and light conversion molecular device (LCMD) [1,3,12–16]. There has also been an increased effort to incorporate luminescent lanthanide complexes into solid matrices for the purpose of developing useful sensors. For this latter purpose, the sol–gel technique offers the possibility to prepare an inorganic matrix possessing extremely good optical, thermal and chemical stability [14,16]. A high-quality optical component can be obtained in the formation of a sol–gel if special care is taken during the drying and

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densification stages to prevent cracking. Our primary interest in this area is the incorporation of chiral luminescent lanthanide complexes into sol–gels, and the development of their use as chiral-optical probes [17]. A major consideration in this regard is the formation of sol–gels of sufficient optical quality to allow the transmission of circularly polarized light. The importance of developing a better understanding of the structure and energetics of these systems is enhanced by recent reports of using lanthanide luminescence from complexes incorporated into sol–gels using molecular imprinting techniques in the development of specific molecular sensors [18].

Although the luminescence from lanthanide complexes with chiral ligands are of some interest, complexes composed of multidendate achiral ligands that form chiral structures upon complex formation are of special interest due to the fact that perturbations from the racemic equilibrium can be easily detected. For example, chiral lanthanide complexes, that occur in the solution as racemic mixtures, can often be studied by circularly polarized luminescence (CPL) spectroscopy by photopreparing an enantioenriched excited state through circularly polarized excitation [19,20]. CPL spectroscopy yields information about the symmetry and structure of the excited state and can provide information concerning energetics and other dynamic processes that occur on the timescale of the emission. This application of CPL involving circularly polarized excitation (CPE) is referred to as CPE/CPL. It is successful only if the excited state enantiomeric excess is at least partially maintained during the excited state lifetime.

Application of CPL spectroscopy to chiral lanthanide complexes prepared in sol–gels does allow one to study chiral systems in which the effect of structural racemization can be neutralized. At the high concentrations that can be obtained in sol–gels, however, the effect of excited state racemization due to radiationless energy transfer can not be neglected [21]. This area of research also has the potential to provide unique information concerning differences in diastereomeric energy transfer rates [22,23]. In these previous works, we reported the observation of CPL from complexes of $\text{Eu}(2,6\text{-pyridine-dicarboxylic acid} = \text{DPA})_3^{3-}$ and $\text{Eu}(2,2'\text{-bipyridine-N-oxide} = \text{bpyO}_2)_4^{3+}$ prepared in sol–gels as a function of concentration. It was shown that the variation of CPL with concentration can be fit to a theoretical energy transfer model, and a value for the critical transfer distance, which is a measure of the energy transfer rate may be estimated.

The present work is a continuation of earlier studies on CPL for Eu(III) and Tb(III) complexes but with more bulky ligand 4-phenyl-ethynyl-dipicolinic acid (PEDPA) incorporated into a sol–gel. This species is less spherical than the parent DPA species, and has been selected for additional study due to the fact that the

Eu(III) complex with PEDPA is exceptionally luminescent. Previous results have suggested that local concentration of the imbedded luminescent complexes into cavities in the sol–gel matrix is present, and that this non-uniform distribution of species has an effect on the optical characteristics of the sol–gel material [22]. Our expectation is that the more extended structure of this ligand would mitigate the formation of these local clusters. We report results from a number of different spectroscopic measurements on Eu(PEDPA)_3^{3-} and Tb(PEDPA)_3^{3-} under a variety of experimental conditions. The results are interpreted in terms of molecular and excited state electronic structural details of the complexes.

2. Experimental

A stock solution of 0.35 M 2,6-pyridinedicarboxylic acid (DPA, Aldrich) in H_2O was prepared, the pH was adjusted to 8 by addition of concentrated NaOH. A stock solution of Eu(III) was prepared by dissolving $\text{Eu-Cl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) into H_2O , the pH was adjusted to 3.5 with concentrated HCl. 4-phenylethynyl-2,6-pyridinedicarboxylic acid (PEDPA) was synthesized as described previously [24]. A stock solution containing this ligand was also prepared and the pH was adjusted to 10 with concentrated NaOH. Eu(DPA)_3^{3-} and Eu(PEPDA)_3^{3-} solutions were prepared by combining aliquots of the two respective stock solutions. The metal to ligand ratio in case of Eu(DPA)_3^{3-} was 1:3.5 and for Eu(PEPDA)_3^{3-} 1:10 since experimental results show that this ratio is required to ensure the tris complex.

The sol–gel samples were synthesized by the acid-catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS) with deionized water. After homogenization the pH of the sol was adjusted to 7 using NaOH. Doping was accomplished by adding sufficient volumes of Eu(DPA)_3^{3-} or Eu(PEPDA)_3^{3-} solution to the stirred sol. The gelation occurred in a few days and then the samples were aged for one month at room temperature. The sol–gel samples were transparent and free of cracks.

Excitation and emission spectra were performed at 293 and 77 K using SLM Aminco SPF 500 spectrofluorometer equipped with 300 W xenon arc lamp, and a liquid N_2 -cooled cryostat in the 200–800 nm spectral range. Fluorescence decay times were measured at 293 and 77 K using a Tektronix TDS oscilloscope, Jobin-Yvon THR 1000 monochromator, and Lambda-Physik 105 excimer laser. Absorption spectra were recorded by a Cary Varian 500 spectrophotometer. Laser excitation and emission measurements were accomplished by using a Coherent-599 tunable dye laser (0.03 nm resolution) with Coherent Innova-70 argon ion laser as a pump source. The laser dye used in all experiments was rhodamine 6G dissolved in ethylene glycol. The optical detection system consisted of a focusing lens, long pass filter,

and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photon counting mode. Circularly polarized luminescence following circularly polarized excitation was measured using an instrument described previously [20,25].

3. Results and discussion

In Fig. 1 we plot the total luminescence spectrum of $\text{Eu}(\text{PEDPA})_3^{3-}$ in an aqueous solution at room temperature, in a frozen solution at 77 K, and dissolved in a sol-gel. In Fig. 2, similar results are presented for $\text{Tb}(\text{PEDPA})_3^{3-}$. The emission transitions displayed originate from the $^5\text{D}_0$ excited level of Eu(III), or the $^5\text{D}_4$ excited level of Tb(III). The samples exhibit typical metal-centered emission following UV excitation at 312 nm corresponding to a strong ligand $\pi \rightarrow \pi^*$ absorption. As can be seen in Fig. 1, the Eu(III) complex exhibit strong luminescence in all three environments. However, a significant reduction in luminescence intensity in the Tb(III) complex in the sol-gel is apparent in the results given in Fig. 2. An explanation for this decrease in intensity will be presented below. In Fig. 3(a) we plot the excitation and absorption spectra of $\text{Eu}(\text{PEDPA})_3^{3-}$ in aqueous solution at room temperature. The excitation

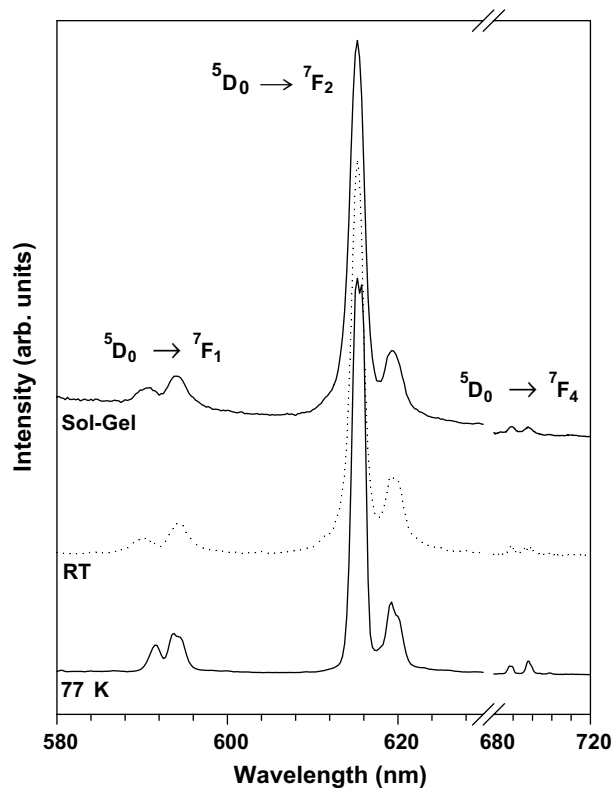


Fig. 1. Luminescence spectra of $\text{Eu}(\text{PEDPA})_3^{3-}$ in aqueous solutions and silica sol-gel; Eu:PEDPA ratio = 1:10.

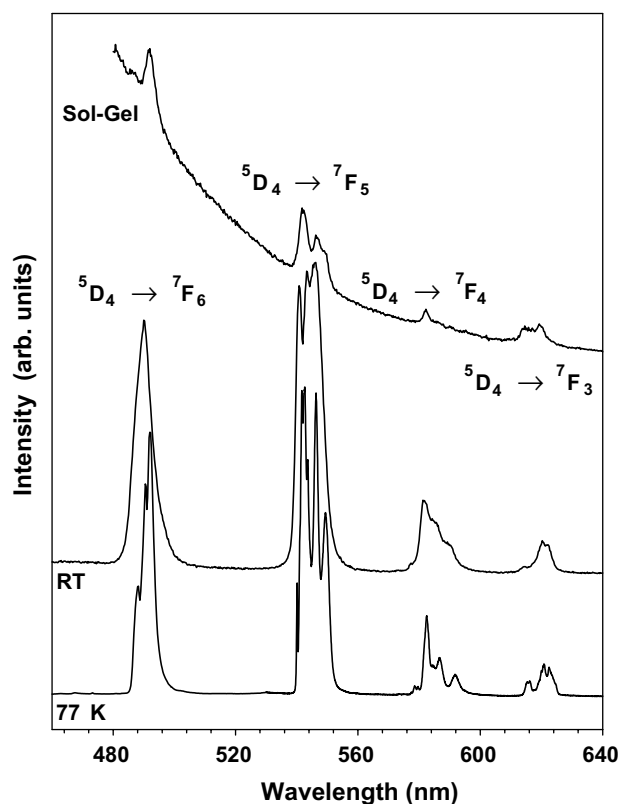


Fig. 2. Emission spectra of $\text{Tb}(\text{PEDPA})_3^{3-}$ in aqueous solutions and silica sol-gel; Tb:PEDPA ratio = 1:10.

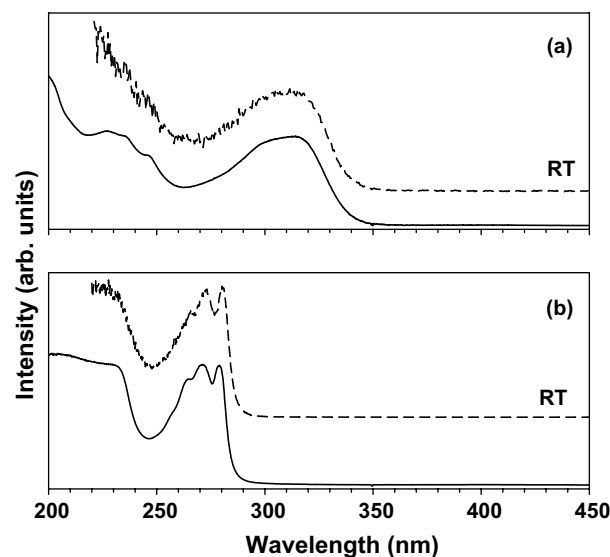


Fig. 3. (a) Absorption (solid line) and excitation (dashed line) spectra of $\text{Eu}(\text{PEDPA})_3^{3-}$ in aqueous solutions. $\lambda_{\text{obs}} = 615 \text{ nm}$; (b) absorption (solid line) and excitation (dashed line) spectra of $\text{Eu}(\text{DPA})_3^{3-}$ in an aqueous solution. $\lambda_{\text{obs}} = 615 \text{ nm}$ (b).

spectrum was obtained by monitoring the strong $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu(III) at 615 nm. For comparison in Fig. 3(b) we plot similar results for tris complex of Eu(III) with the less conjugated ligand DPA. The

broad bands centered at 260 nm for $\text{Eu}(\text{DPA})_3^{3-}$ and 315 nm for $\text{Eu}(\text{PEDPA})_3^{3-}$ are assigned to a $S_0 \rightarrow S_1$ absorption transition within the organic chromophore. Similar results are obtained for aqueous solutions of $\text{Tb}(\text{PEDPA})_3^{3-}$ and $\text{Tb}(\text{DPA})_3^{3-}$ when the emission is monitored at 545 nm corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of $\text{Tb}(\text{III})$. These results confirm the sensitization of the metal-centered luminescence by the efficient energy transfer from organic ligands.

As evident in Figs. 1 and 2, the shape of the emission peaks and relative intensity ratios of the transitions shown are very similar, indicating that incorporation of the complexes into the sol-gel matrix does not significantly modify the structure of the complexes. The existence of only one peak in the spectral region corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of the $\text{Eu}(\text{III})$ ions, as shown in Fig. 4, is consistent with the presence of only one distinct form of the complex, both in aqueous solutions and sol-gels. Similar results has been reported for $\text{Eu}(\text{DPA})_3^{3-}$ in our earlier studies [22,23]. It should be noted that, as mentioned above, tris-PEDPA complexes were formed from solutions containing a large excess ($>1:10$) of ligand, to ensure complete formation of the tris complex. Therefore, these sol-gels contain lanthanide complex and considerable amounts of

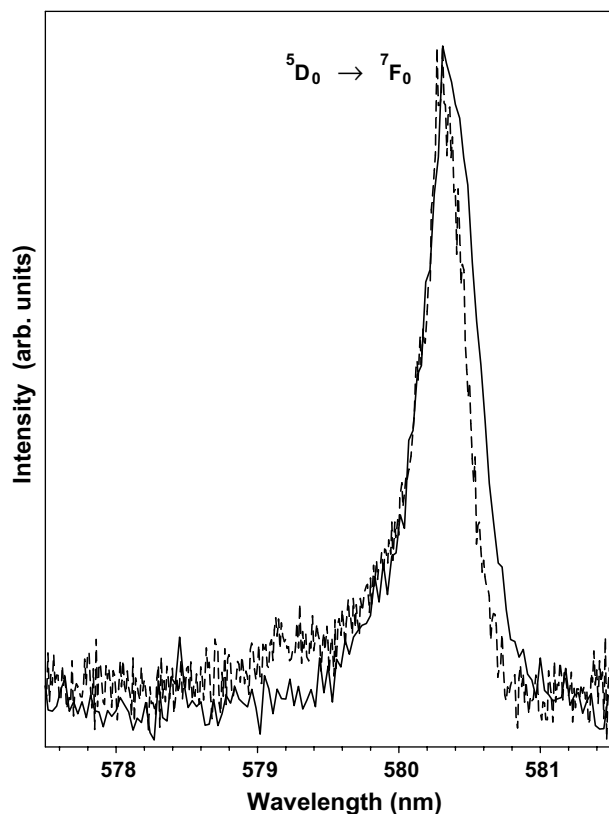


Fig. 4. $^5\text{D}_0 \rightarrow ^7\text{F}_0$ luminescence spectra of $\text{Eu}(\text{PEDPA})_3^{3-}$ at 77 K, in aqueous solution (dashed line) and sol-gel (solid line); $\text{Eu}:\text{PEDPA}$ ratio = 1:10.

Table 1

Luminescence lifetimes, $\lambda_{\text{exc}} = 355$ nm

Experimental conditions	RT τ	77 K τ
	(ms)	(ms)
$\text{Eu}(\text{PEDPA})_3^{3-}$ in H_2O	1.05	1.17
$\text{Eu}(\text{PEDPA})_3^{3-}$ in D_2O	1.64	1.71
$\text{Eu}(\text{PEDPA})_3^{3-}$ in sol-gel molar conc. 0.091	0.84	
$\text{Eu}(\text{PEDPA})_3^{3-}$ in sol-gel molar conc. 0.0045	0.87	

uncomplexed ligand. This will, of course, influence the overall spectroscopic properties of the sol-gel samples.

In Table 1 we list the luminescence lifetimes for $\text{Eu}(\text{PEDPA})_3^{3-}$ in H_2O and D_2O solutions, and prepared in a sol-gel at the concentrations given. Differences observed between measurements at room temperature and 77 K are small. According to established theories of the quenching of excited lanthanide states through O–H and O–D vibrations, the observed differences in lifetimes between H_2O and D_2O solutions indicate some involvement of water molecules in the coordination of the metal ion and/or dynamic of transformation of one enantiomer (Λ) into another one (Δ) involving a hydrated mediating state. No such dependence is seen for the corresponding DPA complexes where complete formation of the tris complex is obtained with only a slight excess of ligand. As described above, more than a ten fold excess of PEDPA is required to completely form the tris complex. The somewhat reduced lifetime observed for the $\text{Eu}(\text{PEDPA})_3^{3-}$ complex in sol-gels is consistent with only a slightly modified environment for the complex as compared to dilute solution.

As can be seen in Fig. 5(a), in addition to the characteristic sharp $\text{Eu}(\text{III})$ luminescence from 575 to 700 nm, the $\text{Eu}(\text{PEDPA})_3^{3-}$ doped silica sol-gel displays a broad band of green (488 nm) ligand-centered luminescence when excited in the visible (~ 410 nm). The luminescence excitation spectrum is also plotted in this figure, and it can be seen that excitation around 320 nm leads only to the metal-centered luminescence. The excitation spectrum of the metal-centered luminescence reveals two energy transfer mechanisms between organic chromophores and $\text{Eu}(\text{III})$ centers. The first is the intramolecular energy transfer (as observed in dilute solution), which often occurs in rare earth ions involving aromatic chelates, and is represented by the band with the maximum at 320 nm. The second band with a maximum of 410 nm is ascribed to intermolecular energy transfer from aggregated uncoordinated ligand. Note that the sample excited around 410 nm, exhibits both ligand- and metal-centered luminescence. The intermolecular energy transfer between organic molecules and lanthanide ions has been reported previously in solution [1,12], and in the solid state [3]. It is expected that uncomplexed ligand molecules may form aggregates in the matrix pores, leading to a shift in absorption and emission wave-

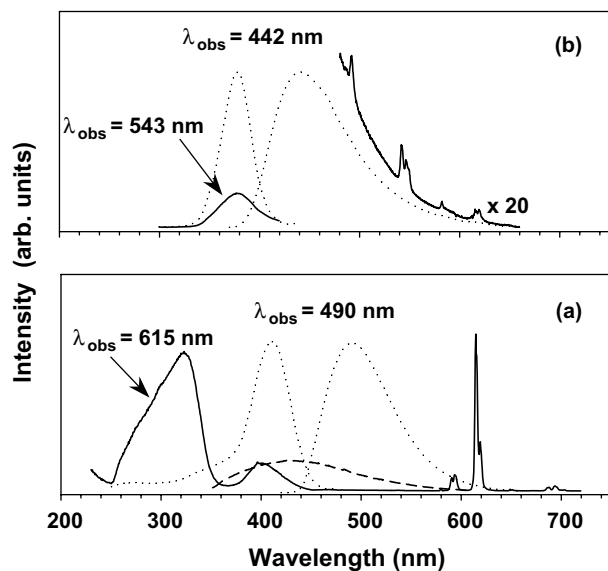


Fig. 5. (a) Luminescence and luminescence excitation spectra of $\text{Eu}(\text{PEDPA})_3^{3-}$ in a doped silica sol-gel; (b) luminescence and luminescence excitation spectra of $\text{Tb}(\text{PEDPA})_3^{3-}$ doped silica sol-gel. Dotted lines represent ligand emission, dashed lines shows sol-gel emission under given experimental condition.

lengths. This secondary excitation peak is therefore assigned to energy transfer from long lived triplet states of the aggregated aromatic PEDPA ligands to the excited energy levels of coordinated molecules and/or to the lanthanide ion levels. The ligand emission band is located in the same spectral region as $\text{Eu}(\text{III})$ ion $^5\text{D}_2$, $^5\text{D}_3$ and $^5\text{L}_6$ excited states, which makes the nonradiative energy exchange probable. It is well known that the transition probability for such an exchange is proportional to the overlap between emission of the donor and absorption of the acceptor.

As can be seen in Fig. 5(b), the $\text{Tb}(\text{PEDPA})_3^{3-}$ doped silica sol-gel displays bright blue ligand-centered luminescence (440 nm) when excited in the UV (~ 320 nm), and contrary to the $\text{Eu}(\text{III})$ sample, almost no metal-centered emission. The excitation spectrum of this blue emission is a broad band with the maximum at 375 nm. In the case of $\text{Eu}(\text{PEDPA})_3^{3-}$ the electronic properties of the aggregated PEDPA ligands provided an additional excitation mechanism for the lanthanide excited state, in the case of $\text{Tb}(\text{PEDPA})_3^{3-}$ it is clear that the aggregated ligands are providing an accessible quenching mechanism for the excited $\text{Tb}(\text{III})$ ion. The very weak metal-centered emission, therefore, can be explained by effective phonon assisted energy back transfer from the lanthanide excited states to PEDPA aggregate states. The energy back transfer is a well known phenomenon, especially for $\text{Tb}(\text{III})$ complexes, and has been reported in a number of solid state and solution samples [2,15,26]. In the $\text{Tb}(\text{PEDPA})_3^{3-}$ complex the energy gap between triplet state and $^5\text{D}_4$ level is close to

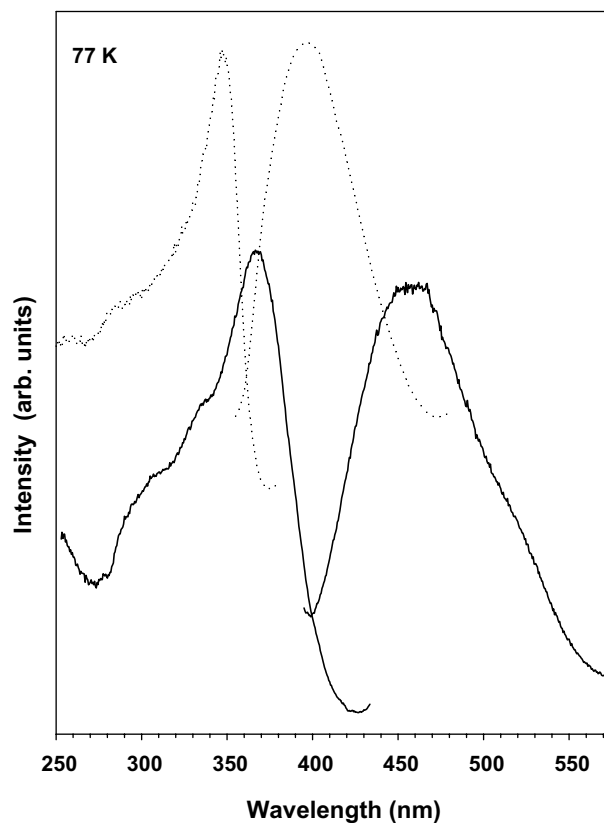


Fig. 6. Phosphorescence and phosphorescence excitation spectra of $\text{Gd}(\text{PEDPA})_3^{3-}$ in aqueous solution (dotted lines) and doped silica sol-gel (solid); $\text{Gd}:\text{PEDPA}$ ratio = 1:10.

4500 cm^{-1} as can be calculated from the phosphorescence spectrum of $\text{Gd}(\text{PEDPA})_3^{3-}$ at 77 K that is presented in Fig. 6. This energy gap is approximately equal to 1.5 OH-phonons.

For comparison we present in Fig. 7(a) and (b), total luminescence and luminescence excitation spectra for sol-gel samples doped with tris complexes of $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ with DPA. We see that in this case the sol-gel samples display both metal- and ligand-centered luminescence. In the excitation spectra of the metal centered luminescence of both samples, a broad band centered at 310 nm may be assigned to the transitions within ligand coordinated to the metal ion, as well as weak narrow bands corresponding to $f \rightarrow f$ absorption transitions of the lanthanide ions. As can be seen, ligand-centered blue emission for the $\text{Tb}(\text{III})$ sample has a maximum around 380 nm and that for $\text{Eu}(\text{III})$ at around 420 nm. Their excitation spectra show two maxima each, and overlap, to some extent, the excitation spectra of metal-centered emission.

Comparison of the absorption and excitation spectra of the complexes in aqueous solutions (see, for example, Fig. 3) shows that the spectra for the complexes of the same metal ion do not differ in relative intensities and positions of the absorption and excitation transition

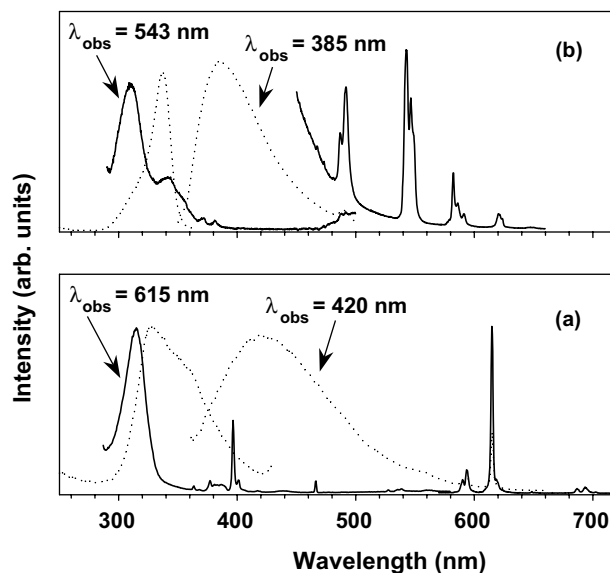


Fig. 7. (a) Luminescence and luminescence excitation spectra of $\text{Eu}(\text{DPA})_3^{3-}$ doped in a silica sol-gel; (b) luminescence and luminescence excitation spectra of $\text{Tb}(\text{DPA})_3^{3-}$ doped silica sol-gel. Dotted line represents ligand emission. Ln:DPA ratio = 1:3.5.

bands. However, comparison of the excitation spectra of the complexes taken for aqueous solutions, and spectra for the complexes imbedded in sol-gels (Figs. 5 and 7), shows significant differences at low wavelengths due to the difference in concentration of the complexes in the liquid and solid samples. In aqueous solutions the molar concentration of the complexes was approximately 10^{-6} M, but in the sol-gel process the volume of the sample is reduced such that the resultant concentration in this sol-gel was approximately 0.1 M. It is well known that for solid and more concentrated solutions the deexcitation processes may be different, and that excitation may only be effective in the tail of the absorption band [4,5,27].

Additional information concerning the electronic state characteristics of free ligand in the sol-gels may be obtained from results displayed in Figs. 6, 8 and 9. In Fig. 6 we plot the phosphorescence spectrum and the phosphorescence excitation spectrum of an aqueous dilute solution of $\text{Gd}(\text{PEDPA})_3^{3-}$. The phosphorescence spectrum may be used to determine the peak of the triplet state emission of isolated PEDPA ligand which is seen to be located at 395 nm. The phosphorescence spectrum of uncomplexed PEDPA imbedded in a sol-gel is presented in Fig. 8. From this spectrum one can see that the maximum of the triplet state emission has shifted to 485 nm. For comparison we show similar emission results for DPA in Fig. 9.

It is interesting to note that the emission of free ligand appears at different energies than the respective ligand-centered emissions recorded for metal complexes. Additionally, (see Fig 5(a) and (b)) the ligand-centered

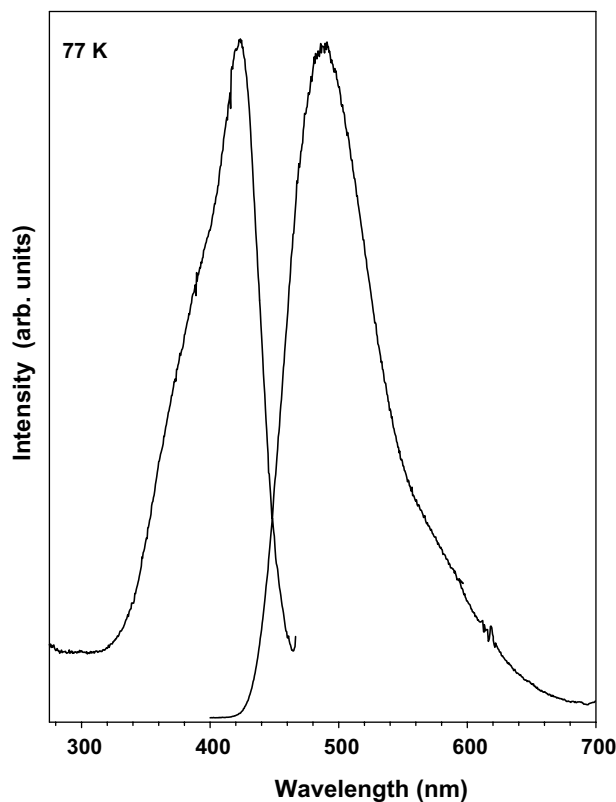


Fig. 8. Phosphorescence and phosphorescence excitation spectra of PEDPA doped into a silica sol-gel.

luminescence of Eu(III) samples with both ligands appears at lower energy than the emission of Tb(III) samples. The excitation spectra show the same tendency. It can lead to the conclusion that the lanthanide ions have some affect on the ligand states, but the effect is slightly different for the two ions.

Information concerning the extent of excited state energy transfer may be obtained through the measurement of CPL following circularly polarized excitation. A circularly polarized excitation beam will generate a non-racemic excited state concentration of $\text{Eu}(\text{PEDPA})_3^{3-}$ species from a racemic ground state by differential excitation. If the difference in excited state concentration is maintained throughout the emission lifetime, then one will observe circularly polarized luminescence. However, if there is efficient excited state energy transfer, and making the reasonable assumption that the rate of heterochiral $\Delta \rightarrow \Lambda$ and homochiral $\Delta \rightarrow \Delta$ or $\Lambda \rightarrow \Lambda$ transfer rates are approximately equal, then the initial excited state differential concentration will be reduced. In Fig. 10 we plot the total luminescence and circularly polarized luminescence for a sol-gel containing approximately 10^{-3} M $\text{Eu}(\text{PEDPA})_3^{3-}$ following circularly polarized excitation of Eu(III). CPL is observed from this racemic mixture, and the observation was confirmed by changing the excitation circular polarization from left to right and noting a completely opposite CPL spectrum

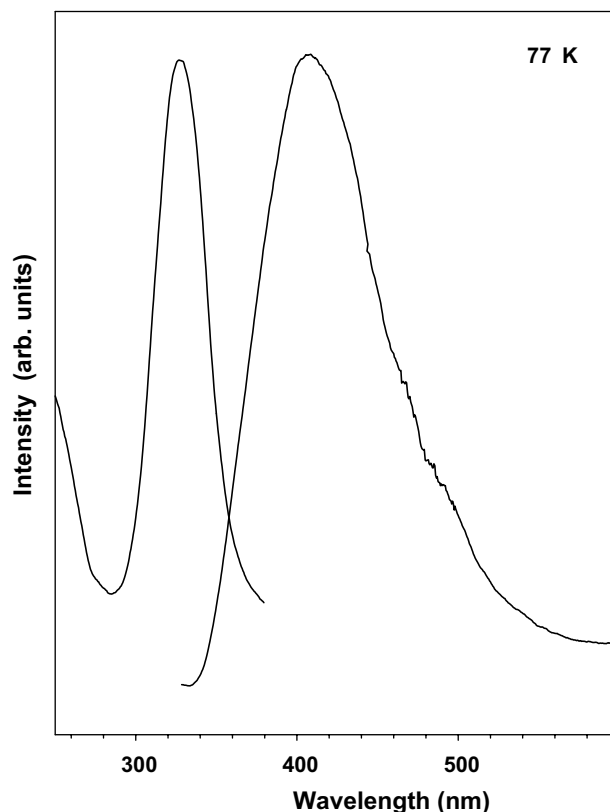


Fig. 9. Luminescence and luminescence excitation spectra of DPA doped into a silica sol-gel.

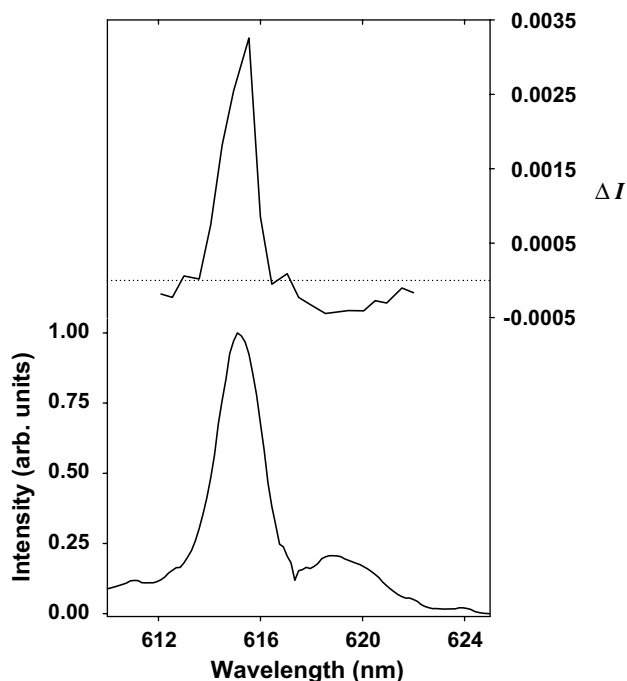


Fig. 10. CPL (upper curve) and total luminescence (lower curve) for $\text{Eu}(\text{PEDPA})_3^{3-}$ doped into a silica sol-gel following circularly polarized excitation at 594 nm.

of approximately equal magnitude. In a previous study on $\text{Eu}(\text{DPA})_3^{3-}$, CPL was measured on samples with a concentration greater than 0.08 M [22]. However, for $\text{Eu}(\text{PEDPA})_3^{3-}$ it was not possible to prepare sol-gel samples suitable for CPL measurements in which the concentration of the complex was greater than 0.1 M. Clearly, for this sol-gel system, containing a large excess of free ligand, there are structural or chemical constraints on the efficiency of incorporation of the complexes.

4. Summary and conclusions

In the design of efficient sol-gel based sensors based on lanthanide (III) emission, one must be concerned with a number of factors associated with the structural stability of the luminescent species, and the spectroscopic properties of the host matrix. We have shown in this and previous work that tris complexes of lanthanide (III) ions, which are known to racemize quickly in aqueous solution, may be imbedded in sol-gels to inhibit racemization without significant modification of the complex structure. Although to date there has been no specific application of this sensor technology to the detection of chiral species, the use of chiral luminescent lanthanide (III) ions for this purpose has significant potential for many of the same reasons that luminescent lanthanide ions are being used in quantitative fluor-immunoassays of biological substances [28].

The complexes described in this work were prepared from achiral ligands and as a result were imbedded in the sol-gels as racemic mixtures. Research is currently under way on the preparation and characterization of sol-gels containing chiral non-racemic complexes. It is anticipated that these gels may be suitable as luminescent sensors of chiral analytes through differential molecular interactions leading to preferential enantiomeric quenching or excitation of the luminescent chiral imbedded complex.

The results presented in the previous section highlight the importance of taking into account the emission of the host material itself, including the spectral properties of excess ligand that are incorporated along with the complex of interest. Emission from host material has been reported by many authors [29–31]. At low temperature (77 K) the sol-gel emits blue light of the intensity three-four times lower than show the investigated ligands (see Fig. 5(a)). Although for the purpose of this study, the host luminescence presented some experimental difficulties in the characterization of the imbedded complex, it may be that such long-lived luminescence of variable wavelength, depending upon the concentration and structure of the aromatic ligand, may lead to the production of interesting luminescent devices. This is also an area of current interest to our research groups.

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