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Investigations of the spectral properties of lanthanide(III) complexes with 3,3'-bi-isoquinoline-2,2'-dioxide (biqO₂) and a biqO₂-cryptate in solution, solids, and gels

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Abstract

Increasing interest has been observed in the spectroscopic properties of lanthanide ions in cryptates and heteroaromatic ligands where the lanthanide ions are encapsulated into the ligand structure [B. Alphov, J.M. Lehn, G. Matkis, *Angew. Chem.* 99 (1987) 259; J.M. Lehn, in: V. Balzani (Ed.), *Supramolecular Photochemistry*, Reidel, Dordrecht, 1987, pp. 29–42; N. Sabbatini, S. Perathoner, V. Balzani, B. Alpha, J.M. Lehn, in: V. Balzani (Ed.), *Supramolecular Photochemistry*, Reidel, Dordrecht, 1987, pp. 187–206]. Of special interest are those cryptates and chelating ligands in which efficient energy transfer between the ligands and the rare-earth ion takes place. The goal of the present studies is the description of the best conditions for this intra-system energy transfer in two types of compounds with 3,3'-biisoquinoline-2,2'-dioxide (biqO₂), and for a cryptate incorporating biqO₂. Results are reported for these complexes prepared in water and non-aqueous solutions, and in gels obtained by different methods. Spectroscopic methods, including absorption, emission and excitation spectra, at 293 and 77 K were used to characterize the type and symmetry of the complexes formed in solutions and gels under different conditions (pH and concentration). It is demonstrated that the type of solvent used in the sol–gel process affects the emission intensity through perturbation of the ligand:metal electronic energy levels, and the symmetry and stability of the complexes. Correlation of the solid state spectroscopic results with those in solution and gel for Eu(III) ions, illustrates the role of the energy back transfer process in emission quenching. This is found to be temperature dependent. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Absorption; Excitation; Emission spectroscopy; biqO₂-cryptate; Energy transfer; Emission quenching

1. Introduction

In the past decade there has been an increase in interest in the photophysical properties of strongly luminescent lanthanide(III) complexes in view of their potential use as laser material, solar concentrators, and molecular labels for biological applications [1–5]. It is well recognized that for these complexes to be useful in these types of applications, they must possess certain critical properties. In particular, much effort is being devoted to the study of complexes which contain ligands that have high absorbance in the UV followed by efficient energy transfer to excited f-electron states of the lanthanide ion, and an overall structure which protects the excited state from water or other solvent molecules which may lead to radiationless deactivation. In

addition, these compounds must be kinetically stable, and relatively asymmetric for increased luminescence intensity. The dominant characteristics which determine the luminescence quantum yield of these complexes are the energy gap law corresponding to the difference in energy between the excited (emitting) state and the highest state of the ground ^{2S+1}L term, the location and influence of ligand–metal charge transfer (LMCT) states, and the competition with other non-radiative decay processes. Inter- and intramolecular dynamics also affect the luminescence properties of lanthanide(III) complexes. These are severely reduced in solid samples, and, more recently, in experiments in which the luminescent species have been incorporated into transparent sol–gels [6–9].

The most luminescent lanthanide(III) complexes are those containing Tb(III) and Eu(III). These ions are frequently sensitized by coordinated aromatic ligands, including a number of hetero-aromatic species [10–14]. Of particular note are macrocyclic ligands incorporating

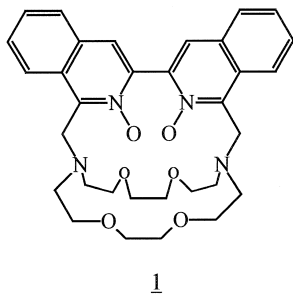
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heterocyclic N-oxides which not only form stable lanthanide complexes, but also may be very efficient sensitizers [1–5,15–17]. In this paper we report on comparative optical studies of Nd(III) and Eu(III) complexes with 3,3'-bi-isoquinoline-2,2'-dioxide (biqO₂), and in a cryptate in which this ligand has been incorporated. These studies have been performed in solutions, solids, and sol-gels. All of the spectroscopic results reported to date on complexes of Eu(III) with a cryptate containing biqO₂ have been performed in solution at room temperature, and as a result, are probing the relatively stable forms that are created under these conditions. Much of our interest is focused on studying the structure of these species and others under high resolution conditions in the solid state at low temperature in order to study the often subtle structural effects that are often necessary to fully understand the complicated photophysics of these systems. Comparison is made to previous measurements of related Eu(III) cryptates [4,5,16,17], and the potential for the use of complexes of this type in various applications is discussed.

2. Experimental

A cryptate (**1**) incorporating 3,3'-bi-isoquinoline-2,2'-dioxide, and complexes of this cryptate with Eu(III) was prepared according to the previously published



procedure. In this work we report results on complexes of Eu(III) with **1** in which the counter ions are CF₃SO₃⁻ and Br⁻. The complex has the formula Eu(**1**)(OSO₂CF₃)₂Br.

Absorption, emission, and excitation spectra were measured in D₂O, and CH₃CN, and in the solid state. The CH₃CN was first purified by distillation over CaH₂. In order to monitor and control the complexation process, the intensity of the absorption spectra corresponding to the ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2} transition were monitored as a function of pH and biqO₂ concentration. Similar control experiments were performed on Eu(III) cryptate solutions by monitoring emission intensity. Sol-gels doped with Eu(III) complexes were prepared using the method described previously [6–9]. Absorption, emission, and excitation spectra were monitored from 77 to 293 K. Absorption measurements were performed on a Cary-Varian 5 spectrophotometer; emission and excitation spectra were recorded on an SLM AMINCO SPF-5000 spectrofluorimeter equipped with a 300 W Xe-lamp, and liquid-N₂ cooled cryostat.

3. Results and discussion

In Fig. 1 we show the emission spectrum of Eu(III):**1** at room temperature and at 77 K. Of particular note is the fact that two distinct components are seen in the spectral region corresponding to the non-degenerate ⁵D₀ → ⁷F₀ transition of Eu(III). This observation is indicative of the presence of non-equivalent Eu(III) centers. This could result from the involvement of Br⁻ counter ions in metal-ion coordination, or by formation of two conformers of the cryptate structure with different energy states. Additional components are also seen in transitions to other ⁷F_J terms, consistent with the above conclusion.

Intraconfigurational *f*–*f* transitions of Eu(III) ions are especially useful as optical probes of ligand or crystal field

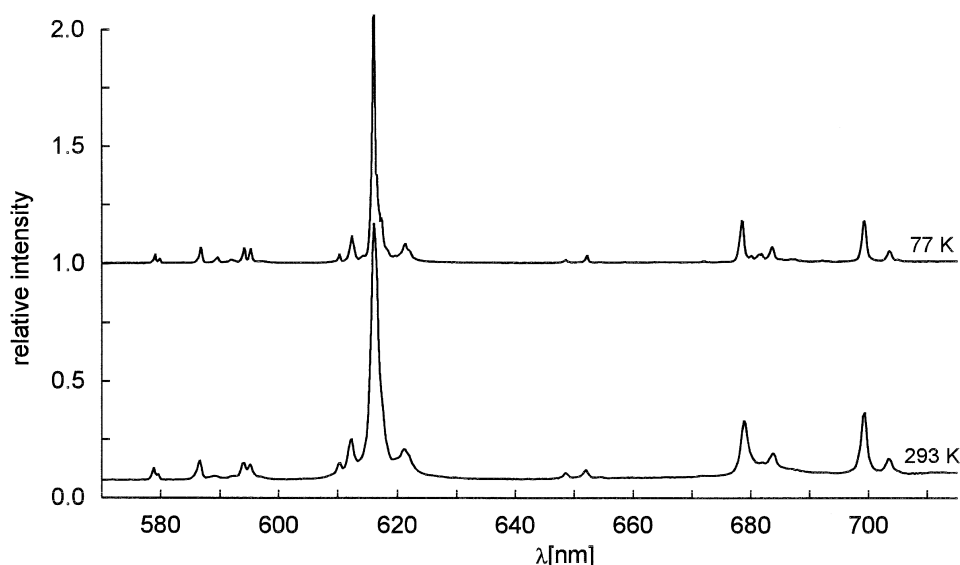


Fig. 1. The emission spectra of Eu(III):**1** solid state at 293 K and 77 K.

perturbation of the 4f electron energy levels, and the magnitude of radiative and non-radiative processes. The relative intensities of the various ${}^5D_0 \rightarrow {}^7F_J$ transitions in emission may be helpful in characterizing the mechanisms responsible for $f-f$ intensities, as well as providing information concerning the site symmetry of the Eu(III) ion. The environment of Eu(III) in this cryptate is expected to be rather asymmetric, and analysis of the intensities of the individual term transitions in the spectra displayed suggest relatively low symmetry. This is due to the observation that the intensity of the ${}^5D_0 \rightarrow {}^7F_2$ transition is very high compared to the ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions which have comparable low intensity. Note also the unexpected wavelength spread of the ${}^5D_0 \rightarrow {}^7F_4$ transition in the 680–720 nm region. This amount of splitting has not been observed by us in numerous related studies. The splitting of the 7F_1 and 7F_2 levels are also unusually large. In addition, the ${}^5D_0 \rightarrow {}^7F_3$ transition, which cannot acquire electric-dipole intensity until at least second order, has a significantly higher intensity than normal. As seen in Fig. 1, a decrease of temperature to 77 K leads to sharpening of the observed spectral lines, and the appearance of weak components which may be vibronic in origin. Although in solid Eu(III):1 cryptate one does not expect the involvement of inner sphere solvent molecules, N–O, C–H and Eu–O,N intramolecular vibrational modes can promote vibronic coupling.

The emission spectrum of Eu(III):1 in D_2O solution, as shown in Fig. 2, broadens, and the splitting of the individual components are different as compared to the solid state results. In fact the splitting is similar to that reported for Eu:1(ClO₄)₃ in CH₃CN [4] and this same compound dissolved in water [16]. This observation is consistent with the suggestion that in the complex studied here, Br[−] coordination is involved in the solid state

structure. Additional evidence concerning the involvement of Br[−] is provided through some preliminary Eu(III) lifetime measurements on Eu(III):1 in CH₃CN involving four different counter ions [16]. These results show similar effects of Cl[−] and Br[−] on the emission lifetimes. Although the spectra reported were performed at higher resolution than in previous reports, the overall shape and relative intensities of the various transitions are, in fact, similar to that of Eu:1(CF₃SO₃)₃ in water. LMCT states, e.g. involving Br[−], can modulate the emission decay times and quantum yields. The emission measured from Eu(III):1 following excitation into $\pi\pi^*$ ligand transitions remains large in D_2O (Fig. 2) solution. The spectrum is similar to that reported for Eu:1(ClO₄)₃ in CH₃CN [4], but with different relative intensities for the ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions. It is also useful to compare the results reported here with those of a different cryptand containing one biqO₂ ligand and two bipyridine units [15]. The splitting and relative intensities of the ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions are the same for these two systems, highlighting the large influence of the biqO₂ group on the spectroscopic properties (Table 1). Energy back-transfer from Eu(III) to the ligand energy levels does take place in the cryptate containing one biqO₂ ligand and two bipyridine units, however, the quantum yield for this system is still larger than that observed for a related cryptate without the biqO₂ unit [15]. The quantum yield is also larger than that observed for Eu(III):1 in CH₃CN [4].

In Fig. 2 we also show the effect of pH on the measured emission spectrum. A decrease of pH following the addition of HCl results in a substantial differences the shape of the spectra and intensity distribution. As can be seen in this figure, new components appear in the spectrum, presumably because protonation of the N–O oxygen decreases the ability of this ligand to coordinate to the

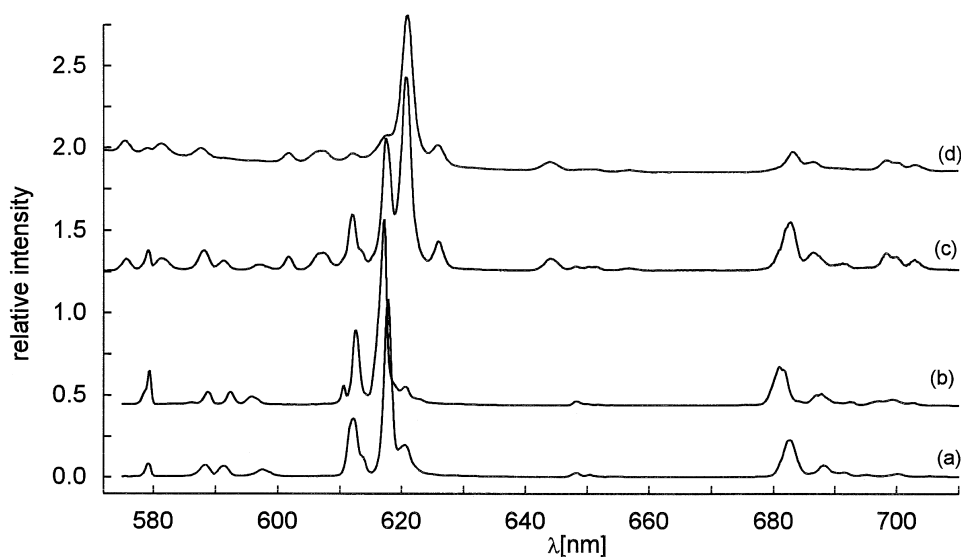


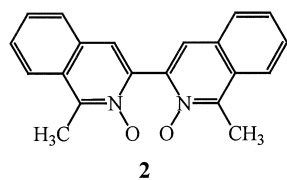
Fig. 2. The emission spectra of Eu(III):1 at 77 K: in D_2O solution (a); in D_2O solution with a addition of HCl (b); incorporated into sol–gel obtained from aqueous solution with addition of NH_4OH (c) and without NH_4OH (d).

Table 1
Relative ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensity ratio in the emission spectra

Complexes	Relative intensity ratio ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$	Temperature [K]	Disolvent
Eu:1(CF ₃ SO ₃) ₂ Br	6.8	293	Solid state
Eu:1(CF ₃ SO ₃) ₂ Br	7.6	293	D ₂ O
Eu:2(ClO ₄) ₃	14.9	293	CH ₃ CN
[Eu:3] ³⁺ [15] ^a	6.6	293	D ₂ O
Eu:1(CF ₃ SO ₃) ₂ Br	10.6	77	Solid state
Eu:1(CF ₃ SO ₃) ₂ Br	6.4	77	D ₂ O
Eu:1(CF ₃ SO ₃) ₂ Br	6.9	77	CH ₃ CN
Eu:2(ClO ₄) ₃	11.0	77	CH ₃ CN

^a Where **3** is a cryptand containing two 2, 2'-bipyridine and one 2, 2'-bipyridine-1,1'-dioxide units. The emission spectrum of [Eu:3]³⁺ is almost identical to that of [Eu:4]³⁺, where **4** is a cryptand containing two 2, 2'-bipyridine and one 3,3'-biisoquinoline-2,2'-dioxide [15].

Eu(III) ion. Additional information concerning the effect of pH on complexation may be obtained from spectroscopic studies involving the isolated biqO₂ ligand (**2**) since this ligand



mimics the complexation of the biqO₂ ligand in the cryptate. In Fig. 3 we show absorption spectra corresponding to the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ hypersensitive transition of Nd(III) for three different ligand:metal ratios in CH₃CN solutions. It is well known that this transition exhibits extraordinary sensitivity to the Nd(III) ion coordination environment. In Table 2, we list oscillator strengths calculated from the measured spectra for a range of pH values and a range of ligand concentrations. As can be seen from these data, a decrease in pH to a value of ≈ 2 through the addition of HCl leads to a decrease in band intensity, whereas an increase of pH to ≈ 6 results in an increase in intensity. As shown, increasing the ligand concentration to a ratio of 1:3 had little effect on the calculated oscillator strengths with the actual value similar but not the same as that obtained for the 1:2 complex. In fact, the values determined for the 1:1 solution are lower in comparison to 1:2 molar ratio but shape of the bands remain similar thus in all of these solutions the 1:2 metal:ligand complex can dominate. The X-ray crystal structure of Eu(biqO₂)₂Cl₃ has, in fact, been reported, confirming the stability of this metal:ligand ratio [18]. It should be noted that Seminara and Masumeci reported extremely large oscillator strengths ($5265 \times 10^{-8} - 5384 \times 10^{-8}$) in the solution spectrum of a 1:4 complex of Eu(III) with ligand **2** without the pendant methyl groups [12]. Obviously, the steric constraints imposed by these methyl groups prevent additional coordination.

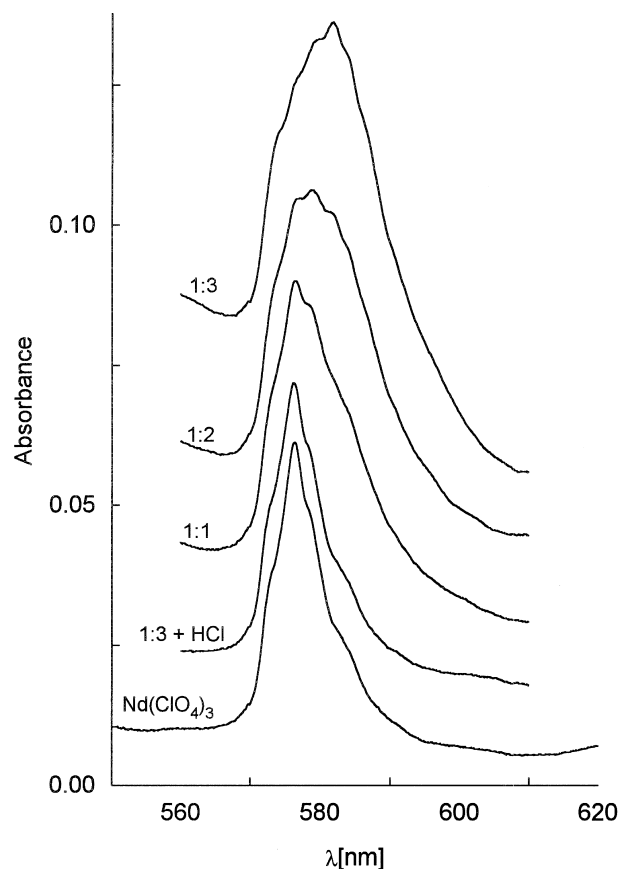


Fig. 3. The absorption spectra of Nd(III):**2** in CH₃CN for various M:L molar ratios and Nd(ClO₄)₃ in CH₃CN at 293 K.

Similar conclusions concerning metal ion coordination can be reached based on analysis of emission spectra. In fact, lowering of the pH in acetonitrile solution results in almost total quenching of the emission from Eu(III):**2**. Addition of HCl, which is used as a catalyst in sol-gel formation, in an effort to incorporate Eu(biqO₂)₂ into a rigid sol-gel quenches the emission from Eu(III) both when exciting directly into the metal energy levels at 394 nm, or when using indirect excitation through ligand absorption at 355 nm. This is illustrated in Figs. 4 and 5a. The disappearance of the Eu(III) emission is accompanied by the appearance of strong green phosphorescence from the organic ligand (see Fig. 5b). Since the emission properties of this system are temperature dependent, one can conclude that the excited state non-radiative processes

Table 2
The oscillator strength values of Nd:**2** (ClO₄)₃ and Nd(ClO₄)₃ in CH₃CN for ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, G_{7/2}$ at 293 K

Molar ratio M:L	Range [nm]	Px10 ⁸
Nd(ClO ₄) ₃	560.0–605.0	2158.3
1:1	560.0–605.0	2961.3
1:2	560.0–605.0	3569.5
1:3	560.0–605.0	3915.7
1:3 with addition of HCl	560.0–605.0	2043.5

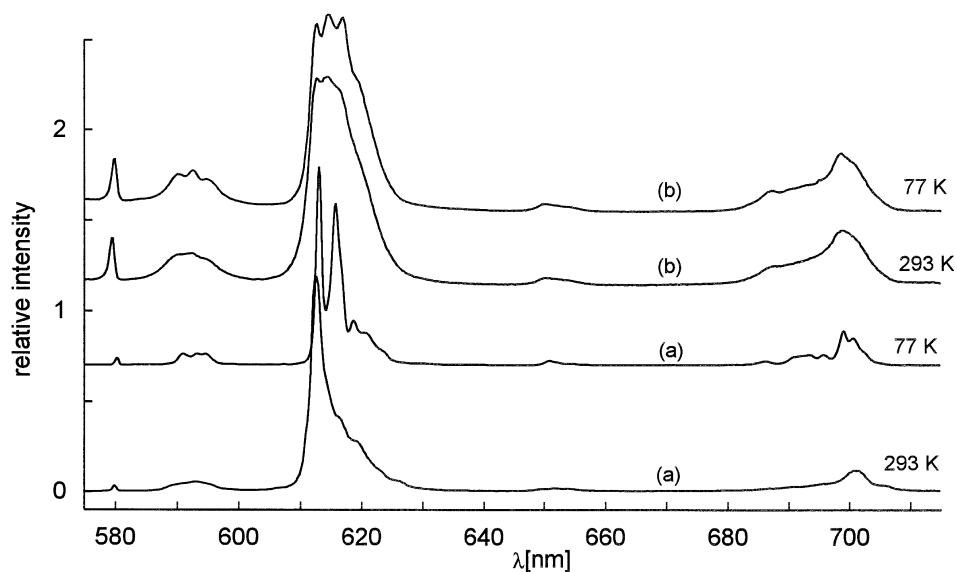


Fig. 4. The emission spectra of Eu(III):2 in CH_3CN at 293 K and 77 K (a); incorporated into silica sol-gel obtained from CH_3CN solution at 293 K and 77 K (b).

involve both the singlet and triplet states of the biqO_2 ligand. Illustrative spectra are given in Fig. 6. Similar effects as those reported above have been observed by us in studies of Eu(III) and Tb(III) complexes with 2,2'-bipyridine-1,1'-dioxide [13,14].

In Fig. 2 we also show the emission spectra of the Eu(III):1 complex which has been incorporated into a sol-gel prepared through catalysis by NH_4OH and by HCl . As can be seen, the measured spectrum under these experimental conditions is very complicated. Note the large number of components as compared to the solution or solid results, and the markedly different emission

intensities for the different transitions. The sol-gels prepared with base catalysis has an emission intensity stronger than the free Eu(III):1 system due to the rigidity imposed by the sol-gel matrix. This indicates that it is possible by this technique to stabilize highly luminescent lanthanide complexes. On the other hand, one should note that in the sol-gel catalyzed by acid, the emission almost completely disappears for Eu(III):2 , consistent with our previous argument on complexation. A more detailed study of the photophysical and structural aspects of Eu(III):1 and related cryptates is underway in order to more fully characterize the excited state dynamics of these systems.

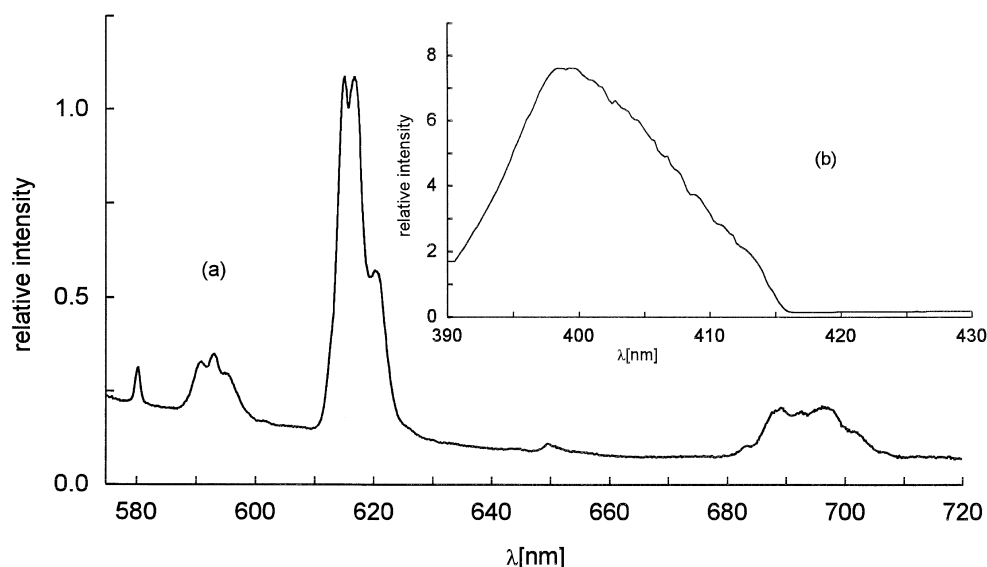


Fig. 5. The emission spectra of Eu(III):2 at 77 K incorporated into silica sol-gel obtained from aqueous solution: with addition of NH_4OH (a); without NH_4OH (b).

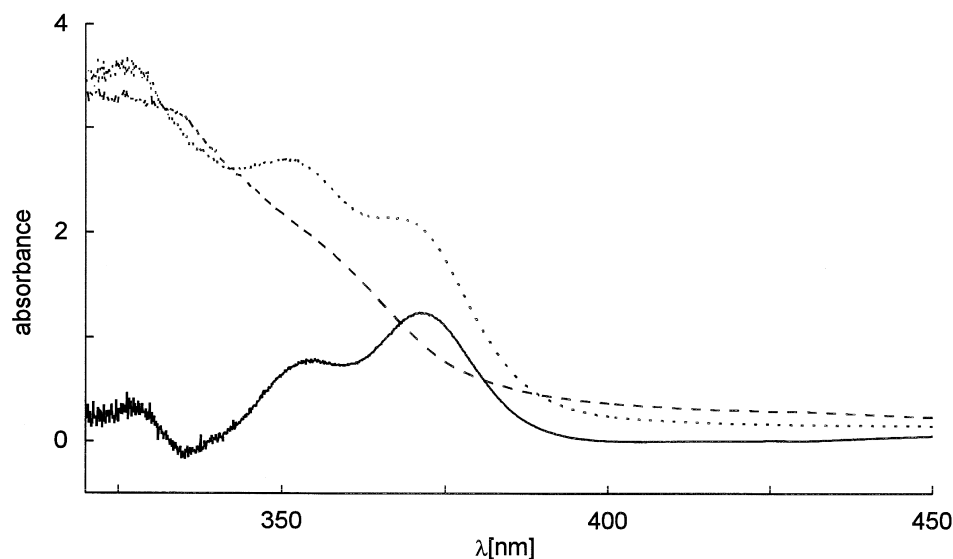


Fig. 6. The absorption spectra— CH_3CN (with air as a reference); \dots BiqO_2 in CH_3CN (with air as a reference); $_$ BiqO_2 in CH_3CN (with CH_3CN as a reference).

Even though the results reported here are preliminary in nature, they do show that complexes of this type may offer a significant advantage over other systems in light conversion efficiency. The role of complex non-radiative processes on luminescence efficiency is an area of active interest, particularly as applied to the study of Tb(III):2 which does not emit in CH_3CN solution. Currently we are probing ligand to metal and metal to ligand energy transfer processes under conditions of high pressure to evaluate the relative contributions of radiationless processes involving charge transfer states, and singlet and triplet ligand orbital states to the excited state dynamics.

Acknowledgements

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