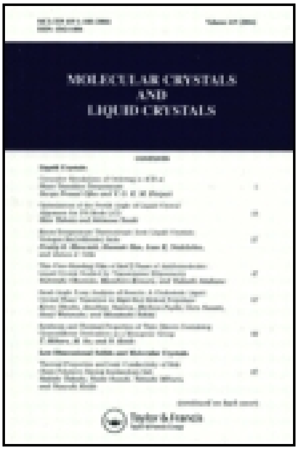

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The Antenna Effect of Eu(III) Cryptate Entrapped in Xerogel Matrices

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The Antenna Effect of Eu(III) Cryptate Entrapped in Xerogel Matrices

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The europium(III) complex with [*biq*.2.2] cryptand, where *biq* is 3,3′-biisoquinoline-2,2′-dioxide and complexes with additional secondary ligands such as 1,10-phenanthroline (*phen*) or triphenylphosphine oxide *(TPPO)* were entrapped by the sol-gel method in silica or silicate xerogel organically modified with methyl groups. The photophysical properties of such materials were studied. The luminescence behaviour of the complexes in the rigid matrix was studied by means of emission, excitation spectra and lifetime measurements. The results indicated that the Eu(III)-[*biq*.2.2] complex in the methylated silicate xerogel displayed a distinctly higher emission intensity and longer lifetime than in the silica matrix, whereas in the case of the complexes with the secondary ligands these changes were not so pronounced. It was also observed for the silica xerogel with Eu(III) complex that the emission intensity increased up to 110 °C with temperature.

Keywords: luminescence; antenna effect; Eu(III) cryptate; xerogel matrix

INTRODUCTION

The sol-gel method has been demonstrated to be a suitable approach for the preparation of novel luminescent materials. The luminescent behaviour of $EuCl_3$ and $Eu(NO_3)_3$ salts absorbed into porous glasses and doped into sol-gel derived hosts has been reported[1,2]. $EuCl_3$-doped silica xerogels have produced highly quenched luminescence. This is due to the strong deactivating power of the luminescent excited states of Eu(III) ions by O-H oscillators present in

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coordinated water molecules. It is therefore of great interest to modify the coordination environment of Eu^{3+} ion to improve its absorption characteristics and to reduce the non-radiative decay from the excited state[3]. In this case cage-like ligands (cryptands) capable of encapsulating the metal ion have been designed. Of special interest are the cryptates with lanthanide ions where energy is transferred from the cryptand to the central ion[4]. This type of energy transfer acts as an antenna. Among the studied cryptands as well as cyclic and acyclic ligands, the best antenna is such cryptand as [*biq*.2.2], where *biq* is *3,3'*-biisoquinoline-*2,2'*-dioxide[5]. This cryptate with Eu(III) is shown schematically in Fig. 1.

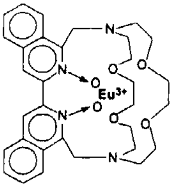


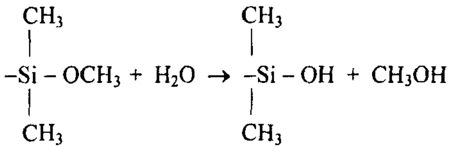
FIGURE 1 Eu(III) cryptate used in the present study

In order to remove OH groups more effectively from the coordination sphere and to isolate tightly the central ion from this type of quenchers, the Eu(III) cryptate was additionally complexed with secondary ligands such as *1,10*-phenanthroline (*phen*) or triphenylphosphinoxide (*TPPO*).

One of the major advantages of the sol-gel process is the possibility of preparing multicomponent systems at low temperature. Sol-gel techniques can be used to synthesize organically modified silicates (ORMOSILs) that represent hybrid systems consisting of an inorganic oxide network and methyl groups[6]. In this process a silicon alkoxide (or methyl-substituted silicon alkoxide) subjected to hydrolysis:

$$\equiv Si-OCH_3 + H_2O \rightarrow \equiv Si-OH + CH_3OH \qquad (1)$$

or

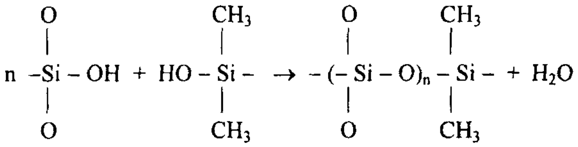


$$\begin{array}{c}CH_3\\|\\-Si-OCH_3\\|\\CH_3\end{array} + H_2O \rightarrow \begin{array}{c}CH_3\\|\\-Si-OH\\|\\CH_3\end{array} + CH_3OH \qquad (2)$$

Hydrolysis is followed by condensation to yield a polymeric material. In this study we synthesized silica ($SiO_{4/2}$)

$$\equiv Si-OH + HO-Si\equiv \rightarrow \equiv Si-O-Si\equiv + H_2O \qquad (3)$$

or a mixed $[SiO_{4/2} + (CH_3)_2SiO_{2/2}]$ xerogel matrix, as below:



$$n\begin{array}{c}O\\|\\-Si-OH\\|\\O\end{array} + \begin{array}{c}CH_3\\|\\HO-Si-\\|\\CH_3\end{array} \rightarrow -(\begin{array}{c}O\\|\\-Si-O\\|\\O\end{array})_n-\begin{array}{c}CH_3\\|\\Si-\\|\\CH_3\end{array} + H_2O \qquad (4)$$

to obtain the above mentioned complexes. The resulting encapsulation and immobilisation effects in such hydrophobic matrix as above should enhance emission intensity[7-9].

EXPERIMENTAL

Sample preparation

Binary Eu(III) complexes with [*biq*.2.2] cryptand, $\{Eu\subset[$*biq*.2.2$]\}(CF_3SO_3)_2Br$, were synthesized according to a previous report[10]. Ternary Eu(III) coordination species with additional, secondary ligands such as *phen* or *TPPO* were prepared separately in methanol solution. Then the ternary complex in solution was added to a starting mixture of alkoxides before gelation (*vide infra*).

The xerogels were prepared by a typical sol-gel procedure[11] from the starting mixture consisting, in the case of a silica matrix, tetramethoxysilane (*TMOS*) from Aldrich Co., methanol as a diluent, distilled water (*TMOS*:H_2O = 1:4) and the Eu(III) cryptate. The starting mixture for the methylated silicate xerogel was *TMOS*, polydimethoxydimethylsilane 200 (*PDMS*) from Aldrich Co., methanol, distilled water (molar ratio as above) and the Eu(III) cryptate. The mixtures were vigorously mixed at room temperature, allowed to gel for 3 days and then dried at room temperature to remove methanol and some water from the pores. The final concentration of the Eu(III) complexes in the materials was $1\cdot10^{-5}$ mole/g xerogel.

Apparatus

Corrected luminescence spectra were recorded with a Perkin-Elmer MPF-3 spectrofluorimeter equipped with dual photon counting set. The luminescence lifetime measurements of Eu(III) were carried out by the detection system described in details previously[12].

Infrared absorption spectra were obtained using a Bruker 113v Fourier Transform Infrared Spectrometer. Spectra were collected after 250 scans at 2 cm^{-1} resolution in the spectral range 4000-2000 cm^{-1}. Samples with the same xerogel concentration were prepared by the standard KBr pellet method.

RESULTS

Excitation fluorescence spectra of the Eu(III) cryptate and the cryptate with one of the secondary ligands entrapped in silica xerogel [Fig. 2(a)] are compared with the excitation spectrum of the Eu(III) cryptate in aqueous solution [Fig. 2(b)].

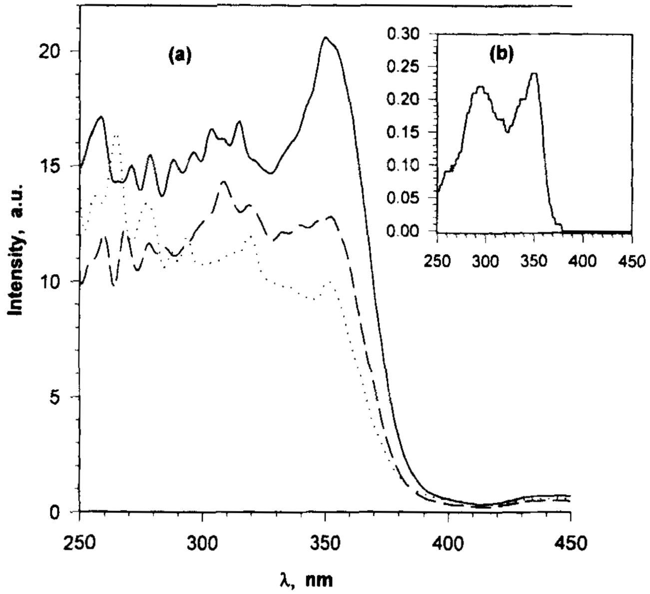


FIGURE 2 Luminescence excitation spectra of: (a) Eu⊂[*biq*.2.2] (.....), Eu⊂[*biq*.2.2] + *phen* (___), and Eu⊂[*biq*.2.2] + *TPPO* (-----) in silica xerogel, (b) Eu⊂[*biq*.2.2] in aqueous solution. $\lambda_{em} = 617$ nm.

Whereas the latter spectrum consists of two characteristic bands, the former spectra present broad bands with a vibronic structure and are much more intense than the one in solution.

The fluorescence emission spectra in Fig. 3(a) - (c) are typical of complexed Eu(III) ions owing to the band at *ca* 620 nm. All materials with the Eu(III) complexes in silica [Fig. 3(a)]

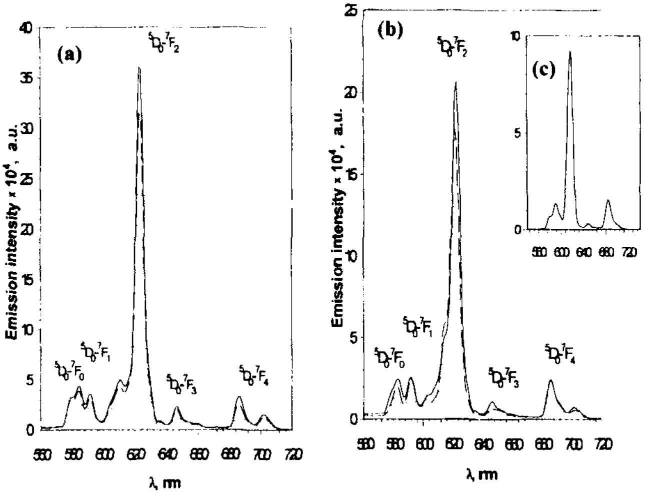


FIGURE 3 Luminescence emission spectra of: (a) Eu⊂[*biq*.2.2] + *phen* (___), λ_{exc} = 358 nm; Eu⊂[*biq*.2.2] + *TPPO* (_ _ _), λ_{exc} = 358 nm Eu⊂[*biq*.2.2] (......), and λ_{exc} = 352 nm in methyl-modified silicate xerogel, (b) Eu⊂[*biq*.2.2] + *phen* (___), λ_{exc} = 358 nm; Eu⊂[*biq*.2.2] + *TPPO* (_ _ _), λ_{exc} = 358 nm; and Eu⊂[*biq*.2.2] (......),λ_{exc} = 352 nm in silica xerogel, as well as (c) Eu⊂[*biq*.2.2] in aqueous solution, c = 1.1·10^{-4} M., λ_{exc} = 350 nm.

and methyl-modified silicate matrices [Fig. 3(b)] display a higher emission intensity than the Eu(III) cryptate in aqueous solution [Fig. 3(c)]. However, among the solid materials, the europium complexes entrapped in the methylated xerogel exhibit a higher intensity [*cf.* Fig. 3(a) and (b)].

The luminescence decay *k* was analyzed as monoexponential. Luminescence lifetime values $\tau = k^{-1}$ are collected in Table 1.

TABLE 1 Luminescence lifetime τ of Eu(III) complexes entrapped in silica and methyl-modified silicate xerogels. Excitation wavelength λ_{exc} = 579 nm

Eu(III) complex with	Matrix	Lifetime τ / μs
[*biq*.2.2]	aqueous solution	227 *
[*biq*.2.2]	$SiO_{4/2}$	351
[*biq*.2.2]	$3\ SiO_{4/2} + Si(CH_3)_2O_{2/2}$	499
[*biq*.2.2]	$SiO_{4/2} + Si(CH_3)_2O_{2/2}$	608
[*biq*.2.2] + *phen*	$SiO_{4/2}$	534
[*biq*.2.2] + *phen*	$3\ SiO_{4/2} + Si(CH_3)_2O_{2/2}$	563
[*biq*.2.2] + *TPPO*	$SiO_{4/2}$	508
[*biq*.2.2] + *TPPO*	$3\ SiO_{4/2} + Si(CH_3)_2O_{2/2}$	507

*After ref. 27.

Thus, for the Eu(III) cryptate in aqueous solution the luminescence lifetime is shorter than for the cryptate in the xerogel matrices. Additionally, the lifetime in the solid matrix increases with content of the methylated component in the case of the cryptate. It is due to reduction of O-H oscillators taking part in the deactivation processes of the Eu(III) excited states. However, for *phen* and *TPPO* as secondary ligands this trend is observed for matrices with the same composition.

The IR spectra of the methylated silicate [Fig. 4(a)] and the silica matrix [Fig. 4(b)] show a broad band at 3350 cm^{-1}. This band is related to SiO-H stretching[13] and in the methylated silicate is reduced in comparison with that of the pure silica matrix.

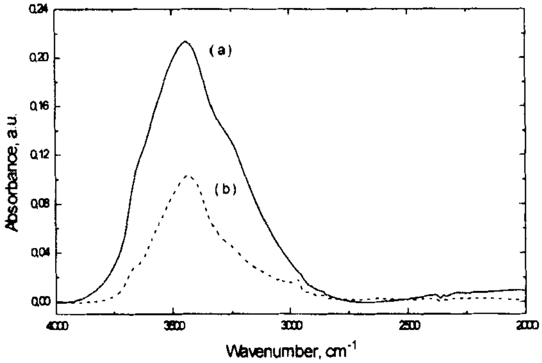


FIGURE 4 IR spectra of: (a) silica (SiO$_{4/2}$) and (b) methyl-modified silicate [SiO$_{4/2}$ + Si(CH$_3$)$_2$O$_{2/2}$]matrices

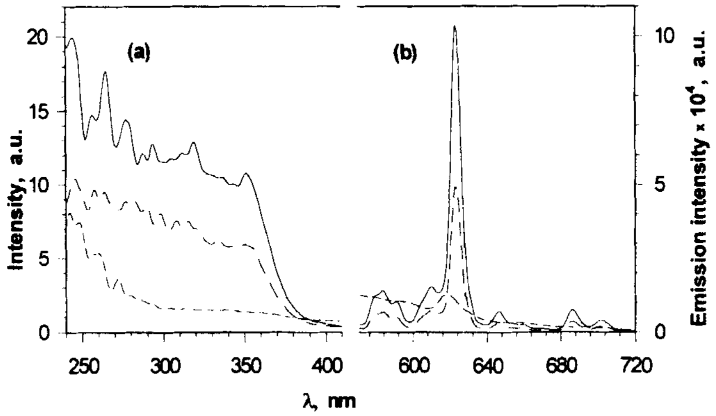


FIGURE 5 (a) Excitation and (b) emission spectra of Eu⊂[*biq*.2.2] cryptate in silica matrix after drying at room temperature (.......) and heating at: 110 (____), 200 (_ . _ .), and 300 °C (_ _ _)

Excitation and emission band intensity for silica xerogel doped with the Eu(III) cryptate are shown in Fig. 5. Their intensities increase with drying temperature; however, in general the temperature should not exceed 110 °C. Changes in emission intensity within the interval from room temperature up to 300 °C are illustrated for the cryptate entrapped in the methylated silicate matrix in Fig. 6. The emission intensity for this material dried at 110 °C reaches a maximum. In the material heated to a higher temperature the intensity falls off owing to the thermal decomposition of the cryptand.

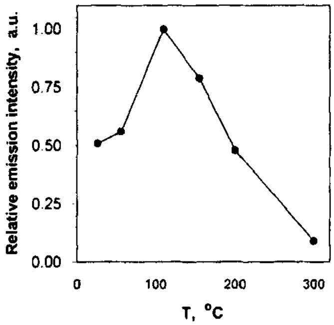


FIGURE 6 Changes in emission intensity of Eu⊂[*biq*.2.2] crypate entrapped in methyl-modified silicate matrix after thermal treatment over various ranges of temperature

DISCUSSION

Many authors have suggested that OH groups are very effective quenchers of Eu(III) ion luminescence[11.14]. The quenching is due to high frequency vibrations resident in the immediate neighbourhood of the ion. This non-radiative loss can be suppressed by encapsulating the central ion in cage-type ligands (cryptands)[15-17]. Of special interest are the cryptates where energy transfer from the cryptand to the central ion takes place. In such a process, known as the "antenna effect", the factors which contribute to the luminescence intensity are (i) the intensity of the ligand absorption, (ii) the efficiency of the ligand-to-metal energy transfer, and (iii) the efficiency of the metal luminescence[4]. In our case this was achieved by using the [*biq*.2.2] cryptand as a ligand of Eu(III) (see Fig. 1).

Some authors observed that the lifetimes of Eu(III) ions complexed with *phen* incorporated into the silica gel become longer than that in the pure complex[18-20]. In our case the luminescence of the Eu(III) ions is markedly increased when their complexes are entrapped in the pores of the xerogels. This is due to a slight immobilisation of the supramolecular device [*cf.* Figs. 3(a) and (b) with (c)][21,22]. Moreover, in the case of materials based on the antenna effect, the luminescence intensity may be much reduced by the water molecules and OH groups present in the coordination sphere if the cryptand cannot occupy all the coordination sites there. The presence and bonding state of OH groups in silica xerogel is closely related to the concentration of non-bridging oxygen (*cf.* ref. 23). The presence of hydrophobic methyl groups in silicate xerogel leads to a much lower concentration of hydroxy groups in the matrix of the Eu(III) cryptate (Fig. 4). In comparison with the silica matrix, the methylated silicate matrix quenches the Eu(III) less effectively, resulting in a higher luminescence intensity and a longer lifetime for the samples [see Fig. 3(a), (b) and Table 1].

Numerous solution studies have shown that the rate of non-radiative de-excitation of the $^5D_0$ level is directly proportional to the number of O-H oscillators in the inner coordination sphere of Eu(III)[24-26]. The de-excitation is due to a weak vibronic coupling of the central ion excited state with high energy O-H oscillations[10,11]. In these studies, the vibronic structure of the excitation spectra [Fig. 2(a)] for the cryptate in silica xerogel provides the evidence for the effective molar interaction with the matrix. Non-radiative de-excitation through O-H oscillations decreases the observed luminescence lifetime, so lifetime changes (Table 1) can be used to deduce the presence of OH groups in the inner coordination sphere of Eu(III).

The additional ligands (such as *phen* an *TPPO*) used in our studies play two roles. Firstly, they replace some of OH groups from the coordination sphere of the central ion and secondly their aromatic groups are additional antenna systems. Thus, in each case their presence in the coordination environment is demonstrated by higher emission intensity (Fig. 3) and longer lifetime of luminescence (Table 1).

The $^5D_0 \rightarrow {}^7F_2$ transition is an electric dipole transition and is extremely sensitive to chemical bonds in the vicinity of Eu(III) ions. The intensity increases as the Eu-O covalence increases and the environment becomes more symmetrical[26]. Fig. 5 shows changes in the band height for $^5D_0 \rightarrow {}^7F_n$ transitions after heating over various ranges of temperature, and in Fig. 6 the band intensity changes related to the same transition are expressed as a function of temperature. The intensity increases if the molecular water and CH_3OH solvent are evaporated, but above 110 °C the antenna effect decreases because the organic environment of the central ion undergoes progressive thermal decomposition.

CONCLUSIONS

By the sol-gel method are prepared materials consisting of Eu(III) complex system (cryptand + secondary ligands) entrapped in silica or methyl-modified silicate xerogels.

In comparison with the cryptate encapsulated in silica xerogel, the intensity of Eu(III) luminescence and its lifetime in excited state increases for:

(i) the cryptate with such secondary ligands as *phen* or *TPPO*,

(ii) the Eu (III) complexes entrapped in the silicate matrix with methyl groups,

(iii) the material dried up to 110 °C.

The lifetime measurements were used to study the effects of Eu(III) complex immobilisation in the xerogel matrices, content of residual hydroxyl oscillators in the matrices and energy transfer from the „antenna" groups on Eu(III) luminescence.

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