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Improvement of emission intensity in luminescent materials based on the antenna effect

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Abstract

Ternary Eu(III) complexes with macrobicyclic and acyclic ligands+co-ligands were encapsulated in silica or methylated silicate xerogels. Additionally, deuterated reagent and solvent were used in the sol–gel procedure. This preparation method with moderate thermal treatment reduced the concentration of OH groups in the materials and simultaneously improved their photophysical properties, i.e. increased luminescence intensity and prolonged luminescence lifetime. The best results were obtained for the Eu(III) complex with a cryptand of the [biqO_2·2·2]+1,10-phenanthroline type (where biqO_2=3,3′-biisoquinoline-2,2′-dioxide) immobilized in methyl-modified silicate xerogel. The effective luminescence properties of this sample make it a promising candidate for use as a luminescent material.

Keywords: Europium complexes; Luminescence; Emission quenching; Xerogel; Immobilization

1. Introduction

Great interest has been shown in modifying the coordination environment of the Eu(III) ion in order to improve its absorption characteristics and to reduce non-radiative decay from the excited state [1]. In this case, cage-like ligands (cryptands) have been designed which are capable of encapsulating the metal ion. On the other hand, photoconversion via an absorption–energy transfer–emission (A–ET–E) sequence realised in Eu(III) cryptates with macrocyclic or macropolycyclic ligands is of special interest. Absorbed by a fluorophore group of the cryptand, UV radiation is efficiently transferred to the central cation, which is very tightly bound in the molecular cavity, and is finally emitted by the cation [2]. This type of ligand acts as an antenna. One of the most efficient ligands in our study is the cryptand [biqO_2·2·2], where biqO_2 is 3,3′-biisoquinoline-2,2′-dioxide.

The principal quenching mechanism is the deactivation of the Eu(III) ion by vibronic coupling to the ligands and hence to the surrounding solvent [3]. In aqueous solution, the dominant mode in which the excited Eu(III) ion is quenched occurs as a result of the vibronic coupling of electronic excitation to the O–H oscillators in the water molecules in the inner coordination sphere of the ion. The replacement of H_2O by other ligand molecules in this coordination sphere reduces the quenching efficiency. The interaction between a ligand and the aquo ion with complex formation requires the removal of bonded water molecules from the inner sphere of the central ion in accordance with the ligand denticity [4]. Hence, the formation of the Eu(III) complex leads to a significant increase in fluorescence intensity [5,6]. In order to remove water, OH groups and other quenchers from the coordination sphere, and to isolate the central ion from them, the Eu(III) complexes (cryptates) were additionally complexed with co-ligands such as 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), salicylic acid and triphenylphosphinoxide (TPPO).

The sol–gel method is a suitable means of preparing hybrid systems consisting of an inorganic oxide network and methyl groups [7]. In this process, silicon alkoxides, as well as methyl-substituted silicon alkoxides, undergo hydrolysis and condensation. Binary complexes (Fig. 1) and ternary Eu(III) complexes with co-ligands were immobilized by the sol–gel method in silica or silicate xerogel

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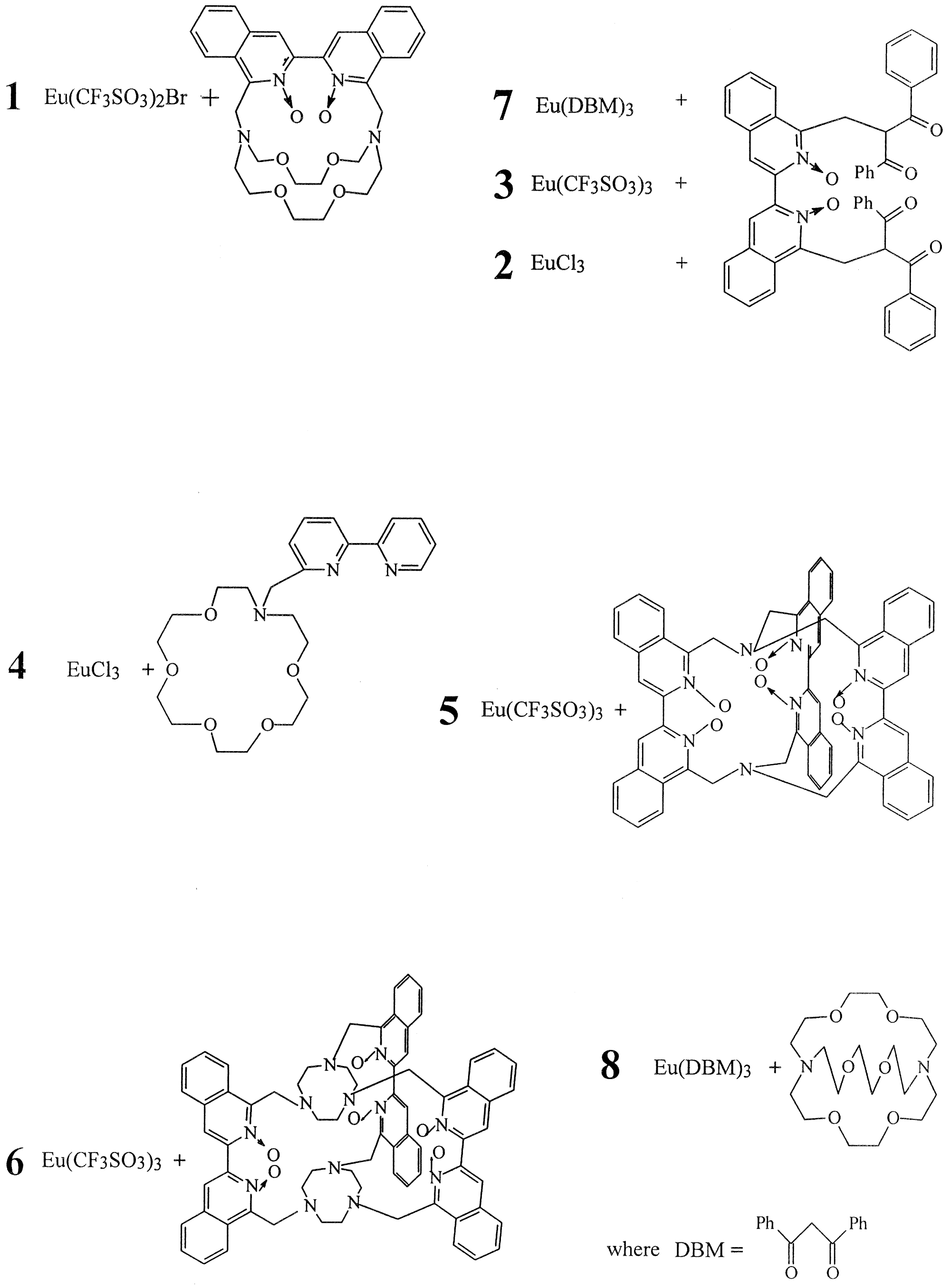

Fig. 1. Eu(III) complexes (cryptates) studied.

organically modified with methyl groups. The luminescence behaviour of the complexes in the rigid matrix was studied by means of emission and excitation spectra as well as luminescence lifetimes.

In this paper, we review our previous results, analyze some recently obtained data, and discuss the problem of designing Eu(III) complexes capable of acting as molecular devices for efficient light absorption and luminescence emission. The results indicate that complex **1** displayed a distinctly higher emission intensity and longer lifetime in the methylated silicate xerogel than in the silica matrix. In addition, the emission intensity of the silica xerogel with the Eu(III) complex was observed to increase following dessication at 110°C.

2. Experimental details

2.1. Sample preparation

Binary Eu(III) complexes of the [EuL]An type, where L is the main ligand (cryptand) and An is an anion, were synthesized in accordance with a previous report [8]. Ternary Eu(III) complexed species with co-ligands were prepared by stirring a methanol solution of the ligand into a methanol solution of the Eu(III) complex with a main ligand (Eu complex/co-ligand=1:1).

The silica gel was prepared by the hydrolysis and condensation (sol–gel process) of tetramethoxysilane (TMOS; Aldrich) in methanol solution [9]. The sol–gel technique was also used to synthesize methylated silicate gel. In this process TMOS+PDMS (polydimethoxydimethylsilane; Aldrich) mixtures in methanol (molar ratio 1:1) were used [10]. In each case, the methanol solutions of Eu(III) complexes were added to the silica or organically modified silica precursor solution. The mixtures were vigorously stirred at room temperature, allowed to gel for 3 days, then dried at room temperature to remove methanol and water from the pores. The final concentration of the Eu(III) complexes in the materials was 1×10^{-5} mol g^{-1} xerogel.

2.2. Apparatus

Optical absorption spectra were recorded on an UV-VIS 160 Shimadzu spectrophotometer. Luminescence emission and excitation spectra were recorded at right angles using a Perkin-Elmer MPF-3 spectrofluorimeter equipped with a dual photon counting set and a holder for crushed xerogel samples. The emission spectra of the xerogel samples doped with the Eu(III) complexes were obtained with excitation wavelengths within absorption band range of the ligands (between 320–380 nm).

Luminescence decays were measured by means of a Perkin-Elmer spectrofluorimeter, an M12FVC51 Edinburgh 199 single photon counter and a set of lasers [KB6211 nitrogen laser (Cobrabid, Poznań) and tunable dye laser] as an exciting light source combined with an MC101 transient recorder and an IBM PC computer.

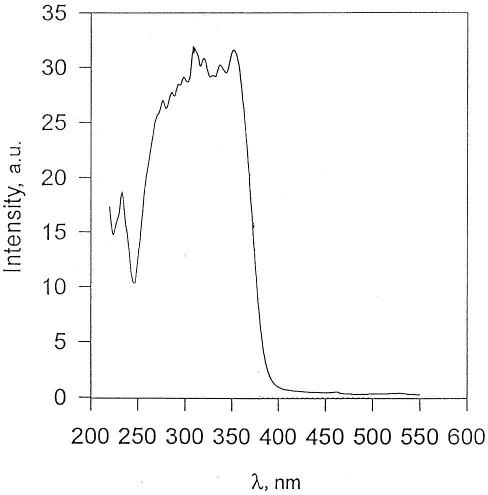

Fig. 3. Luminescence excitation spectrum of the cryptate **1** entrapped in silica xerogel. $\lambda_{em}=617$ nm.

3. Results

Optical absorption spectra of the free [biqO_2·2·2] cryptand and the Eu(III) cryptate **1** (Fig. 2) showed an intense absorption band attributed to ligand centred π-π* transitions. It was also observed a red shift of the absorption maximum for the cryptate compared with the free ligand. In luminescence excitation spectrum of the cryptate **1** entrapped in silica xerogel is present a broad band with vibronic structure (Fig. 3) instead of two bands in this range as for the cryptate in aqueous solution (see Ref. [9]).

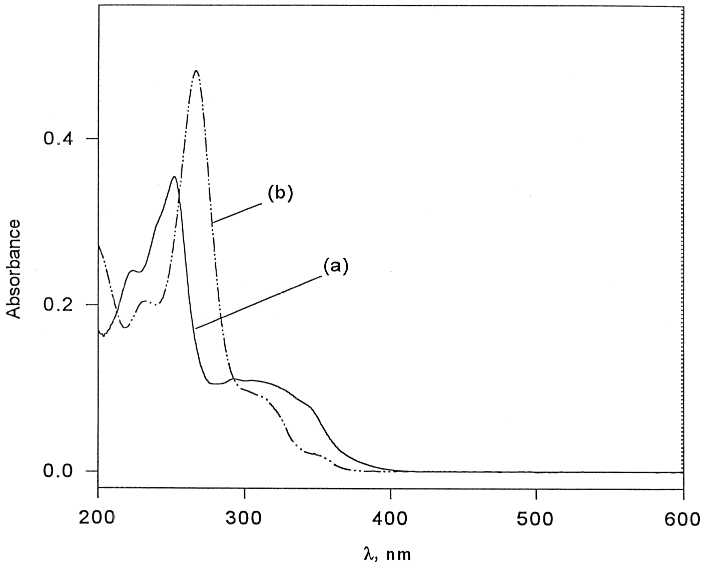

Fig. 2. Optical absorption spectra of: (a) [biqO_2·2·2] cryptand and (b) its complex with Eu(III) (cryptate **1**) in aqueous solution. After Ref. [9].

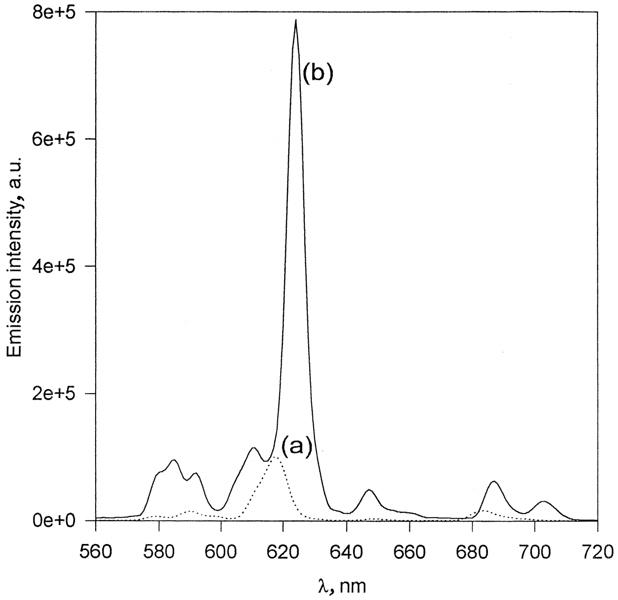

Fig. 4. Comparison of emission intensity of the Eu(III) cryptate **1** in (a) aqueous solution, and (b) silica xerogel. $\lambda_{ex} = 353$ nm.

Luminescence emission spectra are typical of the complexed Eu(III) ion: the most intense band is situated at ≈620 nm. This effect can be seen in the spectra in Fig. 4. They compare the emission intensity of the Eu(III) cryptate with that of the macrobicyclic [biqO_2·2·2] (complex **1** in Fig. 1) in aqueous solution and silica xerogel. Owing to very effective emission quenching by OH groups in aqueous solution, the emission intensity is extremely low.

3.1. Ligands (cryptands)

The compositions of the binary europium complexes (cryptates) **1–8** (in Fig. 1) were confirmed by elemental analysis. Comparison of the luminescence intensity of the complexes or cryptates entrapped in pure silica xerogel (Table 1) shows that the Eu(III) cryptate **1** is the most efficient emitter. Complexes **2** and **3** with acyclic ligands exhibit the same emission intensity, which is nearly one third ($I_{rel} = 0.28$) that of the previous cryptate. Complexes **2**, **3** and **7** possess the same ligand with the biqO_2 group; however, the relative intensities depend on the type of anions in the Eu(III) salts. The complex with the $PhCOCH_2COPh$ (DBM) anion has the lowest I_{rel} value. Table 1 also contains data for Eu(III) complexes with decreasing emission intensity, as follows: complex **4** with an (aza-18-crown-3)-CH_2-(2,2′-bipyridine) ligand, cryptate **5** with a macrobicyclic [biqO_2·biqO_2·biqO_2] ligand, cryptate **6** also with three biqO_2 units but with a greater cavity than previously, and cryptate **8** with a macrobicyclic [2·2·2] ligand.

Table 1
Relative luminescence intensity I_{rel} in the band maximum, excitation and emission wavelengths of Eu(III) complexes (cryptates) immobilized in silica xerogel

Eu(III) complex	Relative intensity (I_{rel})	Excitation wavelength (λ_{ex}, nm)	Emission wavelength (λ_{em}, nm)
1	1.0	352	622.6
2	0.28	344	612.4
3	0.28	345	611.4
4	0.24	320	618.4
5	0.15	350	611.4
6	0.13	350	614.4
7	0.10	380	612.4
8	0.02	380	613.4

3.2. Co-ligands

We observed previously that the emission intensity of species **1** can be improved if the Eu(III) cryptate entrapped in silica xerogel is additionally complexed with such co-ligands as bpy, phen, salicylic acid or TPPO [10]. The phen co-ligand effectively increases luminescence intensity in the Eu(III) complexes, not only in species **1** but also in the weaker emitters like complex **4**, and cryptates **5** and **6** (see Table 2).

3.3. Matrix

In comparison with the cryptate **1** encapsulated in silica xerogel dried at room temperature, the intensity of Eu(III) luminescence and luminescence lifetime increases for the cryptate entrapped in the silicate matrix with increasing concentration of methyl groups [10]. This effect is also present for such ternary complexes as (complex **1**+phen) and complexes with other main and co-ligands.

Table 2
Relative luminescence intensity I_{rel} in the band maximum and excitation wavelength (λ_{ex}) of Eu(III) complexes (cryptates) with co-ligands immobilized in silica xerogel

Eu(III) complex +co-ligand	Relative intensity (I_{rel})	Excitation wavelength (λ_{ex}, nm)
1	0.51	320
1+bpy	0.82	320
1+phen	1.0	320
4	0.68	320
4+*salicylic acid*	0.73	320
4+*phen*	1.0	320
5	0.88	358
5+*phen*	1.0	358
6	0.43	360
6+*TOPO*	0.49	360
6+*salicylic acid*	0.88	360
6+*phen*	1.0	360

Table 3
Preparation procedure and its influence on the relative luminescence intensity I_{rel} in the band maximum and luminescence lifetime τ of the complex **1** immobilized in $[SiO_{4/2}+Si(CH_3)_2O_{2/2})]$ xerogel

Reagents	Solvent	Catalyst	Relative intensity $(I_{rel})^a$	Lifetime $(\tau, \mu s)^b$
$Si(OCH_3)_4+H_2O$	CH_3OH	Acetic acid	0.36	574
$Si(OCH_3)_4+D_2O$	CH_3OH	Acetic acid	0.40	587
$Si(OCH_3)_4+D_2O$	CH_3OD	Acetic acid	1.0	608

[a] $\lambda_{ex}=352$ nm, $\lambda_{em}=622.6$ nm.
[b] $\lambda_{ex}=579$ nm, $\lambda_{em}=615$ nm.

3.4. Sol–gel procedure

In the sol–gel procedure an alkoxide and water are usually used as substrates and alcohol serves as solvent. In order to avoid emission quenching by O–H oscillators we used heavy water D_2O instead of H_2O in the preparation of the methyl-modified xerogel. In the next step the sol was dissolved in deuterated methanol CH_3OD instead of CH_3OH. The results in Table 3 show that by this procedure the relative intensity and emission lifetime increases for the entrapped cryptate **1.**

3.5. Thermal treatment

In our previous paper [10], we reported that drying at elevated temperature increased the luminescence intensity to some extent. However, at higher temperatures (≈100°C) a monotonic decrease in intensity due to thermal decomposition of the materials is observed. There is an improvement in emission intensity for cryptate **1** and **8,** the best and worst of the emitters studied, respectively (Fig. 5). Some of the complexes (see Fig. 1) immobilized in methylated silicate xerogel reach their maximum luminescence at a temperature of 80°C.

4. Discussion

There are a lot of Si–OH groups in silica xerogels because the hydrolysis of alkoxides in the transition from sols to gels is incomplete. Because the vibronic deactivation mechanism involving the O–H groups is so important in the luminescence quenching of Eu(III) complexes entrapped in silica xerogel, various ligands are used with potential shielding properties. Such ligands should isolate the central europium ion from O–H oscillators. The results obtained for cryptates have shown that cryptand ligands shield the lanthanide ion from interaction with O–H oscillators, thereby improving its emitting properties. The cryptand in complex **1** was the most effective of the ligands investigated (Table 1). The shielding properties of other cryptands with three $biqO_2$ groups (in complexes **5** and **6**) were not as efficient as before, since their cavities are either too small (**5**) or too large (**6**). The acyclic ligand with $biqO_2$ (in complexes **2, 3** and **7**) was in general not as efficient a shield as the ligand in complex **1,** and the relative intensity of emission depends on the type of anion in the Eu(III) salts (see I_{rel} for **2**, **3** and **7** in Table 1).

Ternary Eu(III) complexes with an additional co-ligand incorporated into the silica xerogel display a greater emission intensity in comparison with complexes of the Eu(III)+main ligand (cryptand) type (Table 2). Previously, Eu(III) complexes with phen introduced into a silica

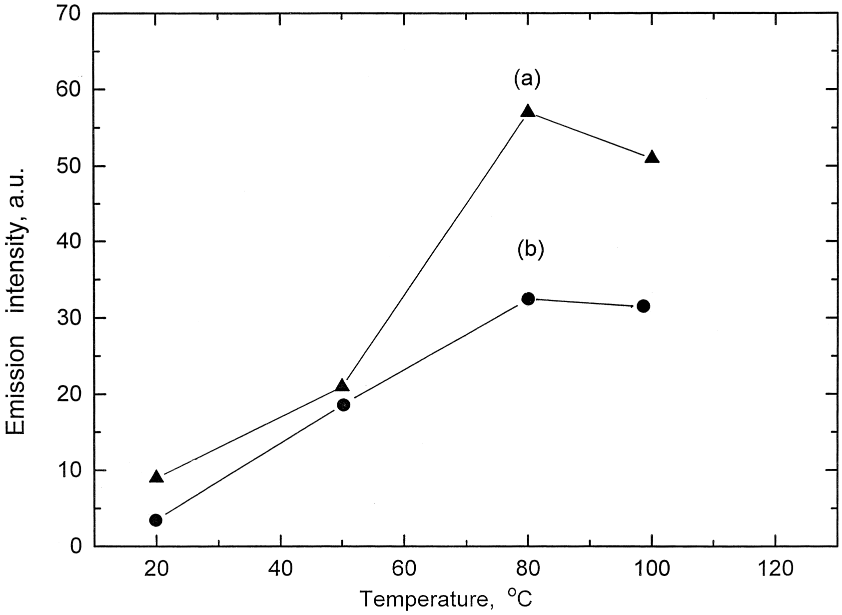

Fig. 5. Changes in emission intensity of: (a) cryptate **1**, and (b) complex **8** entrapped in methylated silicate xerogel after thermal treatment at various temperatures.

matrix [11,12] exhibit excellent luminescence properties. In our studies the phen co-ligand is especially efficient in removing O–H groups from the coordination sphere of the Eu(III) ion. In methyl-modified silicate xerogels, the environment of the Eu(III) complex is poorer in O–H than in pure silica material. Thus, it has been observed that the luminescence lifetime τ of the Eu(III) complexes increases with increasing concentration of methyl groups in the materials [10].

As observed for the cryptate **1** in methyl-modified silicate (Table 3), the lifetime τ and relative luminescence intensity I_{rel} increased if deuterated water and methanol were used in the reaction mixture. This indicates that the O–H groups are replaced by O–D. However, the O–H concentration can be effectively reduced if water is removed at a higher temperature, so long as thermal decomposition of the material is avoided (Fig. 5).

5. Conclusions

The results of this study show that the vibronic deactivation mechanism via O–H groups could be reduced by such factors as:

(1) Effectively shielding ligands (cryptand)

(2) Co-ligands removing water molecules and OH groups from the coordination sphere

(3) A methyl-modified silicate matrix with a low OH concentration

(4) D_2O and CH_3OD as reagent and solvent in the sol–gel procedure

These factors improve the photophysical properties (emission intensity and luminescence lifetime) of the luminescent materials based on the antenna effect.

The effective properties of Eu(III) complexes incorporated in methyl-modified xerogel by the sol–gel method make them promising candidates for use as luminescent materials.

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