Luminescence Properties of Materials with Eu(III) Complexes: Role of Ligand, Coligand, Anion, and Matrix

Andrzej M. Kłonkowski,*,† Stefan Lis,*,‡ Marek Pietraszkiewicz,§
Zbigniew Hnatejko,‡ Katarzyna Czarnobaj,† and Marian Elbanowski‡

*Faculty of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland, Faculty of Chemistry,
A. Mickiewicz University, Poznań, Poland, and Institute of Physical Chemistry,
Polish Academy of Sciences, Warsaw, Poland*

Received March 11, 2002. Revised Manuscript Received October 10, 2002

This study focuses on luminescent materials based on the antenna effect and prepared by the sol−gel method. These materials are composed of a Eu(III) complex (luminescence center) entrapped in a xerogel matrix. Luminescence properties of the lanthanide-based emitting materials depend on the efficiency of energy transfer from the absorption center (ligand) to the emission center (central ion) and on the concentration of quenchers (O−H oscillators) surrounding the central ion. In this study, such luminescence properties as * lifetime and quantum yield were improved by modifying the coordination environment of the central ion and changing anion groups and matrixes. The results of the experiments on the composition of the coordination sphere show that a cryptand ligand with aromatic groups and an aromatic coligand efficiently initiate the antenna effect, thus isolating the central ion from every efficient quencher, e.g., water molecules. Luminescence properties also depend on the anion in the Eu(III) complex salt, the type of matrix material, and the concentration of water and OH groups in the matrix. These luminescent materials have been tested for their photochemical stability under continuous UV irradiation.

Introduction

Materials containing lanthanide ions have been used as phosphors and laser materials because of their sharp, intensely luminescent f−f electronic transitions. In particular, a number of lanthanide complexes display a bright and narrow lanthanide ion emission. These emissions are usually due to the so-called “antenna effect”, defined as a light conversion process via an absorption−energy transfer−emission sequence involving distinct absorption by a ligand (light collector) and emission by a metal ion. In such a process, the quantities that contribute to the luminescence intensity are as follows: (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. This phenomenon has been reviewed by Sabbatini and Guardigli.[1] The luminescence properties of lanthanide complexes in a variety of solutions have been investigated extensively;[2−6] these studies have demonstrated that lanthanide complexes have superior fluorescence properties with respect to simple salts in solutions. However, conventional ligands are incapable of giving rise to inert complexes, especially in aqueous solution, where solvent molecules compete efficiently to occupy coordination sites. In fact, the cryptand ligands possess spheroidal cavities and donor atoms such as oxygen and nitrogen. This type of ligand produces extremely stable complexes with lanthanide ions and can shield the encapsulated ion from interaction with the surroundings.

To increase the intensity of the lanthanide luminescence exploiting the antenna effect, complexes with strongly absorbing cryptands have been designed, for example, cryptands with aromatic segments, e.g., 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 3,3′-biisoquinoline (biq), which show intense absorption bands in the UV region due to $\pi-\pi^*$ transitions.

In an attempt to improve the luminescence properties of Eu(III) cryptates, the bpy or biq units of cryptands were replaced with bpyO_2 or biqO_2.[7] Results of studies on the luminescence of Eu(III) complexes with dioxide derivatives have shown that the included central metal ion is better protected from interactions with water than in the case of the [Eu $\subset$ bpy derivative]$^{3+}$ or [Eu $\subset$ biq derivative]$^{3+}$ cryptate and that these complexes present a significant gain in light conversion efficiency over earlier europium cryptates.

The sol−gel process is a potentially attractive means of synthesizing novel luminescent materials. The incorporation of lanthanide complexes, particularly europium-

---

* To whom the correspondence should be addressed. A.M.K.: (tel) 00-48 58 345-04-05; (fax) 00-48 58 341-03-57; (e-mail) aklonk@chemik.chem.univ.gda.pl. S.L.: (tel) 0048 61 876-81-64; (fax) 0048 61 865-80-08; (e-mail) blis@main.amu.edu.pl.

† University of Gdansk.

‡ Adam Mickiewicz University.

§ Polish Academy of Sciences.

(1) Sabbatini, N.; Guardigli, M. *Coord. Chem. Rev.* **1993**, *123*, 201.

(2) Crosby, G. A.; Whan, R. E.; Alire R. M. *J. Chem. Phys.* **1961**, *34*, 741.

(3) Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.

(4) Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1965**, *42*, 1590.

(5) Dawson, W. R.; Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1966**, *45*, 2410.

(6) Kleinerman, A. D. *J. Chem. Phys.* **1969**, *42*, 1590.

(7) Lehn, J.-M.; Roth, C. O. *Helv. Chim. Acta* **1991**, *74*, 572.

10.1021/cm0202557 CCC: $25.00

(III) complexes, has been investigated in detail.[8−21] Xerogels doped with Eu(III) complexes have been shown to exhibit substantially improved luminescence characteristics with respect to comparable materials containing the simple metal.

According to the theory of nonradiative transitions in lanthanide complexes,[22−24] the nonradiative relaxation between various J states may occur by interaction of the electronic levels of the lanthanide ion with suitable vibrational modes of the environment. The efficiency of these processes depends on the energy gap between the ground and excited states of the lanthanide ions and the vibrational energy of the oscillators.[22,23,25] When solvents containing O−H groups are coordinated to lanthanide ions, efficient nonradiative deactivations take place via vibronic coupling with the vibrational states of the O−H oscillators.[26,27] If the O−H oscillators are replaced by low-frequency O−D oscillators, the vibronic deactivation pathway becomes much less efficient.

To reduce the nonradiative decay from the excited state of Eu(III), we tried to eliminate O−H oscillators in the short range, that is, in the coordination environment of the central ion and in the long range, i.e., in the xerogel matrix. To realize the short-range approach, we tested several ligands for Eu(III) ion luminescence characteristics.[14] Among the ligands used, the best results (i.e., longest lifetime) were exhibited by the [biqO_2.2.2] cryptand, where biqO_2 is 3,3′-biisoquinoline 2,2′-dioxide (Figure 1A, structure **1**). If the coordination sphere is supplemented with coligands such as 1,10-phenanthroline, 2,2′-bipyridine, triphenylphosphine oxide (TPPO),[14,15] or other aromatic systems with donor atoms, quenching water molecules in the first coordination sphere of Eu(III) can be replaced.

To eliminate the O−H quenchers from the long range of Eu(III), we used D_2O instead of H_2O as reagent and deuterated methanol (MeOD) instead of MeOH as solvent in the sol−gel procedure.[14] Good results can also be obtained if the Eu(III) cryptate is encapsulated in methyl-modified silicate xerogel or dried at ~80 °C.[15]

The aim of our present study was to improve the luminescence properties, i.e., to improve the quantum yield, and lengthen the lifetime of the Eu(III) excited state in the materials. We therefore analyzed the influence of ligands, coligands, anions, and matrix materials on the Eu(III) luminescence characteristics in its complexes (cryptates). Components of the matrix materials such as oxide mixtures (titania−silica and zirconia−silica), poly(dimethylsiloxane) (PDMS), and 3-glycidoxypropyl (Glymo)-modified oxide strongly influence the luminescence activity. In general, the Eu(III) ion should be isolated, particularly from effectively quenching O−H groups. On the other hand, O−H oscillators can be eliminated from the materials by a chemical agent or by drying at elevated temperature. Finally, the materials prepared with the Eu(III) cryptate were tested after exposure to UV radiation during a certain period of time, because there is a problem related to the photodegradation of the organic antenna system in a luminescent material during excitation by high-energy quanta.

Experimental Section

Sample Preparation. The [EuLl]An-type Eu(III) complexes (cryptates) used in this work consist of a main ligand L, a coligand l, and an anion An = X or Y; their structures are shown in Figure 1. The Eu(III) complexes without coligands were synthesized in accordance with the previous report.[28] To obtain a Eu(III) complex with a coligand, the primary complex was dissolved in methanol, after which the coligand was added to this solution in a 1:1 molar ratio. After 1 day, the reaction mixture was used as one of the components in the sol−gel procedures.

The hydrolysis and condensation (sol−gel process) of tetramethoxysilane (TMOS, Aldrich Co.) were used for preparing the silica gel in methanol solution.[13] Mixed titania−silica and zirconia−silica xerogels (molar ratio 9:1) were prepared by the hydrolysis and condensation (sol−gel process) of mixtures of TMOS and titanium tetrabutoxide (TTBO; Aldrich Co.) and of TMOS and zirconium tetraisopropoxide (ZTIPO; Aldrich), respectively. The preparation procedure was similar to that described previously.[12] However, to avoid the presence of O−H oscillators in the final products, heavy water (D_2O) as reagent and MeOD as solvent (molar ratio 1:30, respectively) were used. After some days, the resulting wet gels were dried at room temperature.

Methylated silicate xerogel was synthesized in a similar manner. In this case, a 1:1 mixture of TMOS + PDMS 200 (Aldrich Co.) was dissolved in CH_3OD and D_2O was used as reagent.[15]

Organically modified gels with silica, titania, zirconia, and (3-glycidoxypropyl)trimethoxysilane, $CH_2(O)CHCH_2O(CH_2)_3$-$Si(OCH_3)_3$ (Glymo, Aldrich Co.) were synthesized using the same technique. In this process, TMOS−Glymo, TTBO−Glymo, and ZTIPO−Glymo reaction mixtures (molar ratio 1:1) in CH_3OD solution were stirred for 1 h. D_2O was then added to the mixtures; after 24 h the mixture with the Eu(III) complex was stirred vigorously at room temperature. After that, the gel products were dried at room temperature.

---

(8) Levy, D.; Reisfeld, R.; Avnir, D. *Chem. Phys. Lett.* **1984**, *109*, 596.

(9) Fan, X. P.; Wang, W. Q.; Xiong, G. H. *Mater. Sci.* **1993**, *B21*, 55.

(10) Lockhead, M. J.; Bray, K. L. *J. Non-Cryst. Solids* **1994**, *170*, 143.

(11) Jin, T.; Inoue, S.; Machida, K.; Adachi, G. *J. Non-Cryst. Solids* **1998**, *223*, 123.

(12) Fereira, R. A. S.; Carlos, L. D.; Goncalves, R. R. *Chem. Mater.* **2001**, *13*, 2991

(13) Czarnobaj, K.; Elbanowski, M.; Hnatejko, Z.; Kłonkowski, A. M.; Lis, S.; Pietraszkiewicz, M. *Spectrochim. Acta, Part A* **1998**, *54*, 2183.

(14) Kłonkowski, A. M.; Lis, S.; Hnatejko, Z.; Czarnobaj, K.; Pietraszkiewicz, M.; Elbanowski, M. *J. Alloys Compd.* **2000**, *300−301*, 55.

(15) Hnatejko, Z.; Kłonkowski, A. M.; Lis, S.; Czarnobaj, K.; Pietraszkiewicz, M.; Elbanowski, M. *Mol. Cryst. Liq. Cryst., A* **2000**, *354*, 207.

(16) Bekari, V.; Pistolis, G.; Lianos, P. *Chem. Mater.* **1999**, *11*, 3189.

(17) Fan, X.; Wang, M.; Wang, Z.; Hong, Z. *Mater. Res. Bull.* **1997**, *32*, 1119.

(18) Carlos, L. D.; Messaddeq, Y.; Brito, H. F.; Sá Ferreira, A.; de Zea Bermudez, V.; Ribeiro, S. J. L. *Adv. Mater.* **2000**, *12*, 594.

(19) Miyamoto, Y.; Uekawa, M.; Ikeda, H.; Kaifu, K. *J. Lumin.* **1999**, *81*, 159.

(20) Yan, B.; Zhang, H.; Wang, S.; Ni, J. *J. Photochem. Photobiol., A* **1998**, *112*, 231

(21) Sokolnicki, J.; Urbański, B.; Legendziewicz, J. *J. Alloys Compd.* **2000**, *300/301*, 450.

(22) Carnal, W. T. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Eds.; North-Holland; Amsterdam, 1979; Vol. 3, p 237.

(23) Reisfeld, R. *Struct. Bonding*; Springer-Verlag; Berlin, 1975; pp 22 and 123.

(24) Stręk, W. *J. Chem. Phys.* **1982**, *76*, 5856.

(25) Freed, F. K. *Top. Appl. Phys.* **1976**, *15*, 23.

(26) Stein, G.; Wurzburg, E. *J. Chem. Phys.* **1975**, *62*, 208.

(27) Haas, Y.; Stein, G. *J. Phys. Chem.* **1971**, *75*, 3677.

(28) Pietraszkiewicz, M.; Karpiuk, J.; Pietraszkiewicz, O. *Anal. Quim. Int. Ed.* **1997**, *93*, 171.

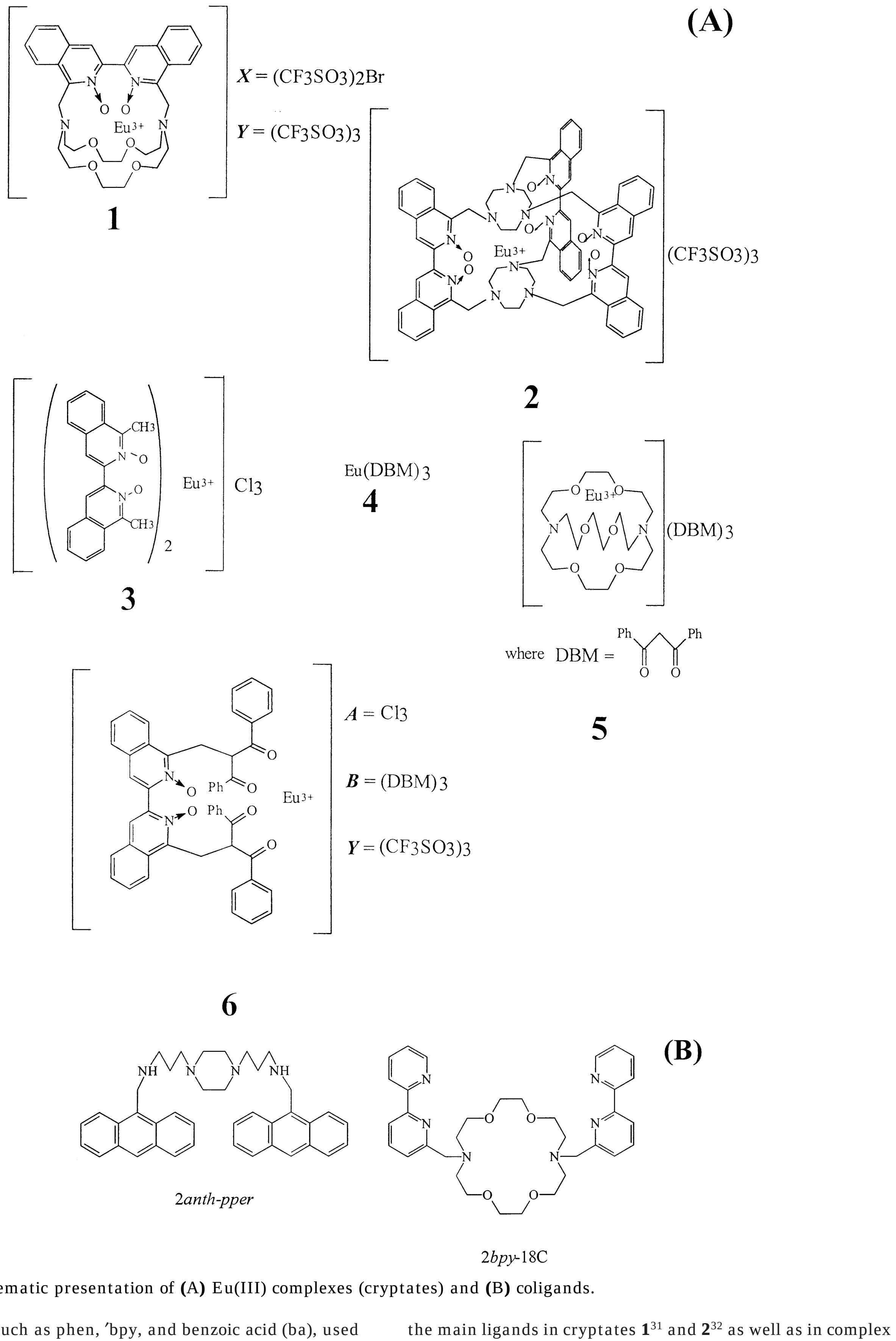

Figure 1. Schematic presentation of (A) Eu(III) complexes (cryptates) and (B) coligands.

Compounds such as phen, ′bpy, and benzoic acid (ba), used as coligands, were purchased from Aldrich Co. Other coligands such as 2bpy-18C (ref 29) and 2anth–pper (see Figure 1B),[30] the main ligands in cryptates **1**[31] and **2**[32] as well as in complex **3**[31] (Figure 1A) were synthesized. Cryptand [2.2.2] and DBM (**4**) were also purchased from Aldrich Co.

---

(29) Rodriquez-Ubis, J. C.; Alpha, B.; Plancherd, P.; Lehn, J.-M. *Helv. Chim. Acta* **1984**, *67*, 2264.

(30) Fabrizzi, L.; Licchelli, M.; Pallavicini, P.; Perotti, A.; Taglietti, A.; Sacchi, D. *Chem. Eur. J.* **1996**, *2*, 75.

The concentration of the Eu(III) complexes (cryptates) in the dried gels (xerogels) is equal to 5×10^{-6} mol·g^{-1}, estimated on pure, dried xerogel obtained from the alkoxides.

Apparatus. Xerogel materials doped with Eu(III) complexes were crushed, and a grain fraction of size 0.25–50 mm were used for measurements mentioned below.

Reflection UV–visible absorbance spectra were recorded on a Shimadzu UV–Vis 240 PC spectrophotometer equipped with a diffuse reflection holder for crushed samples.

Luminescence emission spectra were recorded at right angles using a Perkin-Elmer LS 50B spectrofluorometer with a reflection spectra attachment. The emission spectra of the xerogel samples doped with the Eu(III) complexes were obtained using an excitation wavelength of 358 nm. None of the excitation spectra were corrected for the lamp and photomultiplier response.

Luminescence decays were measured by means of a Perkin-Elmer MPF-3 spectrofluorometer, an M12FVC51 Edinburgh 199 single-photon counter, and a laser system [KB6211 nitrogen laser (Cobrabid, Poznań) and tunable dye laser] as an exciting light source combined with an MC101 transient recorder and an IBM computer.[33]

The luminescence quantum yields of the samples have been determined based on the method described by Wrighton et al.[34] Measurement of absolute luminescence quantum yields of the powdering samples (fraction of 0.3 mm) involved determination of the diffuse reflectance of the sample relative to a nonabsorbing standard (KBr) at the excitation length and then measuring the emission of the sample under the same conditions. The quantum yield, ϕ, as the ratio of the emitted photons to the difference in the number of diffuse reflected photons from the sample and the nonabsorbing standard has been calculated using eq 1, where E is the area of the corrected

$$\phi = E/(R_{\mathrm{std}} - R_{\mathrm{smpl}}) \qquad (1)$$

emission curve of the sample and R_{std} and R_{smpl} are corrected areas under the diffuse reflectance curves of the nonabsorbing standard and samples, respectively, at the excitation wavelength.

The Eu(III) complexes entrapped in xerogels were irradiated by means of a UV lamp of radiation power 0.53 W·cm^{-2}. The luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ band at $\lambda_{\max} = 617$ nm (when $\lambda_{\mathrm{exc}} = 353$ nm) was measured for the materials using the spectrofluorometer.

Results

Ligands. Figure 2 shows excitation spectra of (a) **1**X (cryptate **1** with anion group X) in aqueous solution and (b) cryptate **1**X immobilized in a silica matrix, together with (c) Eu(ClO$_4$)$_3$ dissolved in water. The Eu(III) ion in aqueous solution exhibits no band in the 250–400-nm spectral range. In the case of the cryptate cation **1** in solution, a weak, sharp band at 230 nm and two bands at 280 and 345 nm are present. The latter spectrum consists of a weak, sharp band at 230 nm and a large structured band in the 250–400-nm range.

The luminescence emission spectrum of complex **3** entrapped in methyl-modified silicate has one very large band peaking at ~430 nm and a trace of a band at ~610 nm (Figure 3a). On the other hand, the spectrum of cryptate **1** with X in the same matrix consists of a broad, low-intensity band with a short-wavelength part whose intensity is lower than the Eu(III) bands at ~620 nm (Figure 3b).

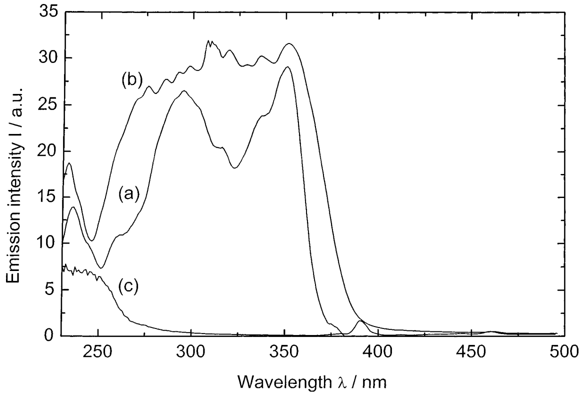

Figure 2. Excitation spectra of cryptate **1** with anion X in (a) aqueous solution, (b) silica xerogel, and (c) Eu(ClO$_4$)$_3$ in aqueous solution. $\lambda_{\mathrm{em}} = 617$ nm.

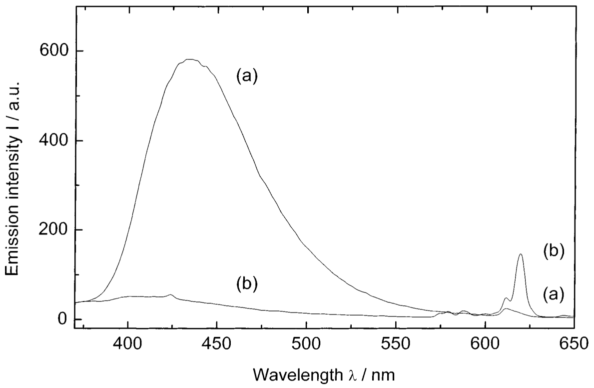

Figure 3. Emission spectra of (a) complex **3** and (b) cryptate **1** entrapped in xerogel silica matrix. $\lambda_{\mathrm{exc}} = 353$ nm.

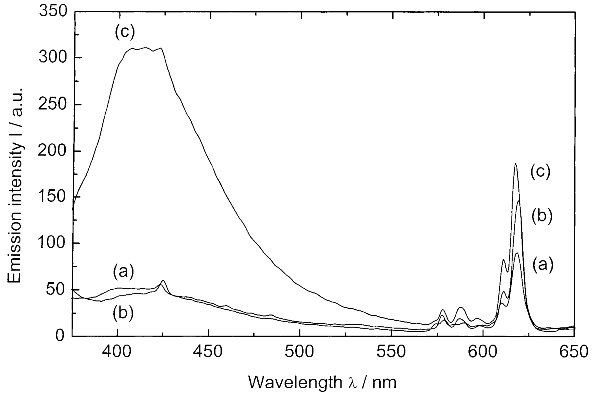

Figure 4. Emission spectra of (a) Eu(III) cryptate salt **1**X incorporated into SiO$_2$–PDMS (1:1) matrix and **1**X with (b) ba and (c) phen as coligands immobilized in the same matrix. $\lambda_{\mathrm{exc}} = 353$ nm.

Coligands. Figure 4 illustrates the changes in the emission intensity in two ranges: 400–450 (characteristic of the ligand) and ~600 nm (characteristic of the Eu(III) ion), if the coordination sphere of Eu(III) consists of [biqO$_2$.2.2] cryptand (a) without coligand, (b) with ba, and (c) phen as coligands.

Anions. Complex salts of type **6** with acyclic ligands (Figure 1A) are good examples that illustrate the influence of an anion on the quantum yield of Eu(III) ion luminescence (Table 1).

---

(31) Lehn, J.-M.; Pietraszkiewicz, M.; Karpiuk, J. *Helv. Chim. Acta* **1990**, *73*, 106.

(32) Pietraszkiewicz, M.; Karpiuk, J.; Gąsiorowski, R.; Pietraszkiewicz, O.; Rout, A. K. *Acta Phys. Pol. A* **1996**, *90*, 207.

(33) Lis, S.; Hnatejko, Z.; Stryła, Z. *Optica Appl.* **2001**, *31*, 643.

(34) Wrighton, M. S.; Ginley, D. S.; Morse, D. L. *J. Phys. Chem.* **1974**, *78*, 2229.

Table 1. Quantum Yield, Lifetime of Eu(III) Luminescence, and Calculated Hydration Numbers of the Eu(III) Complexes 6 with Various Anions (See Figure 1A)

Eu(III) complex salt	excitation wavelength λ_{exc}/nm	quantum yield ϕ	lifetime[a] τ/μs	hydration no./n_{H_2O}
6Y	344	0.25 ± 0.05	286	3.0
6A	345	0.20 ± 0.04	286	3.0
6B	380	0.09 ± 0.02	261	3.3

[a] Excitation wavelength, $\lambda_{exc} = 394$ nm.

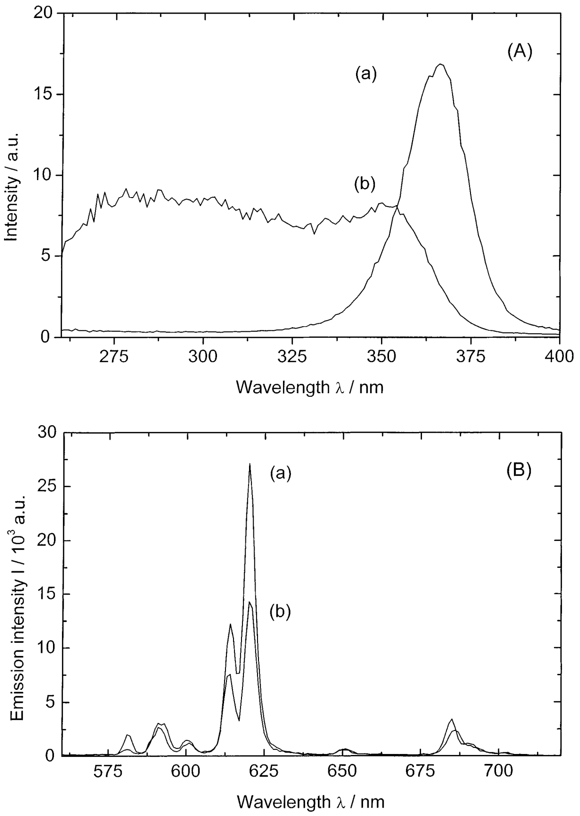

Figure 5. (A) Excitation spectra of cryptate **1** with X entrapped in matrixes: (a) TiO_2-SiO_2 (9:1) and (b) ZrO_2-SiO_2 (9:1), $\lambda_{em} = 620$ nm. (B) Emission spectra of the same cryptate in matrixes: (a) TiO_2-SiO_2 (9:1), $\lambda_{exc} = 365$ nm, and (b) ZrO_2-SiO_2 (9:1), $\lambda_{exc} = 354$ nm.

Matrix. The luminescence excitation spectra of **1** with X in Figure 2 exhibit changes that depend on the type of matrix. In each case, the cryptate shows bands in the 250−400-nm spectral range. However, for the cryptate in a solid matrix (silica xerogel), there is one broad structured band (Figure 2a), while the spectrum of **1**X in aqueous solution consists of two distinct bands (Figure 2b).

The excitation spectrum changes when the cryptate cation **1** with anion group X is incorporated into various mixed-oxide xerogels such as TiO_2-SiO_2 and ZrO_2-SiO_2 (see Figure 5A). Material with the former oxide system shows a large band peaking at 365 nm (spectrum a), unlike the latter one, which has a broad structured band (λ_{max} ~350 nm) (spectrum b). In general, the lifetimes measured for the oxide matrixes are lower than for oxides organically modified by PDMS or Glymo (see Table 2). The only exception is the material with ZrO_2-Glymo matrix.

Silica, zirconia, and titania modified by Glymo alter the excitation spectra in matrixes (Figure 6A). Only the SiO$_2$−Glymo system displays an excitation spectrum with a distinct band at ~360 nm (spectrum b). For each of the materials, the excitation and emission spectra were recorded in the same conditions, therefore allowing comparison of the spectrum intensities in Figures 5 and 6. It shows that the more intense the excitation band of the material, the higher its emission intensity. In the TiO_2-Glymo matrix, the position of the $^5D_0 \rightarrow {}^7F_2$ band is red-shifted in comparison to the matrixes with SiO_2-Glymo and ZrO_2-Glymo.

Table 2. Luminescence Lifetime, τ ($\lambda_{exc} = 579$ nm) and Quantum Yield, ϕ, of Eu(III) Cryptate Salt 1X (see Figure 1A) in Xerogel Matrixes

matrix	lifetime τ/μ	quantum yield ϕ
SiO_2	351	0.18 ± 0.04
TiO_2-SiO_2 (9:1)	547	0.44 ± 0.09
ZrO_2-SiO_2 (9:1)	560	0.26 ± 0.05
SiO_2-PDMS (1:1)	608	0.08 ± 0.02
SiO_2-Glymo (1:1)	629	0.90 ± 0.11
TiO_2-Glymo (1:1)	620	0.21 ± 0.02
ZrO_2-Glymo (1:1)	422	0.09 ± 0.02

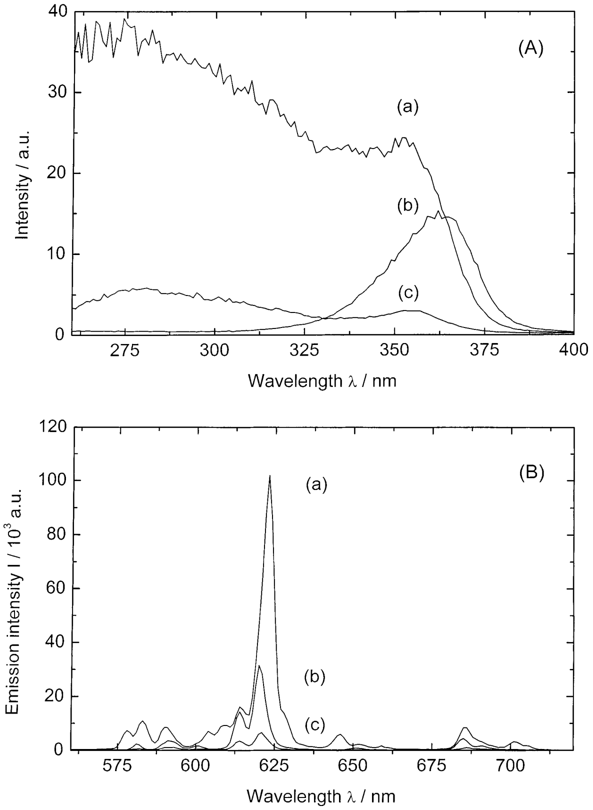

Figure 6. (A) Excitation spectra of **1**X entrapped in matrixes: (a) SiO_2-Glymo (1:1), (b) TiO_2-Glymo (1:1), and (c) ZrO_2-Glymo (1:1), $\lambda_{em} = 620$ nm. (B) Emission spectra of the same cryptate in matrixes: (a) TiO_2-Glymo (1:1), $\lambda_{exc} = 352$ nm, (b) SiO_2-Glymo (1:1), $\lambda_{exc} = 361$ nm, and (c) ZrO_2-Glymo (1:1), $\lambda_{exc} = 354$ nm.

Materials containing **1**X (additionally complexed with phen) incorporated into ZrO_2-SiO_2 (Figure 7) exhibit the same correlation between intensities of excitation (Figure 7A) and emission (Figure 7B) spectra as above.

The results set out in Table 3 indicate that the presence of a coligand such as phen in the Eu(III) coordination sphere increases the luminescence lifetime if the Eu(III) cryptate salt **1**X is entrapped in SiO_2 and methylated silicate (SiO_2 + PDMS) matrixes (cf. Tables 2 and 3).

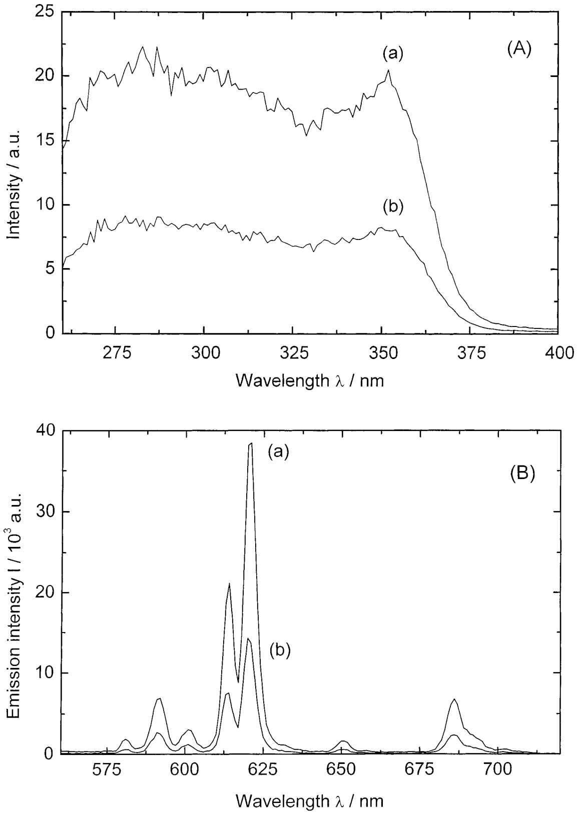

Figure 7. (A) Excitation spectra of **1**X entrapped in matrix: (a) ZrO_2-SiO_2 (9:1) + coligand phen and (b) ZrO_2-SiO_2 (9:1). $\lambda_{em} = 620$ nm. (B) Emission spectra of the same cryptate in matrixes: (a) ZrO_2-SiO_2 (9:1) + coligand phen and (b) ZrO_2-SiO_2 (9:1). $\lambda_{exc} = 353$ nm.

Table 3. Luminescence Lifetime, τ ($\lambda_{Exc} = 579$ nm) and Quantum Yield, ϕ, of Eu(III) Cryptate Salt 1X with phen as a Coligand in Xerogel Matrixes

matrix	lifetime τ/μs	quantum yield ϕ
SiO_2	534	0.30 ± 0.05
ZrO_2-SiO_2 (9:1)	410	0.38 ± 0.07
SiO_2−PDMS (1:1)	672	0.10 ± 0.02
TiO_2−Glymo (1:1)	473	0.34 ± 0.08

In Tables 2 and 3 are collected quantum yield values obtained not only for the cryptate salt **1**X in the oxide and organically modified matrixes but also for the same salt with coligand phen in several of the studied matrixes. The highest quantum yield value is observed for the material with a SiO_2−Glymo matrix (0.90), while the lowest ones show the systems with SiO_2−PDMS and ZrO_2−Glymo. The three-component complex (**1** + phen) in SiO_2 or TiO_2−Glymo presents a higher quantum yield than that in complex **1** without any coligand entrapped in the mentioned matrixes. However, complexes **1** and **1** + phen in matrixes ZrO_2-SiO_2 or SiO_2−PDMS show the same values within experimental error.

Table 4. Luminescence Lifetime τ of Eu(III) Complexes (Cryptates) with Coligands (see Figure 1B) Entrapped in Methylated Silicate Xerogel[a]

complex (cryptate)	coligand	lifetime τ/μs
2	[b]	218
	2bpy−18C	606
	2anth−pper	462
	bpy	476
	ba	513
3	[b]	326
	2bpy−18C	461
	2anth−pper	721
	bpy	485
	ba	466
4	2bpy−18C	651
	ba	461
1	2anth−pper	728

[a] Excitation wavelength $\lambda_{exc} = 579$ nm. [b] Without coligand.

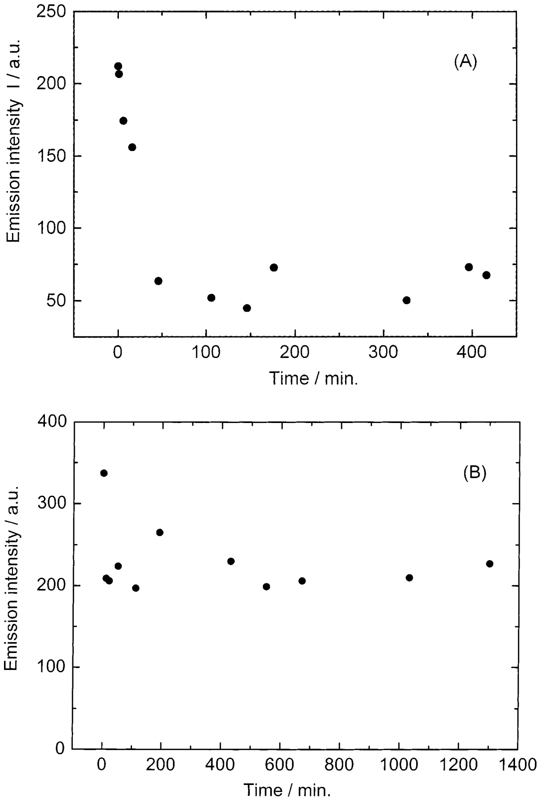

Figure 8. Changes of emission intensity of the $^5D_0 \rightarrow {}^7F_2$ band at 617 nm during UV irradiation of materials consisting of SiO_2−PDMS matrix and immobilized: **(**A**)** complex **3** and **(**B**)** cryptate **1** with X. $\lambda_{exc} = 353$ nm.

Table 4 collects the luminescence lifetime results measured for other Eu(III) complexes with coligands incorporated into methyl-modified silicate xerogels. Some of the coligands, such as *2*bpy−18C and 2anth−pper (see Figure 1B) having large aromatic segments in their structures, show in some cases an effective increase in the luminescence intensity and lifetime. Thus, in the case of the complex with cryptate **2** and coligand *2*bpy−18C, τ is longer than 600 μs, while 2anth−pper is more effective as a coligand for complex **3** (τ = 721 μs). The system with the latter coligand complexed with **1** also reaches nearly the same value (τ = 728 μs), the longest obtained for the materials studied.

Photodegradation. It is shown in Figure 8A that due to UV irradiation (radiation power $P = 0.53$ $W{\cdot}cm^{-2}$) the emission intensity of the material consisting of methyl-modified silicate doped with the Eu(III) complex **3** rapidly decreases and that after an exposure time longer than 50 min a lower intensity level is stabilized (at ~25% of the initial intensity). By contrast, although cryptate **1** with X in the same matrix does exhibit an emission intensity drop after ~50 min, this parameter then remains roughly constant at a relatively high level (over 60% of the initial intensity) for more than 20 h (Figure 8B).

Discussion

Among the ligands studied, the [biqO_2.2.2] cryptand (in **1**, Figure 1) is able most efficiently to isolate the excited state of Eu(III) from the quenching of water molecules; simultaneously, it participates in the antenna effect.[14] In our experiments, cryptate **1** is treated as a fundamental luminescence center characterized by a relatively long lifetime. Although the cryptand in **2** is richer in antenna biqO_2 groups than **1** (see Figure 1), the properties of **2** incorporated into the xerogel matrix are rather poor considering its luminescence emission.[14] Because its cavity is too large in comparison with the complexed Eu(III) ion, the central ion cannot be effectively isolated from surrounding quenchers and therefore does not take effective part in energy transfer from the excited ligand group to the emission center.

When no aromatic group is present around the Eu(III) ion, as in its aqua complex in aqueous solution, no excitation band is observed in the UV range (250−400 nm, Figure 2c). However, a system such as the Eu(III) complex cation with aromatic [biqO_2.2.2] dissolved in aqueous solution or entrapped in a silica matrix exhibits high-intensity excitation bands in the same UV range (Figure 2a and b, respectively). This means that cryptate **1** absorbs sufficient UV energy quanta required for the $\pi-\pi^*$ transition in the aromatic group of the cryptand. It results in the transfer of energy from the ligand to the Eu(III) ion due to an efficient antenna effect in the cryptate.[13]

In some Eu(III) complexes, energy transfer from an excited ligand to the central ion is practically impossible. In this case, emission of the ligand can be observed near the UV region. This effect occurs in the case of Eu(III) complex **3** (see Figure 3). The large emission band is related to the luminescence of the ligand (3,3′-dimethyl-2,2′-biisoquinoline dioxide), but the emission bands characteristic for Eu(III), at ∼620 nm, are in practice not present. On the contrary, for **1**X, the emission band of [biqO_2.2.2] cryptand is of lower intensity than above. However, one of the Eu(III) bands (attributed to $^5D_0 \rightarrow {}^7F_1$) shows nearly the same intensity as the band at 425 nm. This is due to an efficient energy transfer from the cryptand to the metal ion.

The Eu(III) binary system can be additionally complexed with a coligand. It is a well-known effect that aromatic coligands improve the luminescent properties (i.e., the emission intensity and sometimes the lifetime) of the Eu(III) excited state in luminescent materials based on the antenna effect.[35−40] In our experiments, the systems consisting of the ligand and one of the coligands exhibit relatively low emission intensity in the ligand spectral range, while in the Eu(III) range, the emission is distinctly improved in comparison to the system with the ligand only. In the latter system, the intensity proportion in both the spectral ranges is inverted.

Donor atoms of the coligand occupy some coordination sites around the central ion and simultaneously replace remaining water molecules—effective quenchers—coordinated with the Eu(III) ion in the inner sphere. The aromatic group of the coligand can then act as an antenna. These two effects should lengthen the lifetime, as the example of cryptate **1** + phen shows in comparison with **1** (cf. Tables 2 and 3 as well as in Table 4 for other cryptates in SiO_2−PDMS). However, this type of lifetime change is not a rule for all systems studied; e.g., ZrO_2−SiO_2 and TiO_2-Glymo show reduced lifetime.

It has been demonstrated in Table 1 that the type of anion also influences on the luminescence properties of the Eu(III) complex or cryptate. In the studied examples, anions such as $CF_3SO_3^-$ or Cl^- distinctly increase the Eu(III) luminescence lifetime and quantum yield. These anions are able to replace a water molecule (i.e., to remove OH oscillators) from the coordination sphere of the Eu(III) ion and simultaneously reduce the quenching effect. In comparison, larger anions, such as DBM, do not affect the coordination sphere of the metal ion producing spherical hindrance and consequently do not improve luminescent properties of the materials studied.

Regarded as an extensive space surrounding the central ion, the matrix plays an important role in the luminescence characteristics of luminescent materials based on the antenna effect in the entrapped Eu(III) complexes. Two different media (solid and liquid) influence the excitation spectrum of **1** as seen in Figure 2. If **1** is immobilized into a xerogel matrix, a large band with a vibronic structure is present in the excitation spectrum (b) in the 250−400-nm range, while the same cryptate dissolved in water shows two intense bands in this range (spectrum a).

First, the luminescence parameters of the emitting Eu(III) center depend on the concentration of water in the matrix. Thus, in comparison to the cryptate **1**X encapsulated in silica xerogel, the lifetime in excited state increases for the cryptate with such coligands as phen or TPPO entrapped in silicate matrix with methyl groups, as the results in ref 15 demonstrate. The latter case is due to the more hydrophobic character of the methyl-modified silicate and coligand presence. Furthermore, in Table 2 is shown a higher Eu(III) luminescence lifetime value obtained for methyl-modified silicate than for mixed oxides such as ZrO_2−SiO_2 (9:1) and particularly TiO_2−SiO_2 (9:1). Both the mixed oxides with higher permittivity, ϵ (for ZrO_2, $\epsilon = 7.1-10.5$ and for TiO_2, $\epsilon = 14-110$ [41]), exhibit longer a lifetime than SiO_2 ($\epsilon = 4.3$). Another class of organically modified matrixes refers to xerogels with Glymo. In general, the results of our study demonstrate that a lifetime increase depends on the type of matrix, as observed in the following sequence: SiO_2 < mixed oxide (TiO_2−SiO_2, ZrO_2−SiO_2) < organically modified xerogels (SiO_2−PDMS, SiO_2−Glymo, TiO_2−Glymo). Only the material

---

(35) Li, X.; Bian, Z.; Jin, L.; Lu, S.; Huang, S. *J. Mol. Struct.* **2000**, *522*, 117.

(36) Tanner, P. A.; Yan, B.; Zhang, H. *J. Mater. Sci.* **2000**, *35*, 4325.

(37) Yan, B.; Zhang, H.; Wang, S.; Ni, J. *Mater. Chem. Phys.* **1997**, *51*, 92.

(38) Bünzli, J.-C. G.; Moret, E.; Foiret, V.; Schenk, K. J.; Mingzhao, W.; Linpei, J. *J. Alloys Compd.* **1994**, *207/208*, 107.

(39) De Sa, G. F.; Nunes, L. H. A.; Wang, Z.-M.; Choppin, G. R. *J. Alloys Compd.* **1993**, *196*, 17.

(40) Reisfeld, R.; Saraidarov, T.; Pietraszkiewicz, M.; Lis, S. *Chem. Phys. Lett.* **2001**, *349*, 266.

(41) *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1987; p E-53.

with ZrO_2−Glymo matrix is an exception (Table 2). This correlation is not valid for the quantum yield.

In principle, in the case of material with **1**X immobilized in SiO_2−Glymo (1:1), the higher the excitation band near 360 nm, the more intense is the emission spectrum with characteristic band related to $^5D_0 \rightarrow {}^7F_2$ transition of the Eu(III) ion. This effect is present not only if the matrix is changed but also for change in coligands (cf. in Figures 5 and 6).

In comparison to the cryptate **1**X encapsulated in silica xerogel, the lifetime in excited state increases for the cryptate with such coligands as phen or TPPO entrapped in a silica matrix with methyl groups, as the results in ref 15 demonstrate. The presence of phen as a coligand in the coordination sphere does not enhance lifetime and quantum yield in each case. There are examples which demonstrate that only the matrix (Table 3) or the main ligand (cryptand) with a suitable coligand in the same matrix can improve the emission lifetime (see Table 4). In other words, the emission lifetime of the Eu(III) ion−ligand (cryptand)−coligand−solid matrix system depends on the specific interactions between ligand−coligand and coligand−matrix. The former interaction is particularly clearly illustrated by the coligands with large aromatic segments, as for 2bpy−18C and 2anth−pper, in the same matrix (Table 4).

For matrixes such as SiO_2, ZrO_2−SiO_2, and TiO_2−Glymo, quantum yield is higher if coligand phen is present in the materials doped with Eu(III) cryptate. However, this large coligand molecule in some cases cannot be bound quite near the central ion, i.e., into the coordination sphere of Eu(III), due to steric hindrance. This effect influences lifetime changes of the materials with other Eu(III) complexes and aromatic coligands other than phen for the methylated silica (cf. in Tables 3 and 4).

Luminescent materials based on the antenna effect in Eu(III) complexes are excited by UV radiation. Consequently, the relatively high-energy quanta, such as those in UV radiation, are able to decompose photochemically organic groups in an antenna system. Particularly labile in such conditions are N−O bonds in the isoquinoline oxide groups. It is evident that the acyclic ligand in complex **3** in practice loses part of its luminescent properties after brief UV irradiation (Figure 8A). In contrast, [biqO_2.2.2] cryptand in **1** is much more stable. The material (**1** in SiO_2−PDMS) lost about one-third of its original emission intensity after the first minutes of irradiation although the intensity remained at the same relatively high level (Figure 8B). In this case, probably only N−O bonds undergo photochemical decomposition, and the cryptand with aromatic antenna groups should not change due to UV radiation exposure.

Conclusions

In such multiple systems as the luminescent materials with Eu(III) complexes prepared by the sol−gel procedure, the efficiency of their luminescence depends on the presence of quenching O−H oscillators, not only at the shortest distance from the central ion (first coordination sphere) but also farther away, i.e., in the matrix.

(1) To reduce the number of O−H oscillators (water molecules) in the coordination sphere, we prepared the $\{Eu \subset [biqO_2.2.2]\}^{3+}$ cation, additionally with phen as an effective coligand.

(2) The experiments confirm that the type of anion An^- in the complex salt $\{Eu \subset [biqO_2.2.2]\}An_3$ plays also a significant role in the increase of the Eu(III) luminescence lifetime and yield of the prepared materials.

(3) The emission lifetime increases with the change of the matrix materials, as in the following sequence: silica < mixed oxides (such as SiO_2−TiO_2 and SiO_2−ZrO_2) < organically modified oxides (such as SiO_2−PDMS, SiO_2−Glymo, and TiO_2−Glymo). As regards the quantum yield of the materials, the sequence changes as follows: SiO_2−PDMS < (ZrO_2−Glymo and TiO_2−Glymo) < SiO_2 < TiO_2−SiO_2 < ZrO_2−SiO_2 < SiO_2−Glymo. In each sequence, the ZrO_2−Glymo matrix is an exception; this material demonstrates the lowest values of both the luminescence parameters.

(4) The influence of coligands on the emission lifetime depends on two specific interactions, namely, coligand−matrix and coligand−main ligand (cryptand). The former interaction is seen for the mixed oxide and the Glymo-modified matrixes. Such extended aromatic systems as 2bpy−18C and 2anth−pper, which in some cases really improve emission lifetimes of the materials studied, illustrates the latter interaction.

(5) A good working luminescent material, excited by UV radiation, should be photochemically stable during exposure to light. This condition is in practice fulfilled by the material consisting of $\{Eu \subset [biqO_2.2.2]\}(CF_3SO_3)_2Br$ complex entrapped in SiO_2−PDMS matrix.

Acknowledgment. This study was supported by the Polish Scientific Research Council (Grant 1235/*T*09/2002/20).

CM0202557