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# Luminescence properties of materials consisting of Eu(III) or Tb(III) complexes with 2,2′-bipyridine *N*,*N*′-dioxide and coligands entrapped in xerogels

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## Abstract

Ln(III) ions, where Ln(III) = Eu and Tb, were complexed with 2,2′-bipyridine *N*,*N*′*-dioxide* (*bpy*O$_2$) as a ligand. To the coordination sphere were introduced coligands such as 1,10-phenanthroline (*phen*), triphenylphosphine oxide (TPPO), salicylic acid (SA) and phthalic acid (PA) to substitute water molecules (O–H quenching oscillators) from the nearest environment of the central ion. These Ln(III) complexes were encapsulated in silica or methylated silicate xerogels. Additionally, moderate thermal treatment or chemical drying reduced the concentration of O–H oscillators in the matrices and simultaneously improved the photophysical properties of the materials.

The complex ions of the type $[\mathrm{Ln(bpyO_2)_3}]^{3+}$ with some free coordination places were prepared intentionally to study role of coligands in isolating the coordination sphere from the quenching water ligands. Coligands with O donor atoms (PA, SA and TPPO) improve the emission intensity of the ternary Ln(III) complexes entrapped in both the xerogel matrices in comparison with the binary complexes. On the other hand, *phen* with N donor atoms lengthens the luminescence lifetime in the Eu(III) bearing materials and Tb(III) immobilised in SiO$_2$.

*Keywords:* Luminescent materials; Xerogel matrix; Ln(III) complexes; Coligands; Emission intensity; Luminescence lifetime

## 1. Introduction

The emission spectrum of Eu(III) ion consists of lines in the red spectral area. These lines have found an important application in lighting and display and they correspond to transition from excited $^5D_0$ level to the $^7F_J$ ($J = 1$–4) levels of the 4f$^6$ configuration. The splitting of the emission transitions yields the crystal field splitting of the $^7F_J$ levels, while the $^5D_0$ level is not splited by the crystal field (because $J = 0$). If the site of Eu(III) ion has no inversion symmetry, the electric-dipole transitions are no longer strictly forbidden and appear as lines in the spectra. Thus, some transitions, *viz.* those with $\Delta J = 0, \pm 2$, are hypersensitive to this effect and the $^5D_0 \rightarrow {}^7F_2$ emission transition dominates above other ones [1].

The emission of Tb(III) is due to transition $^5D_4 \rightarrow {}^7F_J$ which are mainly in the green. Often there is a considerable contribution to the emission from the higher-level emission $^5D_3 \rightarrow {}^7F_J$, mainly in the blue. Since the $J$ values, involved in the transitions, are high, the crystal field splits the levels in many sublevels that gives the spectrum its complicated appearance [1].

A number of Ln(III) complexes, where Ln = Eu or Tb, display a bright and narrow 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 (antenna) and emission by a lanthanide ion. This phenomenon in solutions is devoted the review written by Sabbatini and Guardigli [2].

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The luminescence properties of Ln(III) complexes in a variety of solid matrices have been investigated extensively [3–7]. The studies have demonstrated that especially Ln(III) complexes with aromatic chelate ligands have superior luminescence properties with respect to conventional chelate ligands. The chelates create stable complexes with Ln(III) ions and can shield partly the encapsulated ion from quenching interaction with water molecules. However, the coordination number 6 is unusual but the higher numbers (*e.g.* 9) are more characteristic [8].

To reduce the nonradiative decay from the excited state of Ln(III), we tried to eliminate O–H oscillators in the short range, *i.e.* in the first coordination sphere of the central ion and in the longer range from the central ion, *viz.* xerogel matrix. If the coordination sphere is supplemented with coligands such as 1,10-phenanthroline, 2,2′-bipyridine, triphenylphosphine oxide [9,10] or other aromatic systems with donor atoms, the Ln(III) center emits more effectively for two reasons. Firstly, the coligand is able to complete the coordination sphere and thus replace quenching water molecules. Secondly, the aromatic group of the coligand plays role of an additional antenna in the Ln(III) complex.

The aim of this study was to improve such luminescence properties of the materials as emission intensity and luminescence lifetime. From this point of view we try to analyze the influence of coligands and matrix xerogels on the Ln(III) luminescence characteristics in its complexes. To study the coligand influence we prepared intentionally Ln(III) complexes with only three bidentate *bpy*$O_2$ ligands, instead of four for the completed coordination sphere [11]. In this case the coordination sphere can be completed either by an isolating coligand molecule or by water molecules with effectively quenching O–H groups. Water molecules can diffuse from a matrix to the entrapped central ion, therefore they should be eliminated from the materials either by drying or organic modification (hydrophobization) of the matrix.

## 2. Experimental

### 2.1. Sample preparation

The $[Ln(bpyO_2)_3 \cdot \boldsymbol{c}]Cl_3$ complexes used in this work consists of a central ion Ln = Eu(III) and Tb(III), a main ligand *bpy*$O_2$ and a coligand ***c***. The Ln(III) complexes without coligands were synthesized in accordance with the previous report [12]. To obtained a Ln(III) complex with a coligand, the primary complex was dissolved in dried methanol, after which the coligand was added to the this solution in a 1:1 molar ratio. After one 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]. 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 gel were dried at room temperature and studied as a xerogel luminescent material.

Methylated silicate xerogel was synthesized in a similar manner. In this case, 1:1 mixture of TMOS and PDMS 200 (Aldrich Co.) was dissolved in MeOD and $D_2O$ was used as reagent [10].

Compounds such as 1,10-phenanthroline (*phen*), triphenylphosphine oxide (TPPO), salicylic acid (SA) and phthalic acid (PA), used as coligands, $EuCl_3 \cdot 6H_2O$ and $TbCl_3 \cdot 6H_2O$ salts, and hexamethyldisilazane $(MeSi)_2NH$ as a drying agent were purchased from Aldrich Co.

The concentration of the Ln(III) complexes in the xerogels is equal to $5 \times 10^{-6}$ mol/g, estimated on pure, dried xerogel obtained from the alkoxides.

### 2.2. Apparatus

Xerogel materials doped with Ln(III) complexes were crushed, and a grain fraction of size 0.25–0.50 mm were used for measurements described below.

Luminescence excitation and 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 Ln(III) complexes were obtained using an excitation wavelength equal to $\lambda_{max}$ in the related excitation spectrum. None of the excitation spectra were corrected for 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 a exciting light source combined with an MC101 transient recorder and an IBM computer [14].

The Ln(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 $\lambda_{max} = 613$ nm for Eu(III) and the $^5D_4 \rightarrow {}^7F_5$ band at 542 nm for Tb(III) ($\lambda_{exc}$ from Table 1A) were measured for the materials using the spectrofluorometer.

## 3. Results

### 3.1. Coligands

Absorption spectrum of the *bpy*$O_2$ ligand immobilized in $SiO_2$ consists of two bands at 250 and 330 nm (Fig. 1A) and absorption spectra of the $[Eu(bpyO_2)_3]Cl_3$ complex and the ternary complex with TPPO coligand both entrapped in silica xerogel are shown in Fig. 1B. The spectra of the materials with $[Tb(bpyO_2)_3]Cl_3$ are presented in Fig. 1C. Positions of the absorption bands in the studied materials change between *ca.* 310 and 330 nm.