# Functionalization of Sol-Gel Zirconia Composites with Europium Complexes

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Different sol-gel strategies based on functionalization of $ZrO_2$:Eu microparticles with 1,10-phenanthroline (phen) and incorporation of colloidal $Eu(phen)_2(NO_3)_3$ into zirconia have been used to obtain hybrid sol-gel composites with controlled optical properties. The process leads to materials with quantum yields of about 48 % monitoring the 615 nm emission line at 350 nm excitation. Excitation/luminescence spectroscopy, diffuse reflectance spectroscopy and X-ray diffraction have been used to characterize the hybrid zirconia composites.

*Key words:* Sol-Gel, Zirconia, Europium, Hybrid Composites

## Introduction

Sol-gel technology is a method for the preparation of hybrid materials at temperatures below 150 °C. The products are powerful light sources with potential application as labels for chemical and biological purposes. The strong luminescence of hybrid materials containing lanthanide complexes incorporated in sol-gel networks is based on an efficient energy transfer. By variation of the synthesis conditions, different kinds of amorphous or nanocrystalline materials like hybrid composites, thin films, xerogels or aerogels can be obtained. Sol-gel chemistry also offers the ability to tailor density, microstructure and shape of samples prepared by control of the rate of hydrolysis and condensation reactions. Sol-gel-derived inorganic network materials doped with rare earth ions display optical properties such as luminescence, coloration and energy transfer [1, 2]. Lanthanide complexes, however, display some disadvantages which have to be compensated during sol-gel preparation by changing the incorporation conditions: pH, temperature, phase behavior and drying. Most lanthanide complexes have low solubility and low kinetic stability in solid matrixes. It is difficult to embed a chelate dye into a solid sol-gel matrix and prepare a monolith with a high level of homogeneity [1]. These factors are a prerequisite for the formation of clusters and aggregates that cause quenching of luminescence or a very low doping level [2, 3]. One way to avoid these effects is the covalent binding of the complex with the matrix, such that the solubility of the lanthanide complex can be significantly increased [4]. For example, the synthesis of functionalized mesoporous MCM-41 prepared by the sol-gel method and doped with Eu(III) chloride, in which covalent bonding of complex and matrix is accomplished and an increase of the luminescence is achieved, is reported in ref. [5].

A new method for the functionalization of $Eu^{3+}$-doped silica nanoparticles with 1,10-phenanthroline has been proposed recently when preparing hybrid composites with quantum efficiency of 20 – 40 % [6]. The idea of this method is to replace the doping procedure of the complex by a surface functionalization of inorganic oxides, doped with lanthanide ions. As a surface functionalization agent organic ligands can be used. By this method we achieved a high time stability and improved the luminescent properties of the material. As an Eu(III) complex we used $Eu(phen)_2(NO_3)_3$, a simple, strongly emitting complex (quantum output 30 – 40 % due to energy transfer) capable of sensitizing the luminescence due to a higher lying triplet level with

respect to the resonance level of $Eu^{3+}$, which leads to an energy transfer [7–9].

Europium-doped zirconia belongs to the promising optical materials which allow a high level of doping due to the zirconia structure. Functionalization of $ZrO_2$:Eu with organic ligands increases the quantum yield because of the ready energy transfer even with a lower concentration of europium [8, 10].

In this contribution the preparation of zirconia composites functionalized with an $Eu(phen)_2(NO_3)_3$ complex is described, and the optical properties depending on the preparation strategy are reported. We used two sol-gel strategies: A) functionalization of $ZrO_2$:Eu microparticles with 1,10-phenanthroline and B) incorporation of colloidal $Eu(phen)_2(NO_3)_3$ into sol-gel zirconia.

## Experimental Section

### Sol-gel preparation conditions

The two main sol-gel preparation procedures used are listed bellow. Functionalization with europium complexes needs a zirconia sol-gel matrix preparation. Recently [9] we developed some sol-gel methods based on Zr(IV) complex formation with acetic acid (AA) and acetylacetone (AcAc) in order to decrease the rate of hydrolysis and the gelation of zirconia. In this study, a Zr(IV)-AcAc complex formation has been used, exactly following the preparation conditions described in [9]. Following the complex formation with acetic acid (AA), transparent zirconia sol-gel materials with an optical band gap of about 4.4 eV can be prepared reproducibly. The solid $[Eu(phen)_2](NO_3)_3$ complex in this study has been prepared exactly following the procedure given in our recent contribution [6].

Procedure A (functionalization of $ZrO_2$:Eu microparticles with 1,10-phenanthroline):

- Preparation of $ZrO_2$:$Eu^{3+}$ ($n_{Eu}/n_{Zr} \approx 0.01-0.05$) of a zirconia gel following exactly the acetic acid (AA) complex preparation route [9]. The doping was performed with a 0.5 mol $L^{-1}$ $Eu(NO_3)_3$ solution with pH $\approx 3$ during gelation.
- Drying at room temperature.
- Homogenization in a mortar to microparticles.
- Impregnation with a 1.1 mol $L^{-1}$ 1,10-phenanthroline solution in ethanol, 48 h at room temperature, $n_{Zr}/n_{PHEN} \approx 0.1$.
- Washing the samples with ethanol to fully remove the 1,10-phenanthroline solution (controlled with UV/Vis spectroscopy).

Procedure B (incorporation of colloidal $Eu(phen)_2(NO_3)_3$ into sol-gel zirconia):

- Synthesis of a $[Eu(phen)_2](NO_3)_3$ colloidal solution in ethanol (Eu concentration $\approx 0.02$ mol $L^{-1}$), starting from $Eu_2O_3$, $HNO_3$ and subsequent addition of 1,10-phenanthroline using stoichiometric quantities.
- Preparation of a zirconia sol following exactly the acetic acid (AA) complex preparation route [9].
- Doping with $[Eu(phen)_2](NO_3)_3$ colloidal solution in ethanol (Eu concentration $\approx 0.02$ mol $L^{-1}$) before gelation, which results in a doping level of 2.55 % Eu.
- Drying at room temperature.

### Sample characterization

All starting materials and solvents were commercial products from Sigma-Aldrich. The europium complex $[Eu(phen)_2](NO_3)_3$ was synthesized according to procedures described in ref. [6]. A SpectraPro 300i spectrophotometer was used for the quantum yield measurement of the red-emitting powdered samples at room temperature. As a standard, the Lumogen T Rot GG from BASF with a maximum wavelength of excitation at 350 nm and a maximum wavelength of emission at 615 nm was chosen. Luminescence/excitation spectra of all samples were also measured with a Varian Cary Eclipse fluorescence spectrophotometer with a vertical powder sample holder. Room temperature UV/Vis reflectance measurements and transmittance spectra of solutions and powdered species were measured on a Perkin Elmer Lambda 35 spectrophotometer with a specular reflectance labsphere RSA-PE-20 using a self-made vertical sample holder, described in detail in ref. [10]. The reflectance measurements were verified with a $Ho_2O_3$ standard. From the diffuse reflectance $R$ (%) the Kubelka-Munk function $F(R)$ was obtained.

The Eu content in all samples prepared was checked using a ICP Ultima2 Horiba-Jobin Yvon unit. All doped gels were investigated with X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer and a LynxEye position-sensitive detector (PSD).

## Results and Discussion

### Functionalization of ZrO:Eu microparticles with 1,10-phenanthroline – procedure A

Luminescence spectra of the prepared functionalized materials show very low emission at 613 nm at an excitation of 350 nm, due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III), in addition to a broad, blue luminescence (Fig. 1).

The luminescence spectrum of the functionalized sample consists of a strong and broad peak at 465 nm. Its position does not coincide with the luminescence of
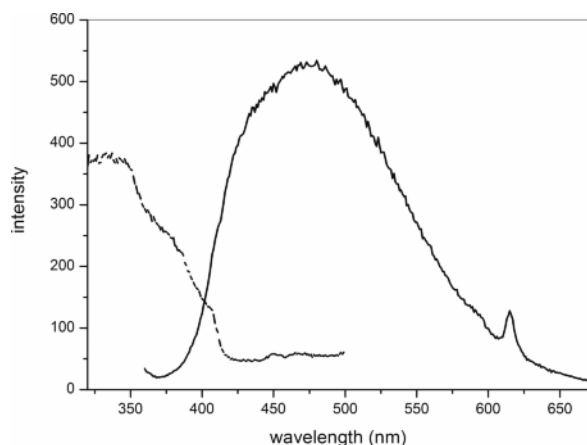
Fig. 1. Luminescence spectrum of $ZrO_2$:0.05$Eu^{3+}$, functionalized with 1,10-phenanthroline using preparation procedure A. Left: excitation spectrum monitoring the luminescence maxium. Right: emission spectrum at 350 nm excitation.
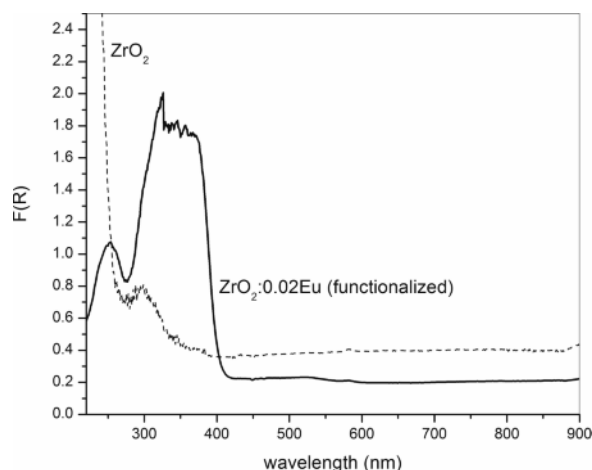


Fig. 2. Diffuse reflectance spectra of pure zirconia and functionalized $ZrO_2$:0.02Eu displayed using the Kubelka-Munk function $F(R)$.

pure 1,10-phenanthroline, which emits in the ultraviolet at 370 nm. The emission observed at 465 nm could be assign according to several hypotheses:

- Luminescence as a result of a ligand-to-metal charge-transfer transition (LMCT) from 1,10-phenanthroline to the $d^0$ level of $Zr^{4+}$ in the complex.
- Sensitization of the emission by lattice defects. Such a luminescence has a very low intensity and is observed in inorganic zirconia systems [8, 10].

It has been shown that $nd^0$ levels ($n = 3 – 5$) play an important role in the observation of emission in the visible region. There are results concerning the $d^0$ levels of the following ions: $Zr^{4+}$, $Nb^{5+}$, $Mo^{6+}$, $W^{6+}$, $Ti^{4+}$, $Ta^{5+}$ and, depending on the $d$-component, emissions are observed extending from 493 to 577 nm (for $Zr^{4+}$, 460 nm), in good agreement with our measurements. In all doped materials a strong Stokes shift is observed [9 – 12]. Zirconium complexes with 1,10-phenanthroline also have been described in ref. [13] using hydrothermal impregnation of $ZrO_2$ with 1,10-phenanthroline, a procedure which leads to a new complex of the type $[Zr(phen)_4(H_2O)_4O_2(V_4O_{12})](phen)_2$. It has been suggested, that the absorption between $250 – 400$ nm of the material can be explained with a ligand to metal charge transfer (LMCT) from the $2p$-AO of $O^{2-}$ to the $d^0$-AO of $Zr^{4+}$ [2].

In Fig. 2 diffuse reflectance spectra of the as-prepared materials are displayed using the Kubelka-Munk function $F(R)$. The spectrum of pure sol-gel zirconia, prepared using acetic acid (AA) protection is given for comparison. The spectrum of the pure zirconia is close to that published in refs. [11, 12].

Two peaks are evident in the spectrum of functionalized $ZrO_2$:0.02Eu, one at 250 nm and a strong peak at 350 nm. The excitation spectrum (Fig. 1) follows the optical absorption in functionalized $ZrO_2$:0.02Eu.

*Optical properties of $ZrO_2$:[Eu(phen)$_2$](NO$_3$)$_3$, prepared by the sol-gel method with colloidal [Eu(phen)$_2$](NO$_3$)$_3$ – procedure B*

In this section we are investigating the luminescence properties and the symmetry of the environment of the activator upon „*ex situ*" incorporation of [Eu(phen)$_2$](NO$_3$)$_3$ in a $ZrO_2$ sol-gel in order to avoid complex decomposition.

It is known that the complex [Eu(phen)$_2$](NO$_3$)$_3$ can be incorporated in $TiO_2$ composites. Room-temperature incorporation favors the complex formation, but heating to 60, 80, 100, and 120 °C causes a decrease of the intensity of the red emission [14]. The good luminescence properties of the complex [Eu(phen)$_2$](NO$_3$)$_3$ lead to an increased interest for incorporating this complex into solid matrices. Previous investigations were carried out in $SiO_2$/PEG400 matrices in PVA films (PVA), and mixed $SiO_2$-$M_xO_y$ matrices ($M$ = Zr, Ta) in Stöber nanospheres [15, 16]. The structure of the complex and a scheme of the
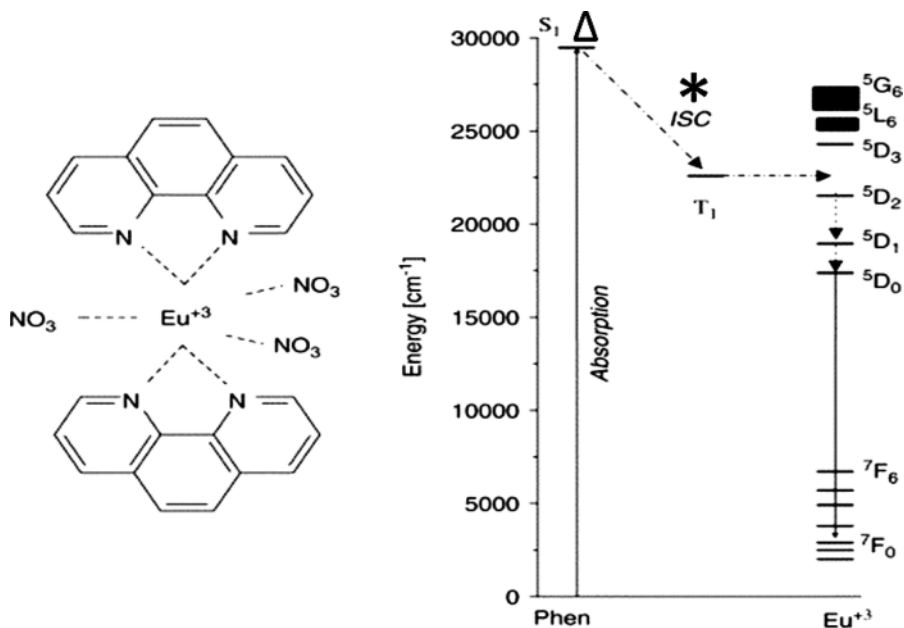
Fig. 3. Structure and energy diagram of the complex $[Eu(phen)_2](NO_3)_3$. The quantum yield of this complex is $30-40\%$ [9, 19–21]. Absorption ($\Delta$) and excitation (*) routes of $ZrO_2$:$[Eu(phen)_2](NO_3)_3$ are also shown.

energy transfer to $Eu^{3+}$ is shown in Fig. 3 according to [17, 18].

Fig. 4 shows the absorption spectrum of a diluted ethanol solution of $[Eu(phen)_2](NO_3)_3$. The peaks in the UV region are due to $\pi \rightarrow \pi^*$ transitions in 1,10-phenanthroline [19]. Two strong peaks are visible at 230 and 265 nm.

The diffuse reflectance spectrum (Fig. 5) of doped $ZrO_2$:$[Eu(phen)_2](NO_3)_3$ shows peaks at 215, 280, 302, and 480–515 nm. There is a change in the relative peak intensities compared to the spectrum of the complex in ethanol, due to incorporation in the sol-gel matrix.

A strong red luminescence, demonstrating the energy transfer from the ligand to the lanthanide ion is shown in Fig. 6. The weak peak at 393 nm in the excitation spectrum indicates the presence of an additional $Eu^{3+}$ optical center, where the rare earth element is directly excited. The excitation spectrum of $ZrO_2$:$[Eu(phen)_2](NO_3)_3$ shows the excitation channels in the complex between 280 and 350 nm [6, 9].

The results of the luminescence spectrum analysis using Gaussian deconvolution show that the activator ion has a non-centrosymmetric environment with most
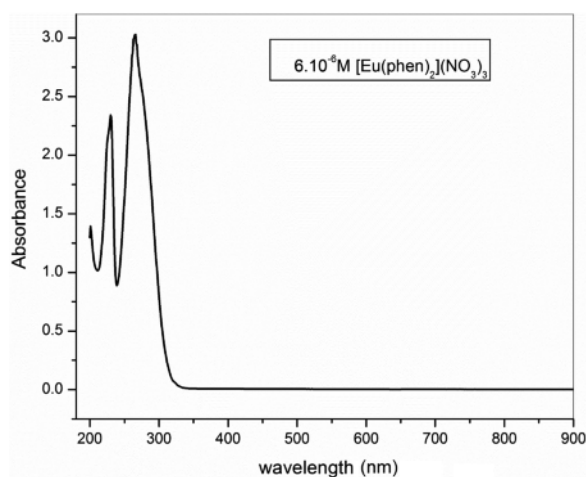


Fig. 4. Absorption spectra of $6 \times 10^{-6}$ M $[Eu(phen)_2](NO_3)_3$ in ethanol. A deuterium lamp together with a quartz cuvette (SUPRASIL) were used to obtain higher intensity in the UV region.

probably $C_{2v}$ symmetry [2, 9, 22]. A similar result was reported for the complex $[Eu(phen)_2]Cl_3$ embedded in a $SiO_2$ matrix, which is characterized by $C_{2v}$ symmetry; after heating it changed to $D_2$ [20, 21]. The spec-

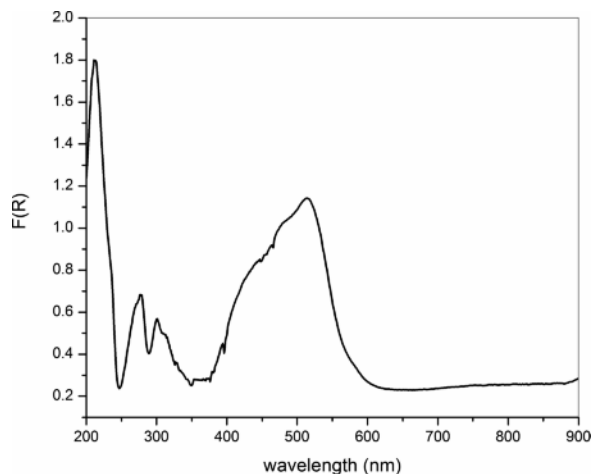Fig. 5. Reflection spectrum of $ZrO_2$:[Eu(phen)$_2$](NO$_3$)$_3$. The Eu content in the powder is 2.55 %.



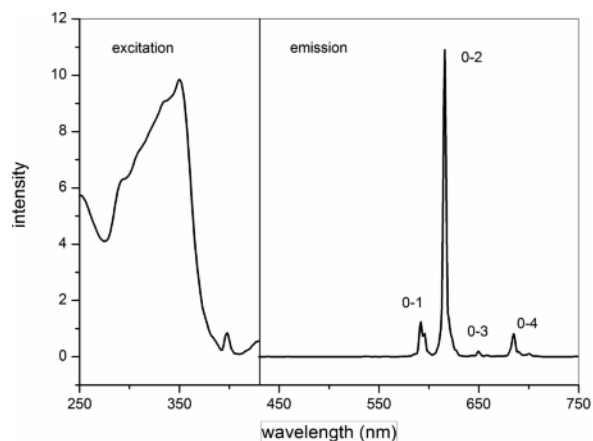Fig. 6. Luminescence spectrum of $ZrO_2$:[Eu(phen)$_2$](NO$_3$)$_3$ (right) at 355 nm excitation and the excitation spectrum monitoring the 615 nm transition (left). The maximum in the excitation spectrum is in good agreement with Fig. 3. The $^5D_0 \rightarrow {}^7F_J$ emission transitions are denoted as 0-1, 0-2, 0-3 and 0-4.



Fig. 7. SEM image of the $ZrO_2$:[Eu(phen)$_2$](NO$_3$)$_3$ composite, containing 2.55 % Eu. The weight analysis indicated about 31 % $ZrO_2$, which is typical of sol-gel zirconia materials prepared at room temperature.



Fig. 8. X-Ray diffraction patterns of zirconia hybrid composites, compared to those of pure [Eu(phen)$_2$](NO$_3$)$_3$ powders [9] and of crystalline 1,10-phenanthroline. Peaks originating from Zr(IV)-1,10-phenanthroline complex formation are shown with astrisks (*).

trum is dominated by the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition, which also proves a non-centrosymmetric environment of the $Eu^{3+}$ ion. The emission spectrum is close to that of other europium-containing hybrid sol-gel materials.

Quantum efficiency measurements of samples $ZrO_2$:[Eu(phen)$_2$](NO$_3$)$_3$ with 2.55 % Eu showed a quantum output of $48 \pm 2$ % at 350 nm excitation, in good agreement with the excitation spectrum (Fig. 6). The quantum yield of the pure solid complex measured
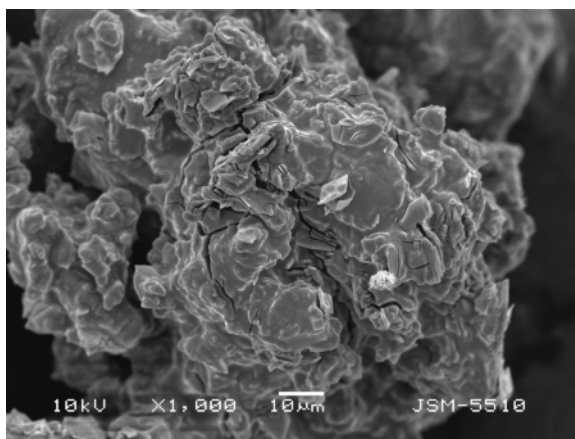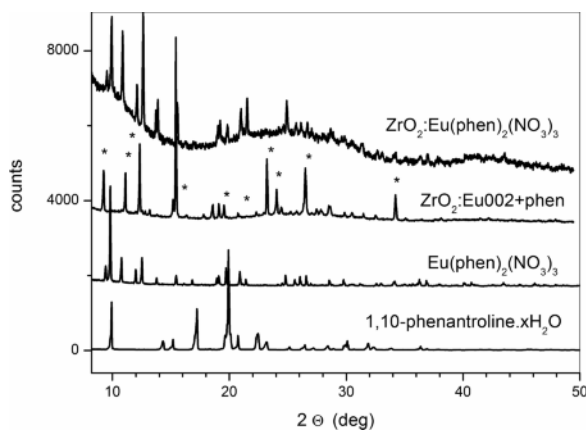
under the same experimental excitation and peak monitoring conditions is about $35 \pm 2$ %. The quantum efficiency measurements demonstrated an increase of the quantum output of the hybrid materials as a result of complex incorporation into the matrix. The quantum yield of the as-prepared materials is close to that of $SiO_2$:[Eu(phen)$_2$](NO$_3$)$_3$, which is about 40 % [6]. In the case of silica an increase of the quantum yield as a result of incorporation of [Eu(phen)$_2$](NO$_3$)$_3$ into the sol-gel matrix has been described.

The morphology of the synthesized composites, investigated with a scanning electron microscope (SEM), is depicted in Fig. 7. The samples have a porous structure with high surface area. The images are typical for sol-gel micropowders.

*Qualitative XRD analysis*

A qualitative XRD analysis has been performed to check the phase composition of the prepared hybrid sol-gel composites. The results are shown in Fig. 8. The diffraction patterns from pure $[Eu(phen)_2](NO_3)_3$ powders [9] and of crystalline 1,10-phenanthroline are given for comparison. It is evident that the as-prepared composites do not contain solid 1,10-phenanthroline contaminations after washing, and zirconia and europium nitrate phases were not detected. The diffraction patterns of the as-prepared zirconia sol-gel materials are close to that given in [9]. The $[Eu(phen)_2](NO_3)_3$ diffraction peaks [9] are visible in the diffraction patterns of $ZrO_2$:$[Eu(phen)_2](NO_3)_3$.

An interesting situation is realized in the product of preparation route A. It is evident that a new oxo/hydroxo-rich species or phase containing Zr(IV) and 1,10-phenanthroline is formed during sol-gel preparation, which results in the appearance of additional diffraction peaks (Fig. 8). Refs. [12, 15, 23] report a related species containing additional carboxylato anions. Quantitative phase analysis and structure determination of hybrid materials like Zr(IV)-1,10-phenanthroline require special diffraction techniques. Further investigations are necessary to clarify exactly the structure of the Zr(IV)-1,10-phenanthroline complex formed as a product of preparation route A.

## Conclusions

The optical properties of hybrid zirconia sol-gel composites functionalized with $[Eu(phen)_2](NO_3)_3$ strongly depend on the mode of incorporation of the europium complex. Blue- or red-emitting sol-gel composites can be obtained because of the formation of Zr(IV) or Eu(III) complexes with 1,10-phenanthroline depending of the doping route. A new promising sol-gel technique for doping of zirconia with colloidal $[Eu(phen)_2](NO_3)_3$ giving products with a quantum yield $48 \pm 2\%$ is demonstrated.

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