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SURFACE FUNCTIONALIZATION OF SILICA SOL-GEL MICROPARTICLES WITH EUROPIUM COMPLEXES

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Abstract. The present contribution is focused on the relation preparation – structure – optical properties of hybrid silica powders containing Eu(III) complexes: SiO_2:[Eu(ntac)$_3$][pphendcn] and SiO_2:[Eu(phen)$_2$](NO_3)$_3$. New methods for surface functionalization of silica microparticles, based on adsorption of 1,10-phenantroline and [Eu(ntac)$_3$][pphendcn], are proposed in the framework of preparation of red emitting hybrid composites with quantum efficiency 20 – 50 %. The optical properties of rare earth ions incorporated in silica composites are used to explore the site symmetry (D_2, C_{2v} or lower) of the Eu^{3+} optical centers in the hybrid composites. Quantum yields of the investigated sol-gel micropowders and quantification of their optical spectra are presented. X-Ray diffraction patterns of the investigated hybrid composites are presented. A short overview of sol-gel technology as a method for preparation of functional nanomaterials is presented.

Keywords: silica, europium complexes, luminescence, sol-gel

Introduction

Sol-gel materials functionalized with rare earth ions and their complexes display important optical properties like luminescence, coloration and energy transfer and give opportunity for wide technical applications. This paper deals with colloidal preparation strategies of silica gels doped with europium complexes. Such materials have potential application as red emitting materials for photo conversion of light, ultraviolet sensors and in labeling of materials (Brinker & Scherrer, 1990). From materials science point of view sol-gel materials functionalized with rare earth ions are hybrid materials as they contain an organic ligand or complex in an inorganic matrix. The oxide matrix is usually prepared using sol-gel chemistry. To transform an inorganic silica or zirconia matrix into a system with desired optical properties it is necessary to incorporate into the matrix an optical active component using a physico - chemical doping procedure. Here, the optical active components are strong red emitting europium (III) complexes (Bünzli, 2014). As a model of europium complexes in this paper following species are used: (a) $[Eu(ntac)_3][pphendcn]$, containing 4,4,4-trifluoro-1-(naphthalene-2-yl) butan-1,3-dione (Hntac) and pyrazino[2,3-f][1,10-phenathroline-2,3-dicarbonitrile (pphendcn). It is a relatively new luminescent complex, detailed described by Bünzli (2014), Petkova et al. (2011a), Petkova et al. (2011b), Danchova & Gutzov (2014), Danchova et al., 2014 and Danchova & Gutzov (2014). The quantum efficiency of the solid complex is 10-15%; (b) $[Eu(phen)_2](NO_3)_3$, europium (III) diphenathroline nitrate. It is a well known luminescent complex, detailed described by Mirochnik et al (2002). The quantum efficiency of the solid complex is 35-40%.

The basic principles of sol-gel chemistry as a tool for preparation of functional nanomaterials are given bellow. Sol-gel technology is a powerful method for preparation of oxide nanomaterials at low temperatures (bellow 150 ^{o}C). Most important advantages of sol-gel technology are the use of liquid chemicals, the possibility for preparation of complicated chemical compositions and the use of low temperature of preparation. Sol-gel chemistry, however, displays some disadvantages like individual preparation schemes for solving each problem, long duration times of gelation and lot of physico - chemical measurements necessary for a reproducible preparation. Sol-gel chemistry offers a possibility for the ambient preparation of optical materials like xerogels or layers doped with rare earth ions. In the same way a wide range of useful ceramic materials like Al_2O_3, ZrO_2 , SnO_2, SiO_2, Al_2O_3 can be easily prepared.

Gels are solids confining a solvent in a three-dimensional network. The solvent may be enclosed as quasi-liquid in a pore system. At this state, the gels are called hydrogels (water as solvent) or alcogels (alcohol as solvent), etc. If the network has nanodimensions or is index-matched, the gel looks transparent. If the solvent is removed without destruction of the porous network, the resulting body is called a aerogel. The density of aerogels is in the range of 0.05 g/cm^3. Drying with destruction of the porous network leads to typical xerogel monoliths with a density in the range of 0.5 – 1 g/cm (Petkova et al., 2011a; Büzli, 2014; Gutzov & Bredol, 2006).

It is known, that sol gel-chemisrty is based on three simple chemical reactions: water hydrolysis of liquid alkoxides followed by condensation. Condensation (better known as gelation), could be performed as a water condensation or alcohol condensation. The results of sol-gel process strongly depend on the reaction conditions: it is possible to obtain micro- or nanopowders, transparent xerogels, transparent thin films or even aerogels by changing reaction conditions.

The europium (III) ion is responsible for the red component of the tricolor luminescent lamps due to a strong emission peak at 615 nm. The optical properties of europium ion are well known, they are explained by the weak crystal field approximation. In addition, the europium ion optical spectra give information about the site symmetry of the europium ion, the so called “spectra structure correlation” (Blasse & Grabmaier, 1994).

The optical transitions of lanthanide ions are weak to produce light and therefore their intensity must be increased. Sensitizer ions or molecules absorb ultraviolet energy and transfer this energy to the europium ion. The europium ion itself goes to an excited state and emits in the red spectral region. In this way the quantum yield can be increased more than ten times. As organic sensitizing ligands many organic molecules like phenathroline or acethylacetone and their derivates are used. Cerium ion is a typical example for inorganic ions with sensitizing properties. More about the energy transfer is given in the monographs (Binker & Scherer, 1990; Büzli, 2014). In the case of an efficient energy transfer the weak sharp Eu(III) peaks in the excitation spectra are replaced by strong, broad features dominated from sensitizers.

In Fig. 1. a typical sol-gel preparation equipment in the laboratory of Functional Optical Materials (FOM) in the Department of Physical Chemistry is shown. The used chemicals are liquids – metal alcoxides, alcohol and water, as well as doping solutions, lanthanide solutions and other solutions. The laboratory is specialized in doping of zirconia and silica gels with lanthanide ions and their complexes. Some details the sol-gel process are: the preparation of oxides consists two steps, hydrolysis of alcoxides and gelataion of the prepared colloidal nanoparticles. The hydrolysis is acid catalized, the condensation / gelation/ step - basic catalized. Drying conditions are very important to obtain gels with desired properties. Reproducibility is one of the most important problems in sol-gel chemistry due to the complicated physic-chemical nature of the processes in sol-gel technology. Parameters which must be controlled during the sol-gel process are pH, temperature and chemical composition to obtain materials with a given chemistry, transparency, phase composition and microstructure.

Fig. 1. Preparation of sol-gel materials: pH control, temperature control and liquid chemicals used for preparation of functionalized gels

In Fig. 2 some results connected with functionalized inorganic silica gels are presented. Silica gels doped with samarium ions are materials with potential application as ultraviolet filters. Left – low doped with samarium ions silica gels are displayed, they are transparent. Increasing the degree of doping leads to a weak yellow color and makes the gels translucent, because nano- crystals of samarium nitrate are formed during the sol-gel process. Under special conditions and using basic condensation conditions, microspheres instead of transparent gels, could be obtained.

The photos of Dr. Gulay Ahmed (Fig. 2) are made through doped gels with a thickness of about 2 mm with a different samarium concentration. In summary, transparency of inorganic sol-gel materials depends on doping concentration and/or porous system properties. Also Fig. 2 shows interesting applications of sol-gel chemistry, preparation of uniform silica microspheres, known as "Stöber's silica". Under special conditions and using basic condensation conditions, uniform microspheres instead of transparent gels could be obtained (Brinker & Scherrer, 1990).

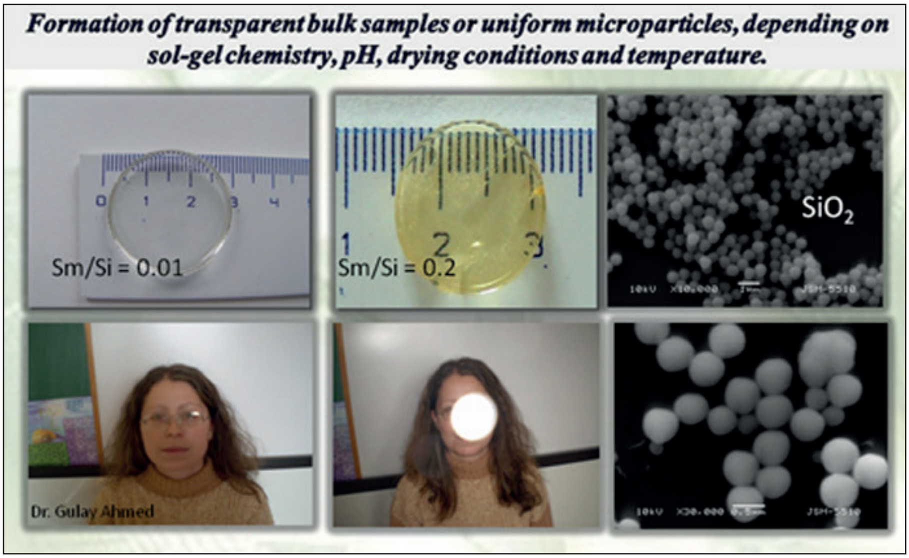

Fig. 2. Inorganic doped silica gels with controlled shape and optical properties. By varying of physico-chemical preparation conditions materials for optical filters (left) or silica microspheres with application as coating materials (right) can be prepared

Zirconia sol-gel chemistry is much more complicated compared to silica chemistry, because of the high reactivity of zirconium alcoxides. In the case of zirconia sol-gel chemistry the rates of hydrolysis and condensation are high and a fast formation of micropowders, as in the case of chemical precipitation takes place. This is why zirconium alcoxides must be protected with organic ligands as acethylacetone or acetic acid, which form chelate complexes with zirconium.

In Fig. 3 three sol-gel approaches for preparation of zirconia sol-gel materials depending on protection conditions of the sol are shown. In the left scheme nanopowders, fast produced without protection are displayed. In the middle scheme a protection with acethylaceton as complex forming ligand is given. The result is a transparent gel with increased ultraviolet absorption. Right an example for production of zirconia gels with protection of acetic acid, the most successful way to produce hybrid materials. The photo of Dr. Nina Danchova (Fig. 3) is made through a zirconia gel to demonstrate the optical transparency of the produced zirconia materials. The high transparency in the case of zirconia is combined with a high refractive index, zirconia is well known as “artificial diamond”. The strong gel coloration in Fig. 3 comes from Zr(IV) – acetyl acetone complexes with a high UV – absorption, ε = 2400 l / mol·cm at 285 nm (Petkova et al., 2011a; Georgieva et al., 2011).

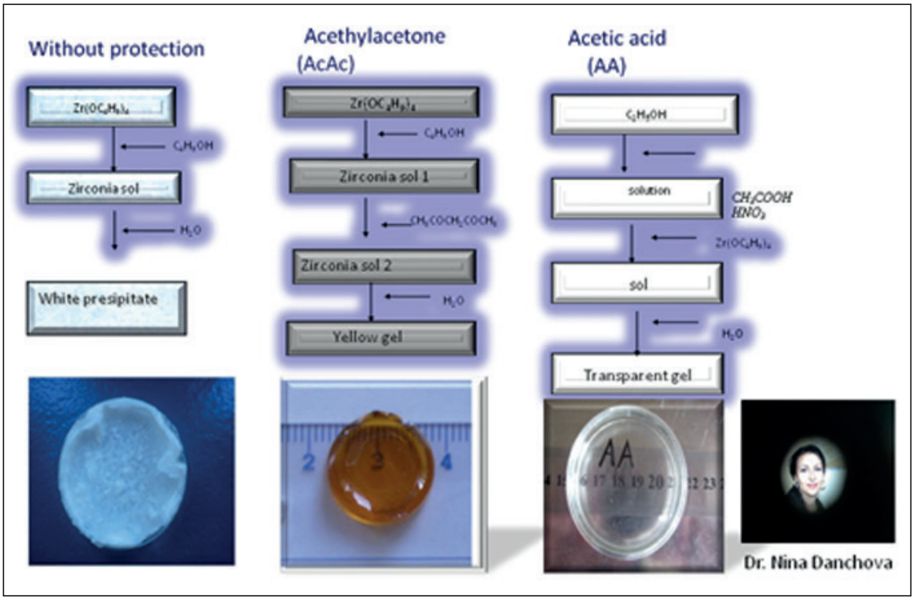

Fig. 3. Three sol-gel approaches for preparation of zirconia sol-gel materials depending on protection conditions of the sol. The acetic acid protection leads to highly transparent materials with an increased refractive index. Zirconia materials are also known as “artificial diamond” because of their high refractive index

Experimental

The europium complexes $[Eu(phen)_2](NO_3)_3$ and $[Eu(ntac)_3][pphendcn]$ were synthesized according procedures by Petkova et al. (2011b). Elemental analysis was performed on a Vario III instrument. A SpectraPro 300i spectrophotometer was used for measurement of diffuse reflectance, excitation / luminescence spectra and quantum yield of powdered samples. As standard, the Lumogen T Rot GG from BASF with maximum wavelength of excitation at 350 nm and maximum wavelength of emission at 615 nm was chosen. The Quantum Yield (QY) of the investigated samples was determined using the comparison method. Emission spectra were integrated between 430 and 750 nm and excitation spectra between 235 and 430 nm. The luminescence and reflectance measurements were used to estimate QY of investigated samples (defined as the ratio of the number of photons emitted to the number of photons absorbed). In this study, the presented luminescence spectra are mathematically threated as overlapping Gaussion curves to obtain relative intensities, peak number, peak maxima and half widths of each luminescence peak. The Eu – content in all samples prepared was checked using a ICP Ultima2 Horiba-Jobin Yvon unit.

To prepare silica microparticles with an intense red emission two physico-chemical functionalization techniques are used:

Surface functionalization of silica micro particles with [Eu(ntac)$_3$][pphendcn] (physical functionalization)

The preparation of hybrid silica micro composites includes the following basic steps: (1) Preparation of SiO_2 matrix, using a classical base catalyzed sol-gel process (Danchova & Gutzov, 2013); (2) Homogenization of the solid matrix in mortar to obtain silica micro particles in size 100-300 μm; (3) Impregnation of silica micro particles with solution of 0.0107 M [Eu(ntac)$_3$][pphendcn] in ethanol (48 h at room temperature).

Preparation of functionalized micro particles starting from SiO_2:Eu (chemical functionalization

The preparation includes the following basic steps: (1) Synthesis of doped SiO_2:Eu^{3+} sol-gel bulk materials with molar ratio n_{Eu}/n_{Si}=0.05 using the procedure by Danchova & Gutzov (2013); (2) Homogenization of silica gel in mortar to obtain SiO_2:Eu^{3+} silica micro particles; (3) Impregnation of doped SiO_2 micro particles with ethanol solution of 1.1M 1,10-phenanthroline (48 h at room temperature with molar ratio $n_{Eu}/n_{phen} = 9.4 \cdot 10^{-3}$, $n_{Si}/n_{phen}= 0.18$; (4) Washing the micropowders with absolute ethanol to remove the excess amount of ligand.

Experimental results and discussion

In **Fig. 4** a typical luminescence spectrum of SiO_2:[Eu(phen)$_2$](NO$_3$)$_3$ powders produced from SiO_2:0.05Eu^{3+} functionalized using adsorption of 1,10-phenanthroline (chemical functionalization) is presented. The relative intensity of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$

transition is high, about 80-82% from the overall Eu^{3+} luminescence intensity between 570 nm and 750 nm. It follows from second derivative luminescence spectra, that the most probable symmetry of Eu^{3+} is D_2 (Görller-Walrand & Binnemans, 1998). Surface formation of $[Eu(phen)_2](NO_3)_3$ as a result of the functionalization of SiO_2:Eu with 1,10–phenanthroline has been confirmed by X-Ray diffraction by comparing data of pure solid complexes and functionalized silica samples. X-Ray diagrams of the investigated samples are presented in **Fig. 5**, here a pure solid complex $[Eu(phen)_2](NO_3)_3$ and solid 1, 10 – phenanthroline are used as a reference. In the case of solid $[Eu(phen)_2](NO_3)_3$ and functionalized $SiO_2:[Eu(phen)_2](NO_3)_3$ we have a very weak $^5D_0 \rightarrow {}^7F_0$ transition at 585 nm, visible in second – derivative spectra, which refers that the most probable site symmetry of Eu^{3+} here is D_2 and / or C_{2v} (Danchova et al., 2014). The presence of two kind of optical centers in the described hybrid materials is also possible. The exact site symmetry evaluation here needs additional investigations.

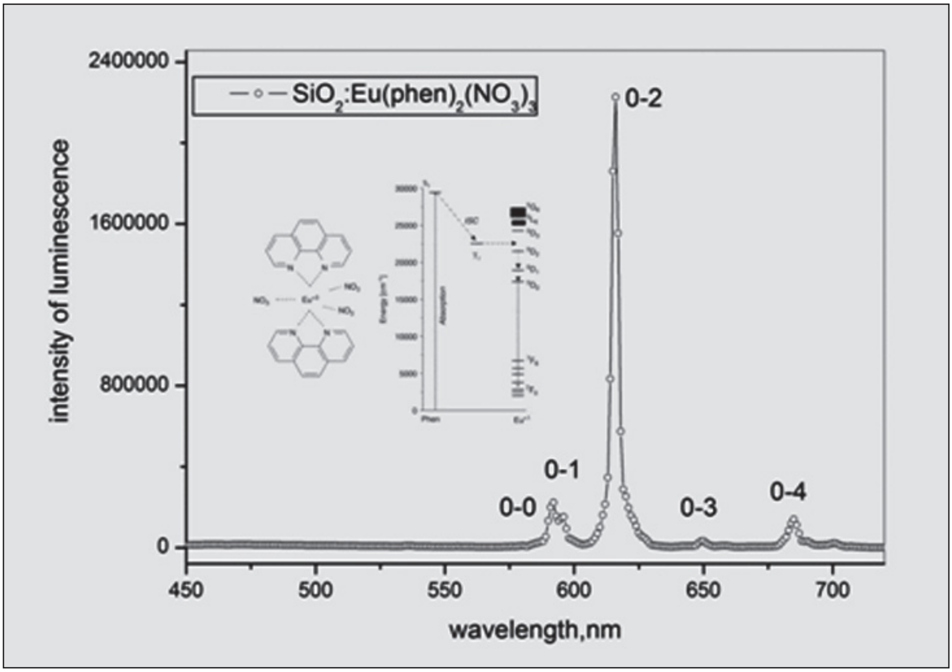

Fig. 4. A typical luminescence spectrum of $SiO_2:[Eu(phen)_2](NO_3)_3$ powders at 352 nm excitation. The Eu^{3+} $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions are denoted as 0-1,2,3,4. The optical properties of the complex are shown (Görller-Walrand & Binnemans, 1998)

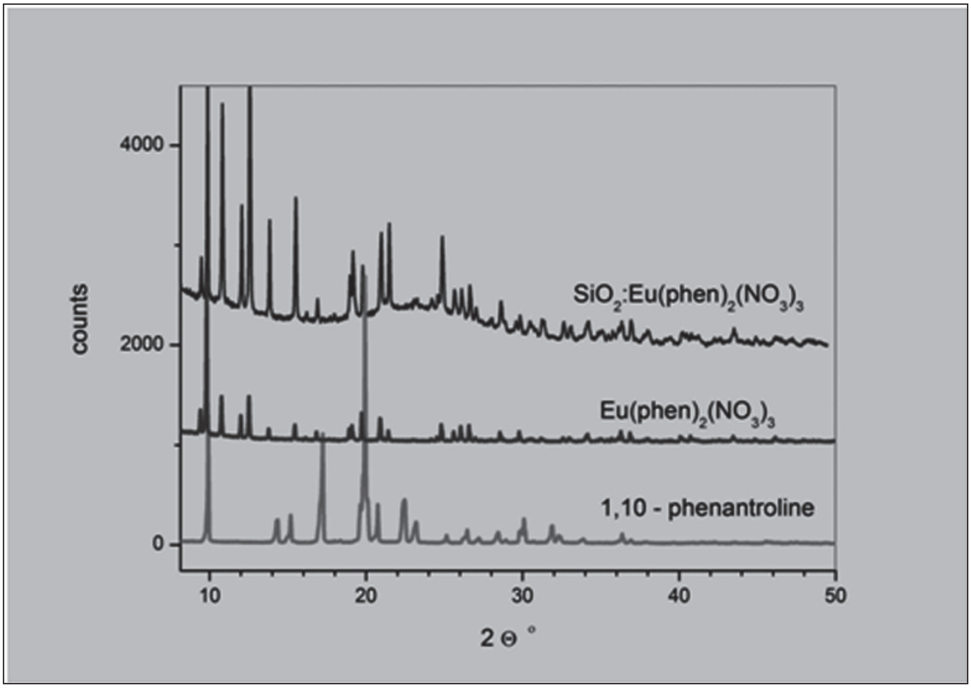

Fig. 5. X-Ray diagrams of the investigated functionalized powders. The diagrams of a pure solid complex $[Eu(phen)_2](NO_3)_3$ and solid 1, 10 – phenanthroline are used as a reference

In **Fig. 6** luminescence spectra of solid $[Eu(ntac)_3]$[pphendcn] and functionalized SiO_2:$[Eu(ntac)_3]$[pphendcn] are presented. The relative intensity of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition is about 83-85%. Differences in the luminescence spectra of solid complex and functionalized sol-gel samples have been detected. The luminescence spectrum of $[Eu(ntac)_3]$[pphendcn] has a relative strong $^5D_0 \rightarrow {}^7F_0$ transition and a site symmetry of Eu^{3+} C_{2v} or lower (Görller-Walrand & Binnemans, 1998). Spectral differences indicate a change of chemical environment and / or site symmetry of Eu^{3+} as a result of the adsorption of $[Eu(ntac)_3]$[pphendcn] on the silica surface. In the terms Eu^{3+} site symmetry/spectra correlation, the most probable site symmetry in SiO_2: $[Eu(ntac)_3]$[pphendcn] is D_2 (Bünzli, 2014). The luminescence spectral maximum changes from 612 nm to 618 nm as a result of functionalization most probable due to lowering of crystal field strength on the silica surface.

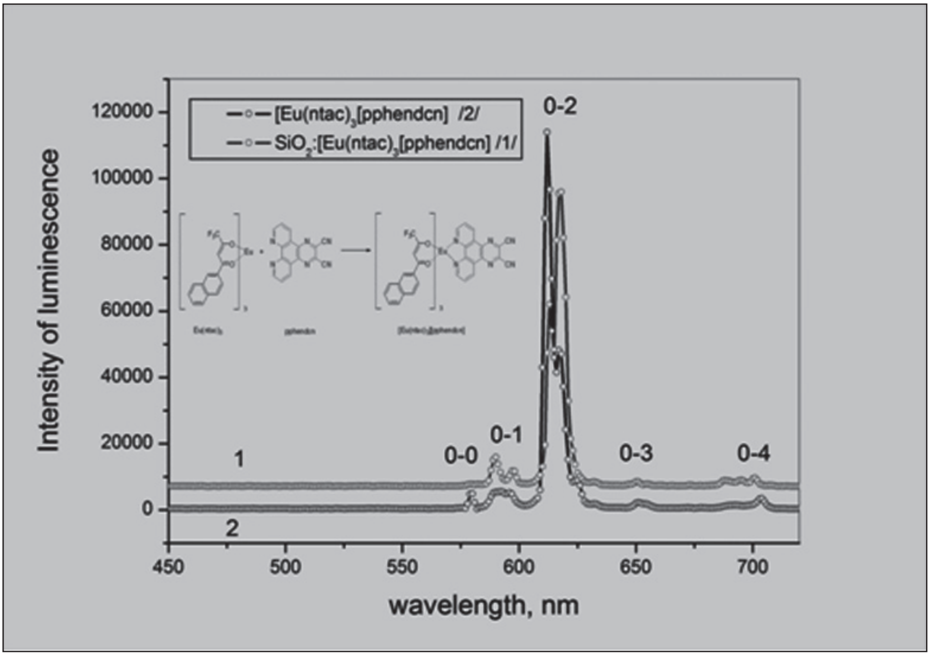

Fig. 6. Luminescence spectra of [Eu(ntac)$_3$][pphendcn] and functionalized SiO$_2$:[Eu(ntac)$_3$][pphendcn] at 400 nm excitation. The Eu^{3+} $^5D_0 \rightarrow {}^7Fj$ transitions are denoted as 0-1, 0-2, 0-3 and 0-4

The luminescence emission of the prepared samples SiO$_2$:[Eu(phen)$_2$](NO$_3$)$_3$ and SiO$_2$:[Eu(ntac)$_3$][pphendcn] are very stable for long period of times (more than 1 year). We do not observed additional blue lines coming from surface complex destruction.

Table 1 presents the quantum yields of the investigated samples together with the doping level of the europium activator. In addition, the most probable site symmetry of the europium ion, exctracted from the luminescence spectra, is given. The high quantum yields confirm unambiguously that a ligand→europium charge transfer take place in all of the samples. The relative error of QY using the described procedure is about 0.1, quantum yields of pure complexes are given for comparison. The relative high quantum yields in table 1. allow the potential application of the described hybrid powders as potential UV – sensors and label materials for chemical and biological applications. The quantum yield of europium complexes increases after incorporation in the sol-gel matrix due to a lack of concentration quenching.

Table 1. Excitation wavelengths, quantum yields (QY) and europium content of the investigated powdered samples at 615 nm emission wavelength. The most probable site symmetry of Eu^{3+} is given

Sample / Chemistry	Excitation [nm]	QY [%]	Eu [%]	Site symmetry of Eu^{3+}
SiO_2:[Eu(ntac)$_3$][pphendcn]	400	**17.4**	**0.1**	**D_2**
SiO_2: [Eu(phen)$_2$](NO$_3$)$_3$	352	**39.6**	**5.4**	**D_2 and / or C_{2v}**
[Eu(ntac)$_3$][pphendcn]	396	**10.8**	**11.4**	**C_{2v} or lower**
[Eu(phen)$_2$](NO$_3$)$_3$	352	**35.4**	**12.7**	**D_2 and / or C_{2v}**

It is well known, that using a quantification of Eu^{3+} luminescence spectra the site symmetry of the activator ion on molecular level can be obtained in different host matrixes, the so called "spectra-structure correlation". In this way the site symmetry of europium doped crystals and amorphous materials can be investigated.

From physical point of view the optical transitions of the Eu^{3+} ion are magnetic dipole transitions or electric dipole transition described by the low crystal field approximation and quantified by the Judd – Ofelt theory. The Judd – Ofelt theory allows to calculate the oscillator strengths of the f-f transitions of lanthanide ions. The intensities of electronic transitions of europium ions incorporated in sol-gel matrices are characterized by their experimental oscillator strength (Görller-Walrand & Binnemans, 1998; Schmidt, 2000; Brinker & Scherer, 1990):

$$f = \frac{4.32 \cdot 10^{-9}}{C \cdot d} \int A(\tilde{\nu}) d\tilde{\nu} \tag{1}$$

where $A(\tilde{\nu})$ is the absorbance, C is the Eu^{3+} concentration in $mol \cdot dm^{-3}$, d is the optical pathlength in cm and $\tilde{\nu}$ is he wavenumber in cm^{-1}. The Judd-Ofelt theory allows for the calculation of oscillator strengths according to:

$$f = 4 \cdot \pi \cdot \varepsilon_0 \frac{8 \cdot \pi^2 \cdot m_e \cdot \nu_0}{3 \cdot h \cdot (2J+1) e^2} [\chi_{ed} \cdot S_{ed} + \chi_{md} \cdot S_{md}] \tag{2}$$

Here, χ_{ed} and χ_{md} are weighting the electric-dipole and magnetic-dipole contributions, respectively. According to the Judd and Ofelt theory the transition moment for electric dipole f→f transitions can be expresses by

$$S_{ed} = \frac{e^2}{4 \cdot \pi \cdot \varepsilon_0} \sum_{k=2,4,6} \Omega_k \left| \left\langle f^N \psi J \middle| U^{(k)} \middle| f^N \psi^/ J^/ \right\rangle \right|^2 \quad (3)$$

and that of the magnetic dipole f-f transition is given by:

$$S_{md} = \frac{1}{4 \cdot \pi \cdot \varepsilon_0} \frac{e^2}{4 \cdot m^2 \cdot c^2} \sum_{k=2,4,6} \Omega_k \left| \left\langle f^N \psi J \middle| L + 2S \middle| f^N \psi^/ J^/ \right\rangle \right|^2 \quad (4)$$

Here, Ω_k are the so-called Judd-Ofelt intensity parameters and $\left| \left\langle f^N \psi J \middle| U^{(k)} \middle| f^N \psi^/ J^/ \right\rangle \right|$ and $\left| \left\langle f^N \psi J \middle| L + 2S \middle| f^N \psi^/ J^/ \right\rangle \right|$ the reduced matrix elements connecting initial and final states J and J', respectively. They are commonly assumed to be independent of the host material and have been calculated by Blasse & Grabmaier (1994) and Görller-Walrand & Binnemans, (1998). Conventionally, the Ω_k (k = 2, 4, 6) are determined from experimental spectra taken at room temperature. Hence, a possible temperature dependence of spectral intensity is not accounted for by the standard Ω_k values.

The quantum yield of europium doped gels QY_{sam} in this paper is calculated from integrated absorption and luminescence intensity using the comparison method as follows (Schmidt, 2000):

$$QY_{sam} = QY_{ref} \cdot \frac{I_{sam} \cdot A_{ref}}{I_{ref} \cdot A_{sam}} \cdot 100 \quad (5)$$

Here, QY_{ref} is the quantum yield of the reference sample; I_{sam} and I_{ref} are the integrated luminescence peaks of the investigated sample and the reference and A_{ref} and A_{sam} are the integrated absorption peaks of the reference and of the investigated sample.

If the Eu^{3+} ion occupies sites with an inversion symmetry, the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ at 590 nm is relatively strong. If the Eu^{3+} occupies sites without an inversion symmetry, the electric dipole transition $^5D_0 \rightarrow {}^7F_2$ at 615 nm is very strong. In addition, the peak number in the region of each Stark multiplet increases when a europium ion occupies sites with a low symmetry. There are quantitative approaches to obtain the site symmetry group from peak numbers in the region of each Stark multiplet, which has been used to determine the most probable site symmetry of Eu^{3+} ion, presented in Table 1.

Conclusions

In this paper surface functionalization of sol-gel SiO_2 microparticles with [Eu(ntac)$_3$][pphendcn] and [Eu(phen)$_2$](NO$_3$)$_3$ complexes is described.

Two colloidal methods of surface functionalization, chemical and physical functionalization for preparation of hybrid optical materials are discussed. All the functionalized samples show a pure, stable in time Eu – luminescence with quantum yield 10 – 40% due to energy transfer from organic ligands. Surface functionalization is accompanied with a site-symmetry change of Eu^{3+} ions followed using luminescence spectroscopy.

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