

Spectroscopic study of the $\text{Eu}(\text{fod})_3$ complex adsorbed on a 3-trimethoxypropylthioethylamine modified silica surface

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Abstract: By using 3-mercaptopropyltrimethoxysilane and ethylenediamine as precursors, the compound 3-trimethoxypropylthioethylamine was synthesized, and then used as a silylating agent to obtain, through a sol-gel process, an organic modification of a silica-gel sample. A surface thus modified was used as a substrate for the adsorption of the luminescent $\text{Eu}(\text{fod})_3 \cdot 2\text{H}_2\text{O}$ complex. $\text{Eu}(\text{fod})_3 \cdot 2\text{H}_2\text{O}$ and the silicon hybrid were mixed in stoichiometric amounts to produce samples with 1 %, 5 % and 10 % (m/m) of adsorbed complex. The adsorbed complex was then studied from the spectroscopic point of view. The lifetimes measured for the emission process are 476, 542 and 566 μs for 1 %, 5 % and 10 % samples, respectively. Furthermore, comparison with experimental data for *n*-[3(trimethoxysilyl) propyl]-ethylenediamine modified silica gel surfaces emphasizes the prominent role of the chemical composition of the silica modified surface on the spectroscopic properties of the adsorbed complex.

Keywords: europium(III) complex, sol-gel, luminescence, hybrids.

INTRODUCTION

Lanthanide complexes have been studied a lot as light conversion molecular devices (LCMDs).¹ In the last years, such complexes have been employed as doping agents for silicon inorganic-organic hybrids,² which are able to coordinate transition metal cations.

It has been verified that sol-gel synthesized matrices can be employed for many purposes, such as for the production of silica glasses with trapped Eu(III) fluorescent compounds.³ As “extra” advantages, silicon hybrids are, from a practical point of view, insoluble in water and many polar and non-polar solvents, exhibit chemical stability towards pH variations, and are of high thermal stability.⁴

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The luminescent $\text{Eu}(\text{fod})_3 \cdot 2\text{H}_2\text{O}$ complex (fod is the anion of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione), has been used as a model system,^{5,6} to study the possible effects of different inorganic-organic hybrid surfaces on the spectroscopic properties of luminescent europium complexes, when submitted to increased external pressure. The spectroscopic properties of luminescent europium complexes on an acrylic resin and silicon alkoxide films have also been investigated.^{7,8}

The aim of this publication is to report a spectroscopic study of the $\text{Eu}(\text{fod})_3 \cdot 2\text{H}_2\text{O}$ complex adsorbed on a 3-trimethoxypropylthioethylamine modified silica surface.

EXPERIMENTAL

Silica gel (Aldrich), (particle size 70–230 mesh) mean diameter 6 nm and $0.75 \text{ m}^3 \text{ g}^{-1}$ pore volume was employed. The silica sample (10.0 g) was stirred with $\text{H}_2\text{SO}_4\text{-HNO}_3$ (2.0 mol dm^{-3}) in a 9:1 ratio. The suspension was left standing for 24 h. The solid was filtered and extensively washed with doubly distilled water until the filtrate had the same pH as water. After this treatment, the silica was activated by heating at 423 K for 10 h under vacuum in a nitrogen atmosphere.

The silylating agent 3-mercaptopropyltrimethoxysilane from Aldrich was used as supplied.

Ethylenimine (etn) was synthesized following a described procedure, by reacting 2-amino-hydrogen sulfate (Aldrich) in hot alkali medium.⁹

The silylating agent, 3-trimethoxypropylthioethylamine (mptt), was synthesized as follows: 3-Mercaptopropyltrimethoxysilane (5.5 cm^3 , 29 mmol) was reacted with etn (6.0 cm^3 , 116.0 mmol) under reflux at 323 K, with magnetic stirring, under an inert dry nitrogen atmosphere for 24 h. The excess etn was removed from the cooled solution under vacuum.

A silica gel surface modified with 3-trimethoxypropylthioethylamine was prepared as follows: The synthesized mptt was allowed to react with 5.0 g of previously activated silica, in dry xylene at 343 K under mechanical stirring for 72 h. Then, the solid was filtered, washed with xylene and acetone until the filtered solution gave no positive test for thiol groups.¹⁰ The sequence of reactions involved in the synthesis of the modified silica are summarized in Fig. 1.

The surface area of the activated and modified silica samples were measured by the BET method in a Flowsord II 2300 Micromeritics apparatus. The carbon, nitrogen, sulfur and hydrogen contents were determined using a Perkin-Elmer microelemental analyser, model PE 2400.

The $\text{Eu}(\text{fod})_3 \cdot 2\text{H}_2\text{O}$ complex (fod is the anion of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione) was of analytical grade (Aldrich) and was used after recrystallization from ethanol.

The europium doped inorganic-organic hybrid samples were prepared as follows: The $\text{Eu}(\text{fod})_3 \cdot 2\text{H}_2\text{O}$ was dissolved in dry ethanol and to the obtained solution was added the insoluble hybrid. The resulting suspension was stirred for 30 min after which solvent was evaporated. The resulting powder was dried at 60°C under vacuum in a stove for 12 h. $\text{Eu}(\text{fod})_3$ and silica-gel hybride were mixed in stoichiometric amounts to produce samples with 1 %, 5 % and 10 % (m/m) of adsorbed complex.

The X-ray diffraction patterns were recorded on Shimadzu diffractometer, Model XD3A, with nickel-filtered $\text{CuK}\alpha$ radiation (35 kV, 25 mA).

The emission spectra were analysed using a Jobin Yvon model double monochromator, model U-1000 and the fluorescence signal, detected using a water-cooled RCA C31034-02 photomultiplier, was processed by a Jobin Spectralink system. The excitation wavelength was 340 nm. To ensure the reliability of the comparison of the intensities of the main bands of the spectra, the geometry of the counting system was maintained constant, *i.e.*, with the same sample container, the same excitation wavelength and the same slit width (0.05 mm).

The lifetime measurements were performed at 298 K exciting the sample with the third harmonic of a Nd-YAG laser ($\lambda_{\text{exc}} = 355 \text{ nm}$) and detecting the emitted light, after dispersion through a Jobin Yvon model H-10 monochromator, with a P28 photomultiplier tube.

The samples for analysis were pressed on a uniaxial press under 380 ± 19 MPa for 30 s. The prepared samples are denoted here as SiSNH₂Eu, SiSNH₂5Eu and SiSNH₂10Eu, for samples containing 1, 5 and 10 % (m/m) of the complex, respectively.

RESULTS AND DISCUSSION

The elemental analysis results give a total amount of 0.8 mmol of the group S-(CH₂)₂NH₂ per gram of hybrid matrix. The obtained X-ray diffraction pattern confirms that the synthesized matrix is amorphous.

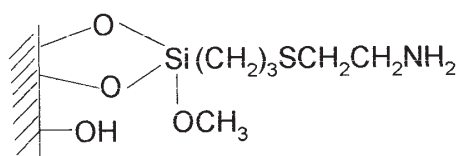
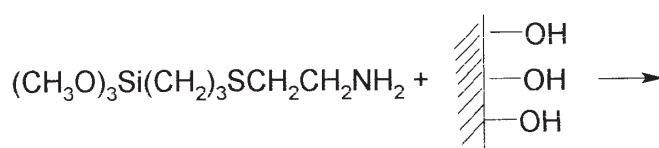


Fig. 1. Schematic representation of the sequence of reactions involved in producing a 3-trimethoxypropylthioethylamine modified silica surface.

All the recorded emission spectra exhibit very similar profiles. As an illustrative example, the spectrum of the SiSNH₂10Eu sample is shown in Fig. 1. The emission bands from 1 to 5, are, respectively: $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$.^{5,6} It was observed that the fluorescence intensity decreases with an increase of the total amount of the adsorbed complex. Such a fact was previously observed for another europium complex-doped hybrid surfaces^{5,6} and could be explained based on both, the organic moiety/complex ratio, as well as a concentration quenching effect.^{5,6}

The lifetimes measured (for lifetime measurements, the main emission band, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, was considered) for the emission process are 476, 542 and 566 μs for samples SiSNH₂Eu, SiSNH₂5Eu and SiSNH₂10Eu, respectively, So, it was verified that the lifetime increases with increasing amount of adsorbed complex. Hence, it can be inferred that the proximity of Eu centers at the surface (higher complex concentrations) favors longer lifetimes.

This behavior is opposite to that observed for Eu(fod)₃·2H₂O adsorbed on Si-Ti⁵ or silicon inorganic-organic hybrids.⁶ The organic moiety in these studies was the -(CH₂)₃-NH-(CH₂)₂NH₂ group, and lifetimes of 414, 384 and 380 μs ⁵ and 500, 468 and 472 μs ,⁶ were measured for 1 %, 5 % and 10 % adsorbed complex samples, respectively. So, the experimental results obtained in this work, when compared with those previously reported^{5,6} provide evidence for the prominent

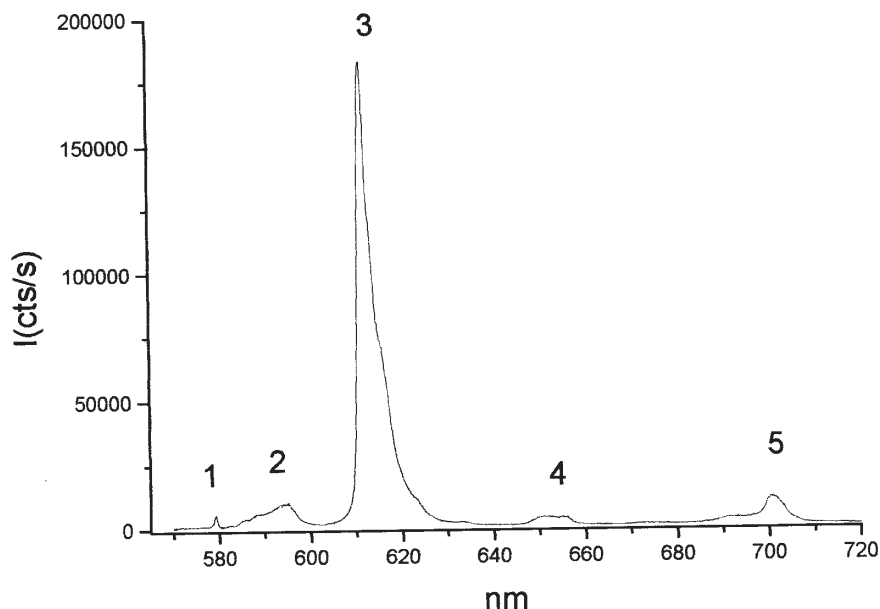


Fig. 2. Emission spectrum of the sample SilSNH₂10Eu.

role of the chemical composition of the silica modified surface on the spectroscopic properties of the adsorbed complex.

It is worth remembering that the $\text{Eu}(\text{fod})_3 \cdot 2\text{H}_2\text{O}$ complex has two water molecules in its coordination sphere, and it is well known that such H_2O molecules can be replaced by another ligands, as exemplified by 1,10-phenanthroline and 2,2'-dipyridyl⁴ (both with nitrogen as the donor atoms). Hence, in previously *n*-[3(trimethoxysilyl) propyl]-ethylenediamine modified surface^{5,6} it was supposed that some water molecules in the coordination sphere of the complex were replaced by the nitrogen atom of the organic moiety. As the complex/hybrid matrix ratio increases, from 1 % to 5 % and finally 10 %, the number of nitrogen atoms available per complex molecule is reduced, and a good hypothesis is to suppose that, because of this, the symmetry of the adsorbed compound undergoes some kind of modification that make the adsorption and transfer of energy from the ligands to the lanthanide less effective. The fact that, for other studied matrices,^{5,6} irregular variations of the fluorescence intensity were observed depending on the duration of the applied pressure,^{5,6} reinforces this hypothesis, since increasing the external pressure induces some kind of reorganization of the organic moiety, as was verified by studying lamellar silica samples.¹¹

For the samples studied in this work, the organic moiety is the $-(\text{CH}_2)_3\text{-S-}(\text{CH}_2)_2\text{NH}_2$ group, *i.e.*, in comparison with the $-(\text{CH}_2)_3\text{-NH-}(\text{CH}_2)_2\text{NH}_2$ group, the only difference is the replacement of a nitrogen atom by a sulfur atom. However, such a difference was enough to modify the tendency (increase or decrease)

of the lifetimes of the emission process and also to increase the lifetimes of the sulfur containing samples. Such phenomena could, at first sight, be attributed to the difference in the hardness¹² of N and S. Hence, it could be concluded that softer bases increase the fluorescence lifetime, whereas hard bases reduce it. In other words, it could be stated that, when adsorbed on an inorganic-organic hybrid surface, the lifetime of the fluorescence process will be increased by polarisable (soft) atoms on the surface and, on the contrary, will be shortened by the presence of hard (less polarisable) atoms.

However, the role of the N–H vibration modes of the ethylenediamine could also be utilized to explain the less efficient quenching of the S–(CH₂)₂NH₂ group. Furthermore, it can also be suggested that the progressive substitution of water molecules for S atoms on the coordination sphere of Eu(fod)₃·2H₂O can result in such a remarkable effect.

CONCLUSION

The obtained experimental results show that a 3-trimethoxypropylthioethylamine modified silica gel surface can be successfully employed as a substrate for luminescent lanthanide compounds. Furthermore, it can be assumed that, by controlling the total amount of available coordination sites on the surface, as well as the external pressure exerted on the doped samples, complete control of the intensity and lifetime of the emitted light could be achieved. Furthermore, comparison with the experimental data for *n*-[3(trimethoxysilyl) propyl]-ethylenediamine modified silica gel surfaces provides evidence for the prominent role played by the chemical composition of the silica modified surface on the spectroscopic properties of an adsorbed complex.

IZVOD

SPEKTROSKOPSKO PROUČAVANJE KOMPLEKSA Eu(fod)₃ ADSORBOVANOG NA POVRŠINI SILICIJUM-OKSIDA MODIFIKOVANOJ 3-TRIMETOKSIPROPIL-TIOETILAMINOM

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Sintetizovano je jediweve 3-metoksipropiltioetilamin korišćenjem 3-merkaptopropiltrimetoksisilana i etilendiamina kao prekursorima i koje je zatim korišćeno kao sililirajuće agens, da bi se sol-gel procesom dobila organska modifikacija uzorka silicijum-oksida-gela. Ovako modifikovana površina korišćena je kao supstrat za adsorpciju kompleksa Eu(fod)₃. Eu(fod)₃·2H₂O i silicijum hibrid pomešani su u stehiometrijskim odnosima tako da su dobiveni uzorci sa sadržajem 1 %, 5 % i 10 % adsorbovanog kompleksa. Adsorbovani kompleks je proučavan

spektroskopski. Izmerena poluvremena emisijonih procesa bila su 476, 542 i 566 μs , za 1 %, 5 % i 10 % uzorka, redom. Upoređujem sa podacima za sa *n*-[3(trimetoksisilil)propil]-etilendiaminom modifikovanom površinom silicijum-oksida, naglašena je dominantna uloga hemijskog sastava modifikovane površine silicijum-oksida na spektroskopske osobine adsorbovanog kompleksa.

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