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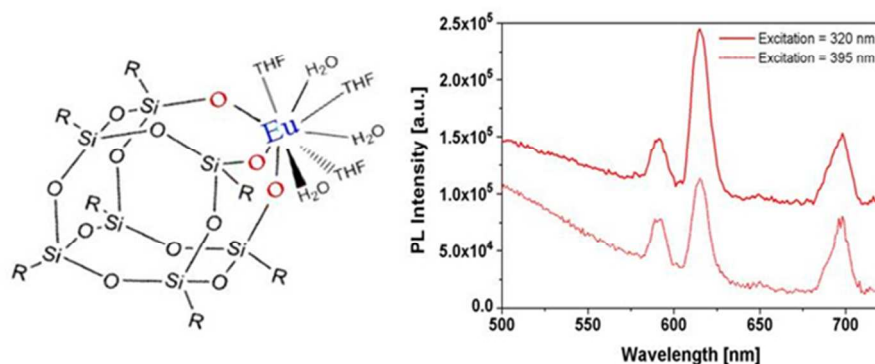


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PAPER

Synthesis and characterisation of a novel Europium(III)-containing heptaisobutyl-POSS

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A novel luminescent metal-containing POSS, bearing in the structure the europium ion, was synthesized and characterized. The corner-capping reaction between the partially condensed isobutyl-POSS (molecular formula $(C_4H_9)_7Si_7O_9(OH)_3$) and the anhydrous $EuCl_3$, under basic conditions, led to a completely condensed Eu(III)-containing POSS. The molecular compound involves in the coordination sphere of Eu(III), THF molecules coming from the reaction medium. A deep optical characterization demonstrated that Eu(III)-POSS sample is characterized by a quantum efficiency of *ca.* 14% and high photostability. Both these properties render this molecular platform an ideal candidate for the construction of luminescent devices and light-harvesting systems.

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are a class of condensed three dimensional oligomeric organosiliceous compounds with cage framework having different geometry and symmetry. As a general feature, the molecular structure of these compounds consists of silicon atoms bonded to one-and-a-half oxygen (“sesqui-”) and hydrocarbon (“-ane”) moieties (hereby reported as R), leading to $(RSiO_{1.5})$ bond units. The most common materials are cubic systems, with general formula $R_8Si_8O_{12}$.¹⁻³

POSS molecules due to their high chemical versatility, good stability and molecular size, attracted grow interest in the last decade as hybrid nanostructured 3D nanomaterials, finding applications in several fields, spanning from catalysis,⁴⁻⁶ to biomedical⁷⁻⁸ and diagnostic uses,⁹⁻¹⁰ to the preparation of nanocomposite materials with improved physico-chemical features.¹¹⁻¹²

Besides fully condensed polyhedral silsesquioxanes, that are generally identified with a cubic $R_8Si_8O_{12}$ structure, open-corner POSS compounds, structurally related to cubic systems where a Si vertex is removed leaving incompletely condensed silanol groups (with general formula $R_7Si_7O_9(OH)_3$), seem to be currently more interesting, because of the capability to link different functionalities through the reaction with specific organosilanes and heteroelements precursors. In particular, partially condensed POSS can be react with a large variety of metal centres (under form of alkoxides or chlorides), thus obtaining completely condensed metal-silsesquioxane species (M-POSS).¹³⁻¹⁷

The “Periodic Table of metal-containing POSS” already covers numerous chemical elements spanning from alkali metals to transition and lanthanide ions and the chemistry of these solids continues to be an area of vigorous research activity. Very

recently, lanthanides-containing POSS (Ln-POSS) attracted interest for their potential uses in homogeneous/heterogeneous catalysis and biomedical field. Indeed, different Ln-POSS containing Ce(III),¹⁸ Er(III),¹⁹ Gd(III)²⁰ with definite architecture have been explored. Nevertheless, as a general comment, information on well-characterized lanthanide silsesquioxane derivatives is still quite limited. Furthermore, luminescent metal centres such as Europium, to the best of our knowledge, have not been deeply investigated in combination with molecular POSS structures.

It is worth to note that luminescent lanthanides are well known as efficient luminophors when combined with specific “antenna” groups (typically based on aromatic functionalities), which emit a long-living narrow band of practically monochromatic radiation through the strong optical absorption in the ultraviolet region. However, they have not so far been used extensively in practical applications mainly due to their poor thermal stability and low mechanical resistance. The encapsulation of these lanthanide ions, through anchoring and embedding procedures, into sol-gel-derived materials²¹ can circumvent these shortcomings and can therefore lead to lanthanide-based luminescent materials. Following this idea, a novel Eu(III)-containing POSS (hereafter named Eu(III)-POSS) was synthesized in this manuscript, starting from a partially condensed isobutyl-POSS. The structure and the optical properties of this molecule were investigated in view of their potential uses in conversion devices such as LEDs, light emitting sensors and imaging diagnostic probes.

2. Experimental Section

2.1 Materials

Heptaisobutyl-trisilanol POSS (1), purchased by Hybrid Plastics Company, was used as precursor for the preparation of E(III)-POSS. All solvents, freshly opened, were used after purification.

Eu(III)-POSS synthesis

Anhydrous EuCl_3 (170 mg, 0.66 mmol, Sigma Aldrich) was added with vigorous stirring to a solution of (1) (500 mg, 0.63 mmol) in 90 mL of anhydrous distilled THF, in the presence of 272 μL of triethylamine (Et_3N $\geq 99\%$, Sigma Aldrich). The reaction solution was carefully purged with nitrogen. The temperature was raised to 50°C and the mixture stirred for 24 h. Finally, the solvent was evaporated until a white powder was obtained. The sample was washed with water and THF in order to remove a large part of un-reacted residual and by-products, thus obtaining Eu(III)-POSS sample (2).

2.2 Characterization

^{13}C NMR spectrum of Eu(III)-POSS, dissolved in CDCl_3 , was recorded with a Jeol Eclipse Plus spectrometer equipped with an 9.4-T magnet.

The amount of carbon and nitrogen was detected by using the EuroVector CHN analyzer "EA3000".

^{29}Si Solid state NMR spectra were acquired on a Bruker Avance III 500 spectrometer and a wide bore 11.7 Tesla magnet with operational frequencies of 99.35 MHz for ^{29}Si . A 4 mm triple resonance probe was employed in all the experiments and the samples were packed on a Zirconia rotor and spun at an MAS rate of 5 kHz. The magnitude of radio frequency field was 42 kHz and the relaxation delay between accumulations was of 120 s.

Infrared (IR) spectra of solid samples in KBr pellets were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ with 4 cm^{-1} resolution, by using a Bruker Equinox 55 spectrometer.

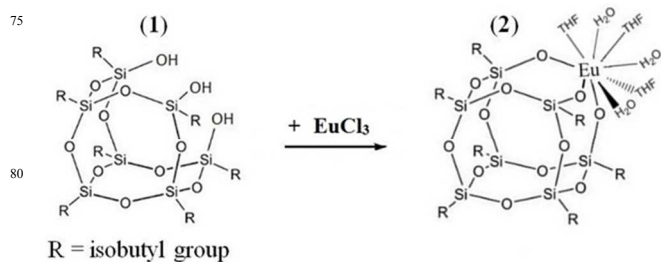
The XRF analysis was carried out with the Rigaku NEX QC (QC1036) Benchtop Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer, equipped with 50kV (4 watt) X-ray tube.

MALDI-TOF analysis was performed with the Mass Spectrometer Voyager DE Pro (AB-Sciex). For MALDI-TOF analysis, 3,5 dimethoxy cinnamic acid (sinapinic acid) (LaserBio Labs, Sophia-Antipolis Cedex, France) was used as matrix in a concentration of 10 mg/mL in 50:50 acetonitrile:water 0.1% TFA. Typically 10 μL sample were mixed with 10 μL matrix solution, of which 1 μL was deposited on the appropriate target. After thorough drying in the dark, 100 shots per spectrum were acquired. The MALDI-MS spectral data were processed using the Data Explorer software from AB-Sciex.

Photoexcitation and photoluminescence emission spectra were recorded on a Horiba Jobin-Yvon Model IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and emission monochromators (2.1 nm mm^{-1} dispersion; 1200 grooves per mm), and a Hamamatsu Model R928 photomultiplier tube. PL spectra were recorded under irradiation at 320 and 395 nm. Eu(III)-POSS was characterized in solid state form and in CHCl_3 solution. Time-resolved measurements were performed by using the time-correlated single-photon counting (TCSPC) option. A 370 nm spectralLED laser was used to excite the sample. Signals were collected using an IBH DataStation Hub photon counting module. Data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH).

3. Results and Discussion

Eu(III)-POSS was prepared following the synthetic procedure adopted in the literature by Eldemann et al. to synthesize the parent Ce(III)-POSS and Er(III)-POSS samples.¹⁸⁻¹⁹ In detail, Eu(III)-POSS synthesis was performed in a single step, through the corner-capping reaction of a partially condensed silsesquioxane, the heptaisobutyl-trisilanol POSS (1), with anhydrous EuCl_3 in distilled THF and in presence of triethylamine (Et_3N). The reaction was carried out at 50°C , under nitrogen flow, for 24 hours (Scheme 1). A white powder was obtained and washed with water and THF solvent in order to remove a large fraction of un-reacted residues and by-products. Eu(III)-POSS sample (2) was successfully obtained. A schematic view of a possible chemical structure of Eu(III)-POSS sample is reported in the Scheme 1.



Scheme 1. Schematic view of the corner-capping reaction of the heptaisobutyl-trisilanol POSS (1) with anhydrous europium salt thus obtaining Eu(III)-POSS (2) sample.

The occurrence of the corner-capping reaction of the open cage POSS was monitored by FT-IR spectroscopy. IR spectrum of Eu(III)-POSS sample, recorded in KBr pellet, was compared to the vibrational profile of the reactant heptaisobutyl-POSS (1) (Fig. 1). The two compounds show very similar IR features in the region of the stretching and bending modes of the isobutyl chains and of the $\nu_{\text{as}}(\text{Si-O-Si})$ of the cage framework ($1500\text{--}1100\text{ cm}^{-1}$). This is a proof that the POSS cage structure was essentially preserved by the chemical point of view during the corner-capping reaction. Nevertheless, it is worth to note that the band centred at 1100 cm^{-1} ($\nu_{\text{as}}(\text{Si-O-Si})$) in the IR spectrum of the product (2) (Fig. 1, down curve), appeared slightly broadened in comparison to the vibrational profile of the reactant POSS (1). This result could be indicative of a local alteration of the cage symmetry occurred in the presence of the coordinated metal centre.

The most important differences between the two samples fall in the $3500\text{--}3000\text{ cm}^{-1}$ and $1000\text{--}500\text{ cm}^{-1}$ IR ranges (Fig. 1).

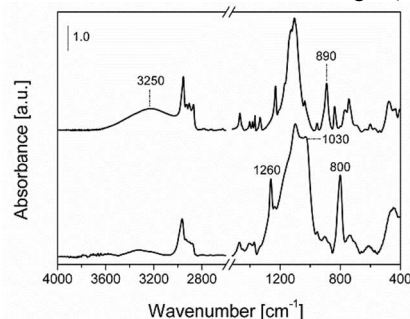


Fig. 1. IR spectra of heptaisobutyl-POSS (up curve) and Eu(III)-POSS (down curve).

In particular, the vibrational profile of sample (1) shows two absorptions at 890 cm^{-1} and 3250 cm^{-1} , relative to the stretching modes of Si-OH and O-H groups, respectively, that are almost completely absent in (2), where the cage is in completely condensed.²² The presence of additional bands, *i.e.* at 1030 and 800 cm^{-1} , in the spectrum of (2), indicates the presence of THF molecules coordinated to the metal centre, as can be assigned to the asymmetric and symmetric modes of the -C-O-C- bonds. An absorption at 1260 cm^{-1} relative to the C-N stretching mode of the Et_3N , deriving by the synthesis procedure, was also observed. The quantification of triethylamine byproduct was estimated by CHN analysis. An amount of *ca.* 4 wt% was detected in the final material.

IR data have been supported by NMR spectroscopy applied to ^{13}C and ^{29}Si nuclei.

High resolution ^{13}C -NMR spectrum of the product (2), dissolved in CDCl_3 (see Figure S1 in the supporting information file), shows peaks at 30.0, 23.9, and 8.6 ppm, ascribed to $-\text{CH}_2$, $-\text{CH}$, and $-\text{CH}_3$ carbon of the isobutyl groups bound to the siliceous framework (Fig. S1). Additional signals at 65.8 and 68.0 ppm are also observed and are ascribed to the $-\text{H}_2\text{C}-\text{O}$ of both free and coordinated (through the formation of $\text{Eu}-\text{O}-\text{CH}_2$ bond) THF molecules to the metal centre, respectively. In addition, peaks at *ca.* 15 and 45 ppm are also present and assigned to the presence of triethylamine by-product deriving by the synthesis reaction (see also IR data above described).

Silicon sites distribution in Eu(III)-POSS sample was monitored by Solid-State MAS-NMR spectroscopy, because of the poor solubility of the product in conventional deuterated solvents. ^{29}Si -MAS NMR spectrum of the heptaisobutyl-POSS shows two well defined signals at -58 ppm (with an abundance of 47%, calculated by the integration of the deconvoluted band), relative to the three silicon sites bound to the -OH groups and at -68 ppm (ascribed to the remaining Si atoms of the POSS cage, with an abundance of 53%), (Fig. 2, curve a). The band at -58 ppm, previously assigned to the silanol species of the partially condensed POSS,²³ drastically decreases in intensity in the ^{29}Si NMR spectrum of the Eu(III)-POSS product (abundance of 6.4%), as a consequence of the almost completely closure of the cage with the metal site (Fig. 2, curve b). The presence of the Eu^{3+} ion in the POSS cage was also supported by the XRF analysis carried out on the Eu(III)-POSS sample (data reported in the supporting information, Fig. S2).

Moreover, two new peaks clearly appear in the -100 - -120 ppm range and can be attributed to the silicon sites directly coordinated to Eu^{3+} ions.

As a general comment, all ^{29}Si NMR signals result broadened as a consequence of both the strong paramagnetic nature of the Eu(III) centre and the alteration of the cage symmetry promoted by the corner-capping reaction.

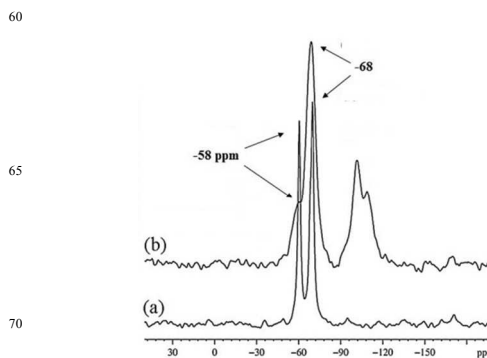


Fig. 2. ^{29}Si MAS NMR spectra of heptaisobutyl-POSS (a) and Eu(III)-POSS (b).

Additional information on the chemical structure of the Eu(III)-POSS sample were obtained by MALDI-TOF analysis. The mass spectrum of (2) shows an intense peak at *ca.* 1205 (m/Z) (Fig. S3). This value looks in agreement with the molecular weight of a monomeric structure in which the Eu^{3+} ion is bound to the Si-O- units of the POSS cage, expanding its coordination sphere with THF (as indicated by the ^{13}C NMR spectrum) and probably water molecules deriving from the purification treatments. An intense peak at *ca.* 1430 m/Z was also observed and correlated to the molecular weight of Eu(III)-POSS bound to the sinapinic acid matrix, used to stabilized the sample prior to the analysis. No evidence of dimeric or multimeric species, often detected for parent Ln-containing POSS are observed for Eu(III)-POSS sample prepared in this work. More insights on the chemical structure of this sample could be obtained through single-crystal X-ray diffraction analysis, but POSS functionalized with highly mobile isobutyl groups are often unsuitable to this analysis due to the scarce tendency to crystallise in properly sized crystals, as observed in our case.

The photophysical properties of Eu(III)-POSS were finally investigated. The excitation spectrum of (2) dissolved in CHCl_3 was collected around the most intense emission line of Eu^{3+} at $\lambda_{\text{em}} = 615\text{ nm}$ (Fig. 3A). The excitation spectrum shows in addition to the narrow peaks relative to the characteristics intra- $4f^6$ electronic transitions of Eu^{3+} (as assigned in the spectra),²⁴ a broad absorption band from 250 and 350 nm with maximum located at 320 nm (Fig. 3A). This absorption, observed both for the sample measured in solid state form (see Fig. S4) and in chloroform solution, was ascribed to the absorption of the host matrix.

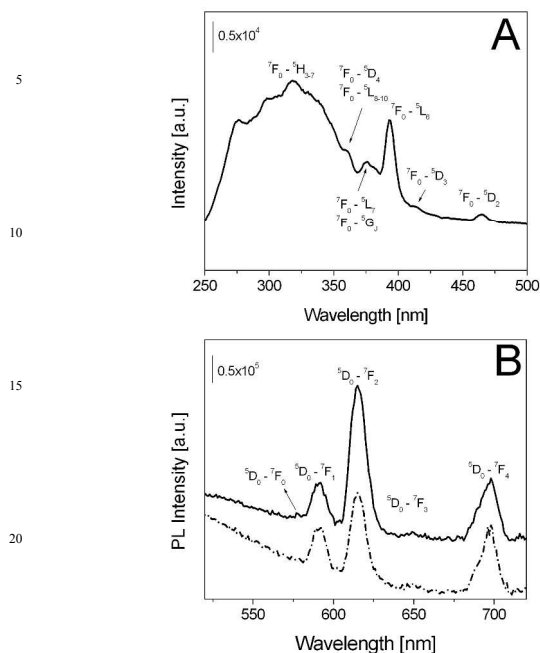


Fig. 3. A) Excitation spectrum of Eu(III)-POSS in CHCl_3 around the most intense emission line of Eu^{3+} at $\lambda_{\text{em}} = 615 \text{ nm}$; B) emission spectra of Eu(III)-POSS under irradiation at 320 nm (solid curve) and 395 nm (dash line).

The photoluminescence spectra of Eu(III)-POSS dissolved in chloroform were measured by exciting the sample at two different excitation wavelengths, 320 (wavelength relative to the absorption of both the Eu^{3+} (${}^7F_0 \rightarrow {}^5H_{3,7}$ transitions) and the host matrix) and 395 nm (only typical of Eu^{3+} ion (${}^7F_0 \rightarrow {}^5L_6$ transition)), respectively (Fig. 3B).

In both cases, the emission spectra are composed of very narrow emission peaks relative to the intra- $4f^6$ electronic levels of Eu^{3+} (${}^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$)).²⁴ However, the intensity of the peak at 615 nm, that is ascribed to the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition, appears more intense when the sample is irradiated at 320 (Fig. 3B).

It is worth to note that the photoluminescence spectrum of the sample irradiated at 320 nm showed a weak band at 579 nm (well evident in the PL spectrum of Eu(III)-POSS in solid state (see Fig. S4, B) related to the ${}^5D_0 \rightarrow {}^7F_0$ transition, unique for a given chemical environment, since both the initial and final states are non-degenerate. The number of components observed for this transition is then related to the number of chemically distinct environments of the Eu^{3+} ion and the transition has been used both in excitation and emission as a probe of sample homogeneity. It is clear that there is only one band in our case, consistent with the presence of a single predominant environment.

Site geometrical aspects can be evaluated using the PL results. The asymmetry factor (R), which is the ratio of the integrated intensity of the ${}^5D_0 \rightarrow {}^7F_2$ (peak at 615 nm) transition with the ${}^5D_0 \rightarrow {}^7F_1$ transition (signal at 592 nm) has been widely used as an indicator of Eu^{3+} site symmetry and it tends to be zero when

the excited ions are located at a symmetry site. It is believed that the value of R becomes larger as the interaction of Eu^{3+} with its neighbours becomes stronger and the Eu^{3+} site symmetry becomes lower.²⁵ The presence of a very intense peak at 615 nm in the PL spectrum of (2), relative to the electric dipole ${}^5D_0 \rightarrow {}^7F_2$ transition, suggests that the chemical environment of the Eu^{3+} ion in Eu(III)-POSS is characterized by a low symmetry degree.²⁶ The asymmetry factor of Eu(III)-POSS is 2.2 when the sample is excited with $\lambda_{\text{exc}} = 395 \text{ nm}$, and 3.8 when irradiated at 320 nm, thus indicating that the Eu(III) ion is characterized in this matrix by a low symmetric coordination environment (see Table 1).

The discussion only involves tendencies, as the method of determining the asymmetry with the ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensity ratio does not allow relying on the exact values.

In order to further investigate the luminescence performance of the sample, the lifetime of excited states of Eu^{3+} ions in (2) was also measured. The decay curve of 5D_0 level is well-reproduced by means of a mono-exponential function. The lifetime value is determined to be 0.34 ms (Table 1) in agreement with the results obtained for parent solids based on silica-type or aluminosilicates matrices (mesoporous silicas, zeolites ...) (Fig. 4).²⁷

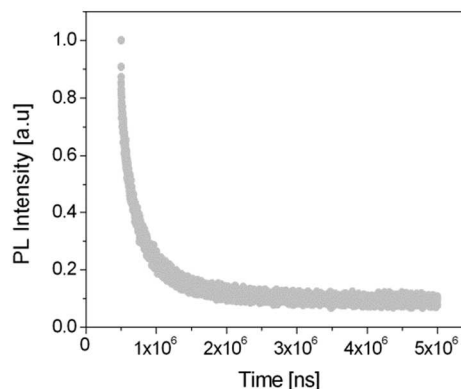


Fig. 4. PL intensity decay over the time of Eu(III)-POSS sample dissolved in CHCl_3 under irradiation at 370 nm (-o-).

Table 1. Asymmetry factor, experimental 5D_0 lifetime, Eu^{3+} quantum efficiency value of Eu(III)-POSS sample.

	asymmetry factor (R)	τ (ms)	$1/\tau_0$ (ms ⁻¹)	τ_0 (ms)	Φ_{Eu} (%)
Eu(III)-POSS	2.2 ($\lambda_{\text{exc}} = 395$)	0.34	0.42	2.37	14.3
	3.8 ($\lambda_{\text{exc}} = 320$)				

The 5D_0 quantum efficiency (Φ) is estimated taking into account the emission spectrum and lifetime of 5D_0 state and by using the following equation (1):²⁸

$$\text{Eq. 1: } \phi_{\text{Ln}} = \tau/\tau_0$$

where τ and τ_0 are the lifetime and the radiative lifetime of the Eu^{3+} luminescence, respectively.

Equation 2 provides a means to calculate the radiative lifetime directly from the corrected emission spectrum without the intervention of the Judd-Ofelt theory.²⁹

Eq. 2:
$$1/\tau_0 = A_{MD,0} n^3 (I_{tot}/I_{MD})$$

In this equation, n is the refractive index of the solvent (CHCl_3), $A_{MD,0}$ is the spontaneous emission probability for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition in vacuo, and I_{tot}/I_{MD} the total area of the (corrected) Eu^{3+} emission spectrum to the area of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ band. It was theoretically calculated and experimentally verified that $A_{MD,0}$ has a value of 14.65 s^{-1} .²⁹

The intrinsic quantum efficiency of europium (Φ_{Ln}), based on the emission spectra obtained in solution under irradiation at 320 nm and on the value of lifetime previously obtained, was calculated to be 14.3% (Table 1), in agreement with the data obtained for other Eu^{3+} -containing silica frameworks.²⁴

In order to further investigate the photostability of the hybrid material in CHCl_3 solution, bleaching tests have been performed (Fig. 5). Photodegradation of Eu(III)-POSS sample is strongly limited (*ca.* 5%) after 1 h of light irradiation at 395 nm, confirming that the sample is characterized by high photostability.

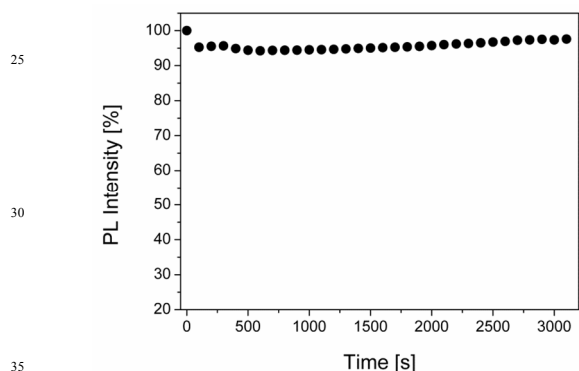


Fig. 5. Photostability test on Eu(III)-POSS solution in CHCl_3 irradiated at 395 nm.

Conclusions

In conclusion, the synthesis and characterization of a novel completely condensed Eu^{3+} -containing POSS (Eu(III)-POSS) is reported in this work. A detailed investigation of the physico-chemical properties of Eu(III)-POSS sample, by NMR applied to ^{13}C and ^{29}Si nuclei, FT-IR and MALDI-TOF analyses, has provided information on the reaction steps and on the nature of the final product and highlighted that the synthetic protocol can be selective towards the preparation of Ln-containing POSS. Structural and spectroscopic results indicated that Eu^{3+} ion caps the POSS unit by the dangling oxygen groups of the open corner and expands its coordination sphere by linking THF molecules (from the reaction medium).

By the optical point of view, the compound presented interesting luminescent properties. Eu(III)-POSS was characterized by quantum efficiency of *ca.* 14%, in agreement with parent samples based on silica matrices, and high photostability to photobleaching. These features along with the molecular size and the high versatility deriving by the presence of organic groups

bound to the POSS cage which can be opportunely modified or functionalized, render Eu(III)-POSS sample a potential candidate for the development of luminescent probes and light-harvesting systems.

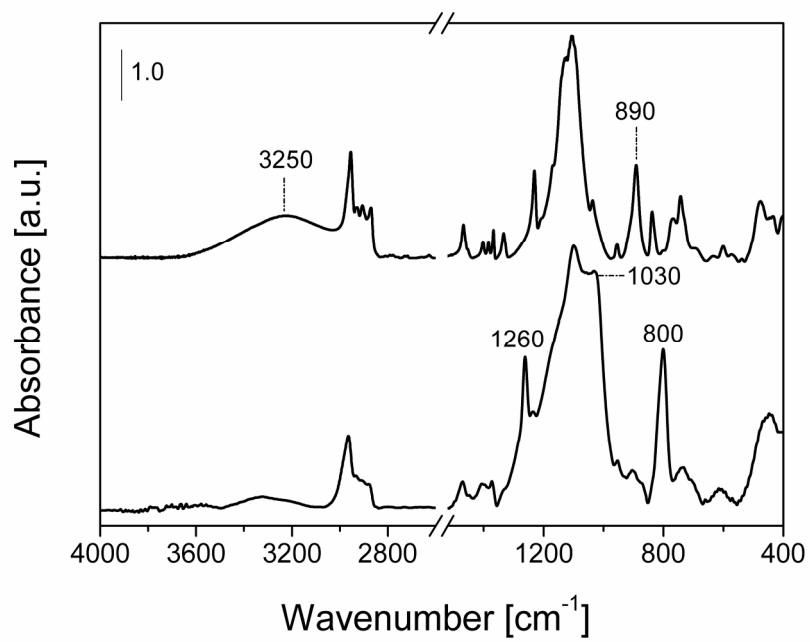
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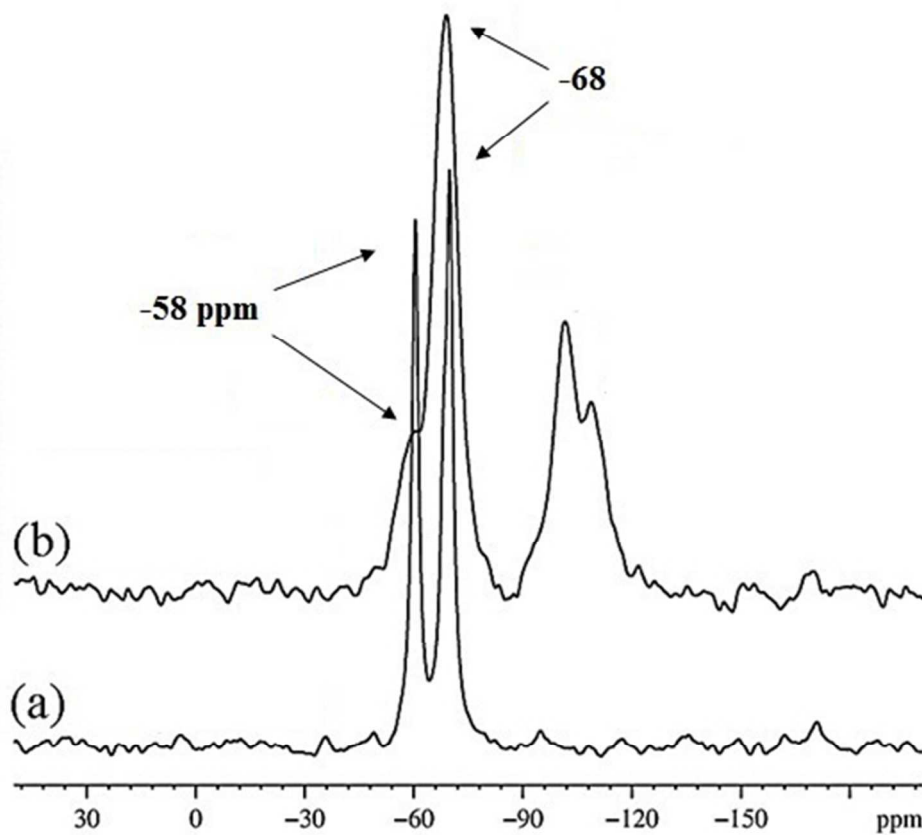
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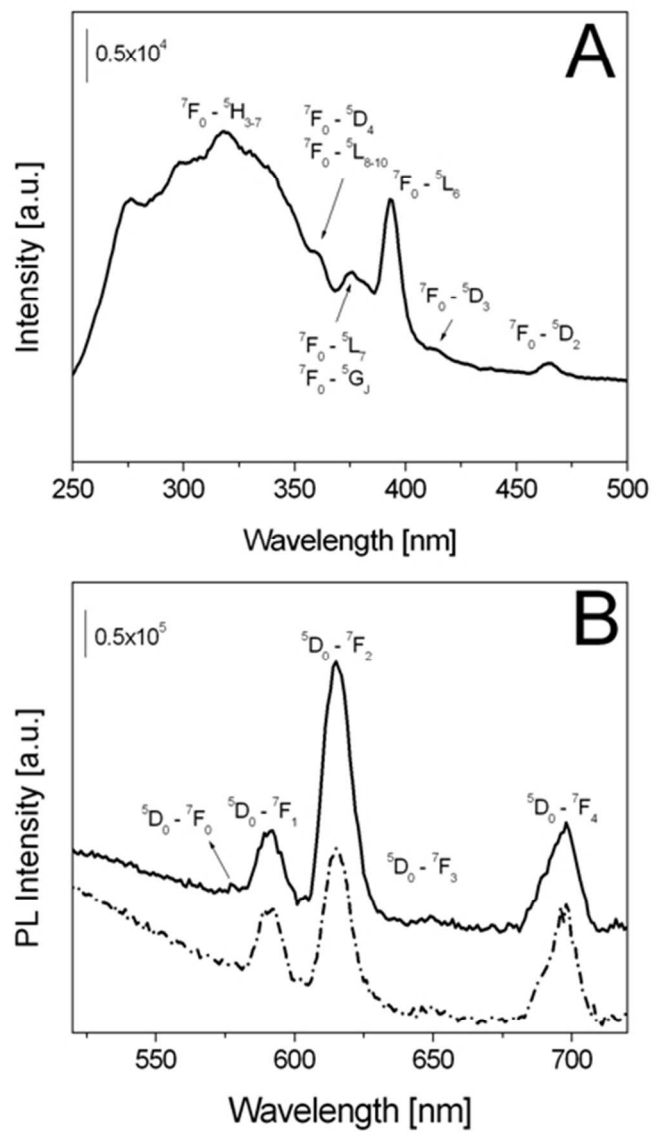
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- † Electronic Supplementary Information (ESI) available: [details on the physico-chemical characterization of Eu(III)-POSS are included here]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
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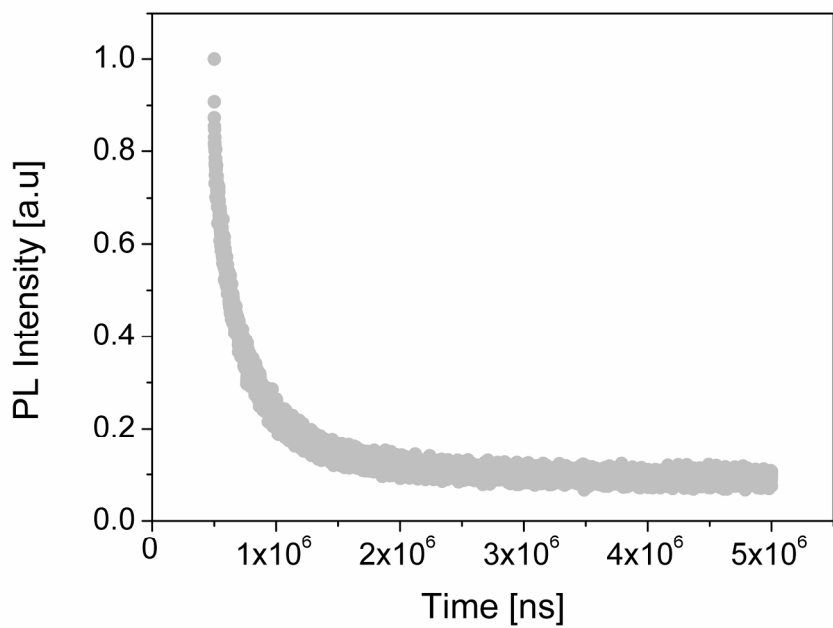
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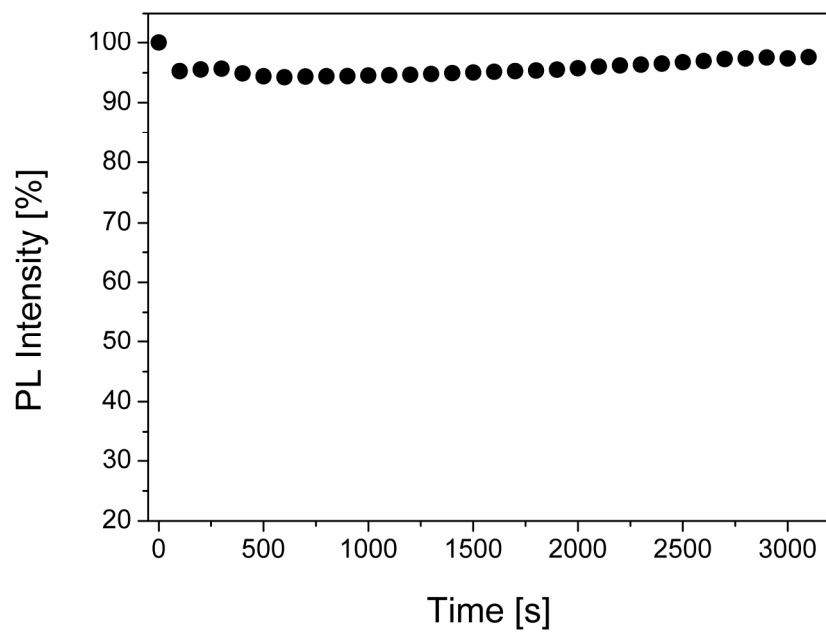
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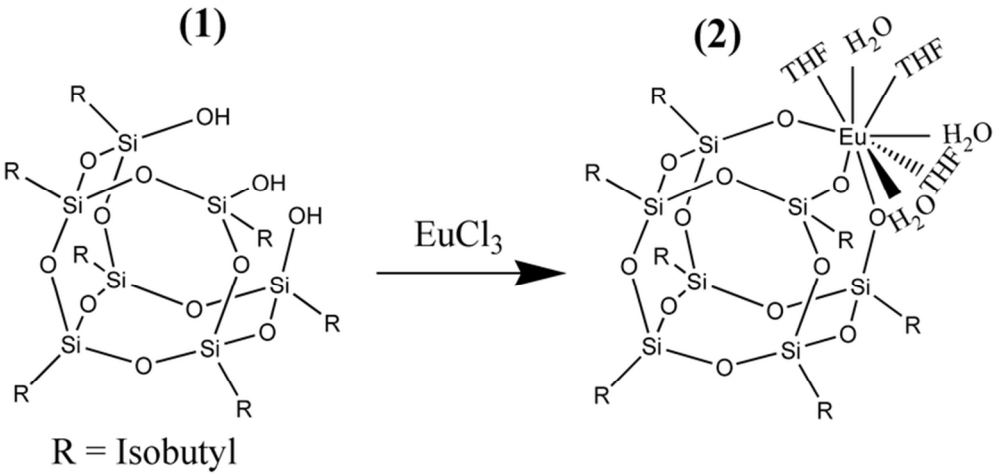




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