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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 THF molecules, coming from the reaction medium, in the coordination sphere on Eu(III). A deep optical characterization demonstrated that the 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 the cage framework having different geometries and symmetries. 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 (herein denoted 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 have attracted growing interest in the last decade as hybrid nanostructured 3D nanomaterials, finding applications in several fields, spanning from catalysis,[4–6] to biomedical[7,8] 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 their capability to link different functionalities through the reaction with specific organosilane and heteroelement precursors. In particular, partially condensed POSS can react with a large variety of metal centres (in the form of alkoxides or chlorides), thus affording a 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, lanthanide-containing POSS (Ln-POSS) have attracted interest because of their potential use in homogeneous/heterogeneous catalysis and the biomedical field. Indeed, different Ln-POSS containing Ce(III),[18] Er(III),[19] and 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 noting that luminescent lanthanides are well known as efficient luminophores 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 materials[21] 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 its potential use in conversion devices such as LEDs, light emitting sensors and imaging diagnostic probes.

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2. Experimental section

2.1 Materials

Heptaisobutyl-trisilanol POSS (**1**), provided by Nova Res S.r.l. (Novara, Italy), was used as a precursor for the preparation of Eu(III)-POSS. In general, all solvents, freshly opened, were used without any further purification. Particular care was taken only for THF, that was purified before use by distillation on Na/benzophenone to remove traces of radicals and water.

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 ≥99%, Sigma Aldrich). The reaction solution was carefully purged with nitrogen. The temperature was increased 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 residues and by-products, thus obtaining the Eu(III)-POSS sample (**2**).

2.2 Characterization

The ^{13}C NMR spectrum of Eu(III)-POSS, dissolved in $CDCl_3$, was recorded using a JEOL Eclipse Plus spectrometer equipped with a 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 in a zirconia rotor and spun at an MAS rate of 5 kHz. The magnitude of the radio frequency field was 42 kHz and the relaxation delay between accumulations was 120 s.

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

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

MALDI-TOF analysis was performed using 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 a matrix in a concentration of 10 mg mL^{-1} in 50 : 50 acetonitrile : water 0.1% TFA. Typically the 10 μL sample was 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.

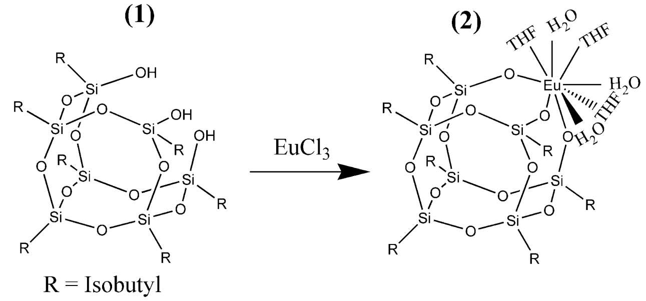
Photoexcitation and photoluminescence emission spectra were recorded on a Horiba Jobin-Yvon Model IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and emission monochromators (2.1 nm mm^{-1} dispersion; 1200 grooves per mm), and a Hamamatsu Model R928 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 spectraLED 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 Edelmann *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 the 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. The Eu(III)-POSS sample (**2**) was successfully obtained. A schematic view of a possible chemical structure of the Eu(III)-POSS sample is reported in Scheme 1.

The occurrence of the corner-capping reaction of the open cage POSS was monitored by FT-IR spectroscopy. The IR spectrum of the Eu(III)-POSS sample, recorded in KBr pellets, 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 ν_{as}(Si–O–Si) of the cage framework (1500–1100 cm^{-1}). This is proof that the POSS cage structure was essentially preserved from the chemical point of view during the corner-capping reaction. Nevertheless, it is worth noting that the band centred at 1100 cm^{-1} (ν_{as}(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 occurring in the presence of the coordinated metal centre.

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



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

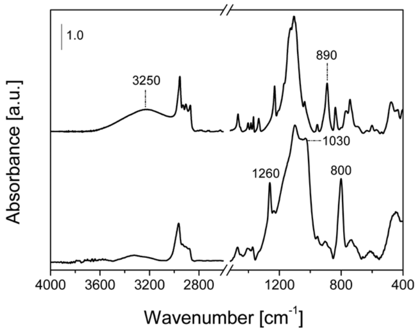


Fig. 1 IR spectra of heptaisobutyl-POSS (up curve) and Eu(III)-POSS (down curve).

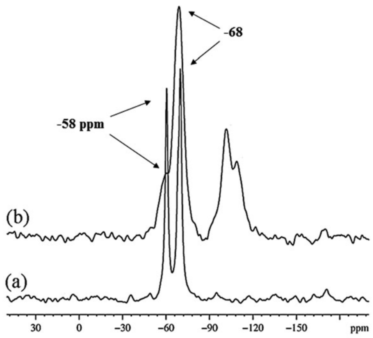


Fig. 2 ^{29}Si MAS NMR spectra of heptaisobutyl-POSS (a) and Eu(III)-POSS (b).

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 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, derived from the synthesis procedure, was also observed. The quantity of the 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.

The high resolution ^{13}C-NMR spectrum of product **2**, dissolved in $CDCl_3$ (see Fig. S1 in the ESI†), shows peaks at 30.0, 23.9, and 8.6 ppm, ascribed to –$\mathit{C}H_2$, –$\mathit{C}H$, and –$\mathit{C}H_3$ carbon of the isobutyl groups bound to the siliceous framework (Fig. S1, ESI†). Additional signals at 65.8 and 68.0 ppm are also observed and are ascribed to the –$H_2\mathit{C}$–O of both free and coordinated (through the formation of the Eu–O–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 the triethylamine by-product derived from the synthesis reaction (see also IR data described above).

Silicon site distribution in the Eu(III)-POSS sample was monitored by solid-state MAS-NMR spectroscopy, because of the poor solubility of the product in conventional deuterated solvents. The ^{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 complete 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 ESI,† Fig. S2).

Moreover, two new peaks clearly appear in the −100 to −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 are 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.

Additional information on the chemical structure of the Eu(III)-POSS sample was obtained by MALDI-TOF analysis. The mass spectrum of **2** shows an intense peak at *ca.* 1205 (*m*/*z*) (Fig. S3, ESI†). This value is 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 derived 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, is observed for the Eu(III)-POSS sample prepared in this work. More insights into 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 for this analysis due to their poor tendency to crystallise into appropriately 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 λ_{em} = 615 nm (Fig. 3A). The excitation spectrum shows in addition to the narrow peaks relative to the characteristic intra-4f^6 electronic transitions of Eu^{3+} (as assigned in the spectra),[24] a broad absorption band from 250 to 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, ESI†) and in chloroform solution, was ascribed to the absorption of the host matrix.

The photoluminescence spectra of Eu(III)-POSS dissolved in chloroform were measured by exciting the sample at two different excitation wavelengths, 320 nm (wavelength relative to the absorption of both the Eu^{3+} ($^7F_0 \rightarrow {}^5H_{3-7}$ transitions) and

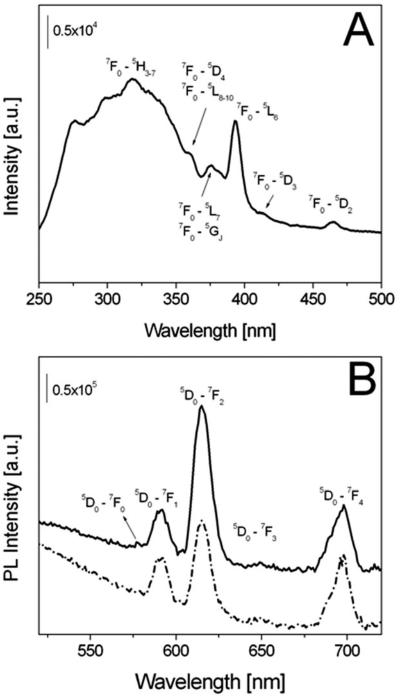


Fig. 3 (A) Excitation spectrum of Eu(III)-POSS in $CHCl_3$ around the most intense emission line of Eu^{3+} at λ_{em} = 615 nm; (B) emission spectra of Eu(III)-POSS under irradiation at 320 nm (solid curve) and 395 nm (dash line).

the host matrix) and 395 nm (only typical of the 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, which is ascribed to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, appears to be more intense when the sample is irradiated at 320 nm (Fig. 3B).

It is worth noting 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 the solid state (see Fig. S4B, ESI†)) 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 to 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 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 at λ_{ex} = 395 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).

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

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

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 the $^5D_0$ 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 aluminosilicate matrices (mesoporous silicas, zeolites...) (Fig. 4).[27]

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

$$\Phi_{Ln} = \tau/\tau_0 \tag{1}$$

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

Eqn (2) provides a means to calculate the radiative lifetime directly from the corrected emission spectrum without the intervention of the Judd–Ofelt theory.[29]

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

In this equation, n is the refractive index of the solvent ($CHCl_3$), $A_{MD,0}$ is the spontaneous emission probability for the $^5D_0 \rightarrow {}^7F_1$ transition *in vacuo*, and I_{tot}/I_{MD} is the total area of the

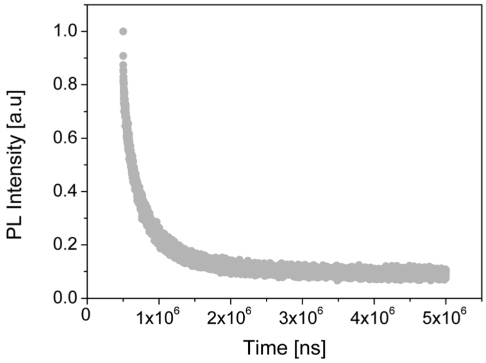


Fig. 4 PL intensity decay over time of the Eu(III)-POSS sample dissolved in $CHCl_3$ under irradiation at 370 nm (–○–).

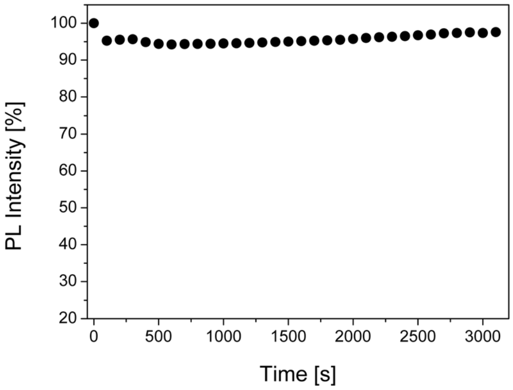


Fig. 5 Photostability test on Eu(III)-POSS solution in $CHCl_3$ irradiated at 395 nm.

(corrected) Eu^{3+} emission spectrum to the area of the $^5D_0 \rightarrow {}^7F_1$ 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 the 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 the 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.

4. Conclusions

In conclusion, the synthesis and characterization of a novel completely condensed Eu^{3+}-containing POSS (Eu(III)-POSS) are reported in this work. A detailed investigation of the physico-chemical properties of the 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 the 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).

From the optical point of view, the compound presented interesting luminescent properties. Eu(III)-POSS was characterized by a 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 derived from the presence of organic groups bound to the POSS cage, which can be opportunely modified or functionalized, render the Eu(III)-POSS sample a potential candidate for the development of luminescent probes and light-harvesting systems.

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Notes and references

1 R. H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, 1995, **95**, 1409.
2 P. G. Harrison, *J. Organomet. Chem.*, 1997, **542**, 141.
3 P. P. Pescarmona and T. Maschmeyer, *Aust. J. Chem.*, 2001, **54**, 583.
4 S. H. Phillips, T. S. Haddad and S. J. Tomczak, *Curr. Opin. Solid State Mater. Sci.*, 2005, **8**, 21.
5 R. Duchateau, *Chem. Rev.*, 2002, **102**, 3525; V. Lorenz and F. T. Edelmann, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1147; V. Lorenz and F. T. Edelmann, *Adv. Organomet. Chem.*, 2005, **53**, 101.
6 H. C. L. Abbenhuis, *Chem.–Eur. J.*, 2000, **6**, 25.
7 J. D. Lichtenhan, *Comments Inorg. Chem.*, 1995, **17**, 115.
8 R. W. J. M. Hanssen, R. A. van Santen and H. C. L. Abbenhuis, *Eur. J. Inorg. Chem.*, 2004, 675.
9 F. J. Feher and J. F. Walzer, *Inorg. Chem.*, 1991, **30**, 1689.
10 V. Lorenz, A. Fischer, S. Gießmann, J. W. Gilje, Y. Gun'ko, K. Jacob and F. T. Edelmann, *Coord. Chem. Rev.*, 2000, **206–207**, 321.
11 R. Duchateau, *Chem. Rev.*, 2002, **102**, 3525.
12 J. Annand, H. C. Aspinall and A. Steiner, *Inorg. Chem.*, 1999, **38**, 1931.
13 V. Lorenz, S. Giessmann, Y. K. Gun'ko, A. K. Fischer, J. W. Gilje and F. T. Edelmann, *Angew. Chem.*, 2004, **116**, 4703; V. Lorenz, S. Giessmann, Y. K. Gun'ko, A. K. Fischer, J. W. Gilje and F. T. Edelmann, *Angew. Chem., Int. Ed.*, 2004, **43**, 4603.
14 F. J. Feher, T. A. Budzichowski, K. Rahimian and J. W. Ziller, *J. Am. Chem. Soc.*, 1992, **114**, 3859.
15 M. Crocker, R. H. M. Herold, A. G. Orpen and M. T. A. Overgaag, *J. Chem. Soc., Dalton Trans.*, 1999, 3791.
16 K. Wada, M. Bundo, D. Nakabayashi, N. Itayama, T. Kondo and T. Mitsudo, *Chem. Lett.*, 2000, 628.
17 M. Chabanas, E. A. Quadrelli, B. Fenet, C. Coperet, J. Thivolle-Cazat, J. M. Basset, A. Lesage and L. Emsley, *Angew. Chem.*, 2001, **113**, 4625; M. Chabanas, E. A. Quadrelli, B. Fenet, C. Coperet, J. Thivolle-Cazat, J. M. Basset, A. Lesage and L. Emsley, *Angew. Chem., Int. Ed.*, 2001, **40**, 4493.
18 Y. K. Gun'ko, R. Reilly, F. T. Edelmann and H.-G. Schmidt, *Angew. Chem., Int. Ed.*, 2001, **40**(7), 1279.
19 V. Lorenz, S. Blaurock, C. G. Hrib and F. T. Edelmann, *Eur. J. Inorg. Chem.*, 2010, 2605.
20 M. Tan, Z. Ye, E.-K. Jeong, X. Wu, D. L. Parker and Z.-R. Lu, *Bioconjugate Chem.*, 2011, **22**, 931.
21 L. Liu, H. Lu, H. Wang, Y. Bei and S. Feng, *Appl. Organomet. Chem.*, 2009, **23**, 429.
22 F. Carniato, E. Boccaleri, L. Marchese, A. Fina, D. Tabuani and G. Camino, *Eur. J. Inorg. Chem.*, 2007, 585.

23 F. Carniato, E. Boccaleri and L. Marchese, *Dalton Trans.*, 2008, 36.

24 Y. Wang and N. Lin, *Photochem. Photobiol. Sci.*, 2011, **10**, 42.

25 S. F. Tang, A. Babai and A. V. Mudring, *Angew. Chem., Int. Ed.*, 2008, **47**, 7631.

26 P. Zhang, Y. Wang, H. Liu and Y. Chen, *J. Mater. Chem.*, 2011, **21**, 18462.

27 X. Guo, H. Guo, L. Fu, H. Zhang, L. D. Carlos, R. Deng and J. Yu, *J. Photochem. Photobiol., A*, 2008, **200**, 318.

28 S. I. Klink, G. A. Hebbink, L. Grave, P. G. B. Oude Alink, F. C. J. M. van Veggel and M. H. V. Werts, *J. Phys. Chem. A*, 2002, **106**, 3681.

29 M. H. V. Werts, *Luminescent Lanthanide Complexes, Visible Light Sensitised Red and Near-Infrared Luminescence*, PhD thesis, The Netherlands, 2000.