Synthesis of Novel Luminescent Double-Decker Silsesquioxanes Based on Partially Condensed TetraSilanolPhenyl POSS and Tb^{3+}/Eu^{3+} Lanthanide Ions

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Abstract: In this study, novel lanthanide-containing double-decker polyhedral oligomeric silsesquioxanes (POSS) were prepared by combining the partially condensed TetraSilanolPhenyl POSS with terbium (Tb^{3+}) and europium (Eu^{3+}) ions. This open-cage POSS possesses four diametrically opposite silanol groups that are able to coordinate, under mild conditions, different luminescent ions through a simple corner-capping method. The two metal-containing POSS functionalized with Tb^{3+} and with an equimolar combination of Tb^{3+} and Eu^{3+} show a completely condensed structure with different luminescent properties. Their emission features depend on the chemical nature of the metal ions incorporated in the framework. An improved stokes shift was detected in the bimetallic compound containing both the Tb^{3+} and Eu^{3+} ions, promoted by the occurrence of a Tb^{3+}→Eu^{3+} energy transfer mechanism. These characteristics identify this metal-functionalized silica platform as a potential candidate for the development of novel luminescent devices.

Keywords: silsesquioxane; double-decker silsesquioxane; POSS; metal-functionalized POSS; corner-capping; lanthanide; europium; terbium; luminescence; energy transfer

1. Introduction

Metal-containing polyhedral oligomeric silsesquioxanes (M-POSS) [1–6] are an important class of inorganic compounds consisting of a condensed oligomeric silica structure with a typical cage shape and bearing a metal ion in one vertex of the structure [7,8]. The remaining edges of the cage are occupied by silicon atoms that are covalently bonded to oxygen and to organic arms, thus generating a three-dimensional Si-O-Si skeleton with tetrahedral units $((RSiO_{1.5})_n)$ (n = 4, 6, 8, 10, 12; R = H or organic substituents) [9–13]. In addition to fully condensed POSS, which is commonly identified by a $R_8Si_8O_{12}$ cubic structure [9–12], the most common cage-like silsesquioxanes used for the synthesis of M-POSS are the partially condensed TriSilanol POSS with the $R_7Si_7O_9(OH)_3$ molecular formula [14–16]. The latter shows a siloxane structure containing three reactive silanol groups that are able to coordinate a broad spectrum of metal centres through a corner-capping procedure [12,17]. Following this synthetic approach, the metal ions are directly incorporated within the POSS inorganic core [6,12,17]. Another interesting strategy for the preparation of M-POSS is based on the chelation of the metal precursors, which is promoted by the presence of ligand arms attached to the silicon vertices [18–20].

POSS and their metal-functionalized derivatives typically exhibit molecular sizes, high chemical versatility and good mechanical and thermal stabilities [8,21]. Furthermore, these solids attracted an increasing interest in several scientific and technological fields, finding applications as heterogeneous catalysts [5,6,22,23] for biomedical and diagnostic uses [18,21,24–27], for the fabrication of 3D nanostructured materials with well-defined

physico-chemical features [28–35] and for the development of original cage-based materials with different porosity and host–guest chemistry [36–39].

The *Periodic Table of Metallasilsesquioxanes* already covers an abundant amount of metal elements included in the M-POSS structures, ranging from alkali and alkaline-earth metals [1,40–46] to metalloid ones [2,47–54], from transition and post-transition metals [21,23,43,50,55–59] to lanthanides [36,43,60–70] and actinides [41,43]. Transition metals, such as Ti^{4+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and $Pt^{2+/4+}$, have been investigated for their catalytic behavior, which shows high activity and selectivity in different reactions [71–73]. M-POSS combined with Co^{2+}, Ni^{2+}, Cu^{2+} and $Fe^{3+/2+}$ have been studied for their unique paramagnetic properties, which are exploitable for the generation of spin-glass and single-molecule magnet systems [74–79].

In the last years, lanthanide-containing POSS (Ln-POSS) attracted growing attention from the scientific community for their potential uses in many fields, although the number of studies on this topic is still relatively small. Encapsulation of lanthanide ions within the cage of POSS [80] can circumvent their innate low thermal stability and mechanical resistance, leading to more stable lanthanide-doped silica-based systems. From an optical point of view, it is widely known that lanthanides exhibit sharp absorption bands with unique well-defined optical emissions in the NIR-UV-Vis range, long-lived excited state lifetimes and remarkable photostability [81,82]. Furthermore, lanthanide ions, such as Gd^{3+}, Dy^{3+} and Ho^{3+}, possess specific chemical properties in terms of high effective magnetic moment and variable electronic relaxation times, which make them suitable for bioimaging [83–86] and electronic applications [87–92].

Ln-POSS are commonly prepared by reaction of the TriSilanol POSS with lanthanides salts. However, this procedure is designed to prepare M-POSS containing in the structure a single type of lanthanide ion. In this respect, samples with different chemical structures, from mononuclear cubic-like systems [39,43,63,65,67,69] to sandwich-type cages are developed [93–96]. On the contrary, the idea to include in the same inorganic cage two different metal ions with intrinsic properties is more promising but still rarely studied in the literature. Very recently, Professor J. Larionova and co-workers described a first example of bifunctional tetranuclear Tb^{3+}-Eu^{3+} silsesquioxanes with a prism-like structure and good magnetic and luminescent properties [97,98]. This solid was prepared through a multi-step reaction procedure, starting with the lanthanides and silicon precursors. An analogous bifunctional structure containing both Dy^{3+} and Y^{3+} ions was also proposed by the same authors as potential single-molecule magnet system [99].

As an alternative to the compounds reported above, in this study, we propose a novel example of bifunctional double-decker POSS (DDSQ) that contains two different lanthanide centres (Tb^{3+} and Eu^{3+}) in the same inorganic framework (TbEu-PhPOSS). The solid was prepared through a simple single-step reaction, starting with the TetraSilanolPhenyl POSS (PhPOSS) and the terbium and europium acetate precursors. This partially condensed POSS [100–105] possesses a pre-formed cubic cage with four diametrically opposite silanol groups (Figure S1) that are able to coordinate the two different lanthanide ions simultaneously. An analogous solid bearing in the structure Tb^{3+} ions was also prepared (Tb-PhPOSS). Finally, the chemical composition and the optical properties of the two samples were investigated.

2. Materials and Methods

2.1. Materials

2.1.1. Synthesis of Tb-PhPOSS (1)

The Tb-PhPOSS sample was prepared by a corner-capping reaction of the partially condensed TetraSilanolPhenyl POSS (Figure S1) [100] with anhydrous terbium acetate, using a molar ratio of 2:1.

In detail, anhydrous terbium acetate ($Tb(CH_3COO)_3$; 78.5(5) mg, 0.234 mmol; Sigma-Aldrich, Burlington, MA, USA) was added with vigorous stirring to a solution of TetraSilanolPhenyl POSS (Ph-POSS; 500 mg, 0.467 mmol; Hybrid Plastics, Hattiesburg, MS, USA)

in 90 mL of anhydrous tetrahydrofuran (THF; ≥99%, Sigma-Aldrich, Burlington, MA, USA) in the presence of 272 μL of triethylamine (TEA; 4.17 mmol; ≥99%, Sigma-Aldrich, Burlington, MA, USA). The reaction was carefully purged with nitrogen for 10 min. After the addition of the reactants, the temperature was fixed to 50 °C, and the mixture was stirred for 24 h. Then, the solvent was removed. The powder was washed with THF and ultrapure water to remove unreacted compounds and by-products, thus obtaining the Tb-PhPOSS (1) sample.

2.1.2. Synthesis of TbEu-PhPOSS (2)

The TbEu-PhPOSS sample was prepared following the same synthetic protocol described before for sample (1) with a relative molar ratio of the reactants of 2:0.5:0.5 (POSS:Tb^{3+}:Eu^{3+}).

In detail, a solid mixture of anhydrous terbium acetate (Tb(CH_3COO)$_3$; 39.32 mg, 0.117 mmol; Sigma-Aldrich, Burlington, MA, USA) and europium acetate (Eu(CH_3COO)$_3$; 38.50 mg, 0.117 mmol; Sigma-Aldrich, Burlington, MA, USA) was added to 90 mL of anhydrous tetrahydrofuran (THF; ≥99%, Sigma-Aldrich, Burlington, MA, USA), containing TetraSilanolPhenyl POSS (Ph-POSS; 500 mg, 0.467 mmol; Hybrid Plastics, Hattiesburg, MS, USA) and 272 μL of triethylamine (TEA; 4.17 mmol; ≥99%, Sigma-Aldrich, Burlington, MA, USA). The reaction was carefully purged with nitrogen for 10 min. The temperature was fixed to 50 °C, and the mixture was stirred for 24 h. Then, the solvent was evaporated, and the final solid, hereafter named TbEu-PhPOSS (2), was washed with THF and water.

2.2. Analytical Methods

Elemental analyses were carried out on a Thermo Fisher Scientific X5 Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Waltham, MA, USA). Before the analyses, the compounds were carefully mineralized by treating them with a mixture of nitric acid (5 mL) and hydrofluoric acid (5 mL) at 100 °C for 8 h.

CHN elemental analyses were accomplished with an EA3000 CHN Elemental Analyzer (EuroVector, Milano, Italy). Acetanilide, which was purchased by EuroVector (Milano, Italy), was used as the calibration standard (C% = 71.089, H% = 6.711, N% = 10.363).

Fourier-transform infrared spectroscopy (FT-IR) measurements were performed on a Bruker Equinox 55 Spectrometer operating in the 4000–400 cm^{-1} range with a resolution of 4 cm^{-1}. IR spectra of the solids mixed with potassium bromide (KBr) pellets were measured in absorbance mode at room temperature. The absorbance values are reported in absolute unit [a.u.].

X-ray powder diffractograms (XRPD) were collected on unoriented ground powders on a Bruker D8 Advance Powder Diffractometer, equipped with a Linxeye XE-T detector. The X-ray tube of the instrument operates with a Cu-K$_{\alpha 1}$ monochromatic radiation (λ = 1.54062 Å), with the current intensity and operative electric potential difference set to 40 mA and 40 kV, respectively, and with variable primary divergent slits and primary and secondary Soller slits of 2.5°. The X-ray profiles were recorded at room temperature in the 5–70° 2θ range with a coupled-2θ–θ method, fast and continuous scan mode, time per step/rate of 0.05°/min, increment/step size of 0.02° and with automatic air scatter and slits.

Photoluminescence (PL) spectra (excitation and emission) of the compounds at solid-state 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. Time-resolved measurements were carried out, instead, by using the time-correlated single-photon counting (TCSPC) option. A 370 nm SpectraLED laser was employed to excite the samples at solid-state and in H_2O and D_2O. The signal was collected using an IBH DataStation Hub photon counting module, while data analysis was accomplished with the commercial DAS6 software (HORIBA Jobin Yvon IBH Ltd., Glasgow, UK).

3. Results and Discussion

The two luminescent POSS, incorporating Tb^{3+} and a combination of Tb^{3+} and Eu^{3+} ions, were prepared by a one-step corner-capping reaction between the PhPOSS and the lanthanide precursors. The reaction was performed under simple conditions, in anhydrous solvent THF, in the presence of a small amount of TEA at 50 °C for 24 h. During the reaction, the four reactive Si-OH groups of PhPOSS reacted with lanthanide ions' reactants.

The Tb^{3+} and Eu^{3+} contents in both samples were determined by an inductively coupled plasma mass spectrometry (ICP-MS), while the amount of carbon was quantified by a CHN analysis (Table 1). The amount of Tb^{3+} ions was found to be 0.63 mmol/g and 0.26 mmol/g for Tb-PhPOSS and TbEu-PhPOSS, respectively, while the Eu^{3+} loading was equal to 0.30 mmol/g in the bimetallic POSS. The carbon content was equivalent to 42.24 mmol/g and 41.30 mmol/g for Tb-PhPOSS and TbEu-PhPOSS, respectively, in agreement with the chemical composition of the reactant PhPOSS. By combining the data obtained from the ICP and CHN analyses, it was possible to extrapolate the number of lanthanide ions per POSS cage. In detail, for Tb-PhPOSS, we calculated a molar ratio between the number of cages and the Tb^{3+} ion of 1.4. This could suggest that Tb-PhPOSS is composed by a polycondensed structure in which each Tb^{3+} is shared by two coordinated POSS cages (Figure 1). A similar result was obtained for TbEu-PhPOSS, considering for the quantification the total amount of the two lanthanide ions embedded in the structure (Figure 1).

Additional structural information on the metal-containing POSS samples was obtained by infrared spectroscopy. IR spectra of the samples, recorded in the 4000–400 cm^{-1} range, are reported in Figure 2. The vibrational profiles of Tb-PhPOSS and TbEu-PhPOSS are compared with the spectrum of PhPOSS sample.

**Table 1.** Amount of Tb^{3+}, Eu^{3+} and C elements (in mmol/g) in Tb-PhPOSS and TbEu-PhPOSS.

Sample	Tb^{3+} Content [mmol/g]	Eu^{3+} Content [mmol/g]	C Content [mmol/g]
Tb-PhPOSS	0.63	-	42.24
TbEu-PhPOSS	0.26	0.30	41.30

The IR spectrum of PhPOSS (Figure 2, a) shows the typical signals of phenyl groups at 3100–3000 cm^{-1} (stretching of C-H groups) and at 1595, 1490 and 1430 cm^{-1}, assigned to the stretching modes of C=C [100,106]. The main absorption of the POSS cage is detectable at 1100 cm^{-1}, and it is ascribed to the asymmetric stretching of the siloxane (Si-O-Si) groups of the inorganic framework [100,106,107]. Finally, the absorptions at 3250 and 895 cm^{-1} are characteristics of the stretching modes of OH and Si-OH functionalities, which are typical of partially condensed POSS molecules [100,106,107].

After reaction with the Tb^{3+} precursor (Figure 2, b) or the mixture of terbium and europium salts (Figure 2, c), the IR spectra of both solids show a complete erosion of the bands located at 3250 and 895 cm^{-1}, as a consequence of the condensation of Si-OH groups with the lanthanide ions. The bands of phenyl groups are still visible, proving that the organic groups attached to the POSS cage are preserved during the corner-capping reaction. Finally, it is worth noting that the band at 1100 cm^{-1} appears more defined and narrower with respect to the POSS reactant. This is undoubtedly indicative of an orderly and regular organization of the Si-O-Si network, promoted by the presence of the lanthanide ions during the condensation reaction. This comment is qualitatively supported by the X-ray powder diffraction (XRPD) data shown in Figure 3.
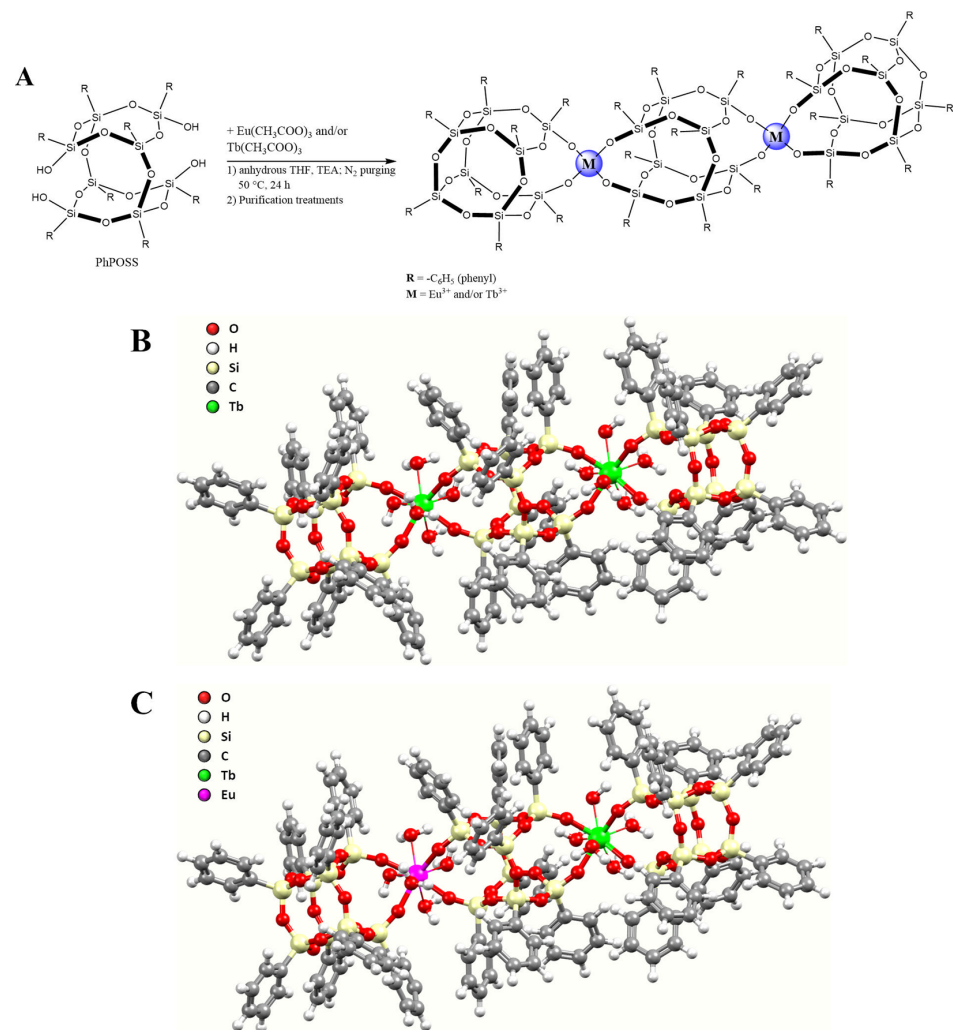
Figure 1. (**A**) Synthesis of metal-containing PhPOSS. Schematic view of a possible structure of Tb-PhPOSS (**B**) and TbEu-PhPOSS (**C**).
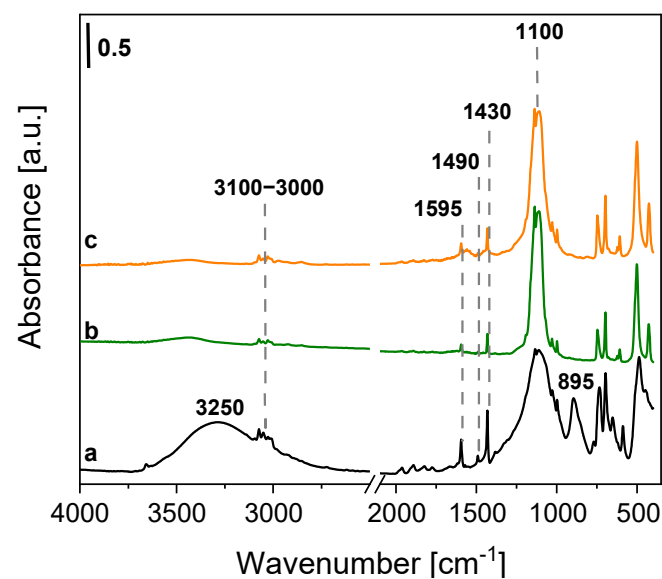
Figure 2. FT-IR spectra of PhPOSS POSS (a), Tb-PhPOSS (b) and TbEu-PhPOSS (c), collected in KBr matrix (10 wt%).
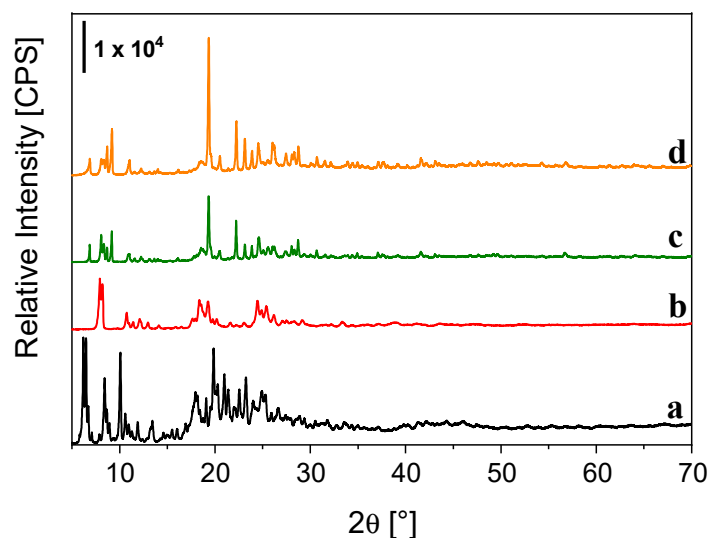
Figure 3. X-ray powder diffraction profiles of PhPOSS (a), the commercial condensed OctaPhenyl POSS (b), Tb-PhPOSS (c) and TbEu-PhPOSS (d). The diffractograms were collected in the 5–70° 2θ range.

The diffractogram of the PhPOSS is composed by well-resolved peaks in the 5–70° 2θ range, as is typically observed for crystalline POSS (Figure 3, a). After the corner-capping reaction, the X-ray profiles of Tb-PhPOSS and TbEu-PhPOSS show new well-defined peaks, and both profiles differ from that of PhPOSS and the analogous completely condensed OctaPhenyl POSS (Figure 3, b and Figure S2). The coordination of Tb^{3+} and Eu^{3+} ions promoted a different ordered structural arrangement of the POSS molecules with respect to the PhPOSS (Figure 3, c and d). Furthermore, the two diffraction patterns are comparable to each other, thus testifying that both Tb-PhPOSS and TbEu-PhPOSS have a similar crystallographic arrangement. More structural information can be obtained by single crystal X-ray diffraction, but, unfortunately, we did not obtain suitable crystals for the analysis. Furthermore, NMR analysis is difficult to apply to samples containing "shift agents".

The photophysical properties of the luminescent Tb-PhPOSS and TbEu-PhPOSS products were carefully investigated by photoluminescence (PL) spectroscopy. The excitation spectra at solid-state of Tb-PhPOSS (Figure S3) and TbEu-PhPOSS (Figure 4A), measured at the most intense emission line of terbium at 545 nm, are essentially composed by the characteristic peaks of the intra-$4f^8$ electronic transitions of Tb^{3+}, assigned to: $^7F_6$-^5D_J (J = 1–4), $^7F_6$-$^5I_8$, $^7F_6$-$^5F_{4-5}$, $^7F_6$-^5H_J (J = 4, 7), $^7F_6$-^5L_J (J = 7–10) and $^7F_6$-^5G_J (J = 3, 5, 6) [108–110]. The maximum absorption band of Tb^{3+} displayed in both samples is located between ca. 280–290 nm, and it was ascribed to a combination of $^7F_6$-5d and $^7F_6$-$^5I_8$/$^5F_{4-5}$/$^5H_4$ electronic transitions. The solid-state excitation spectrum of TbEu-PhPOSS, monitored at the most intense emission line of Eu^{3+} at 615 nm (Figure 4B), instead, showed (*i*) the presence of the same Tb^{3+} signals before indicated, and (*ii*) additional peaks ascribed to the intra-$4f^6$ electronic transitions of Eu^{3+} ($^7F_0$-^5H_J, $^7F_{0,1}$-^5D_J, $^7F_0$-^5G_J and $^7F_0$-^5L_J), with a λ_{max} at 395 nm ($^7F_0$-$^5L_6$) [108–111]. The presence of the Tb^{3+} transitions in Figure 4B represent a clear indication of the presence of a metal-to-metal energy transfer from $Tb^{3+} \rightarrow Eu^{3+}$ ions [110,112–114].
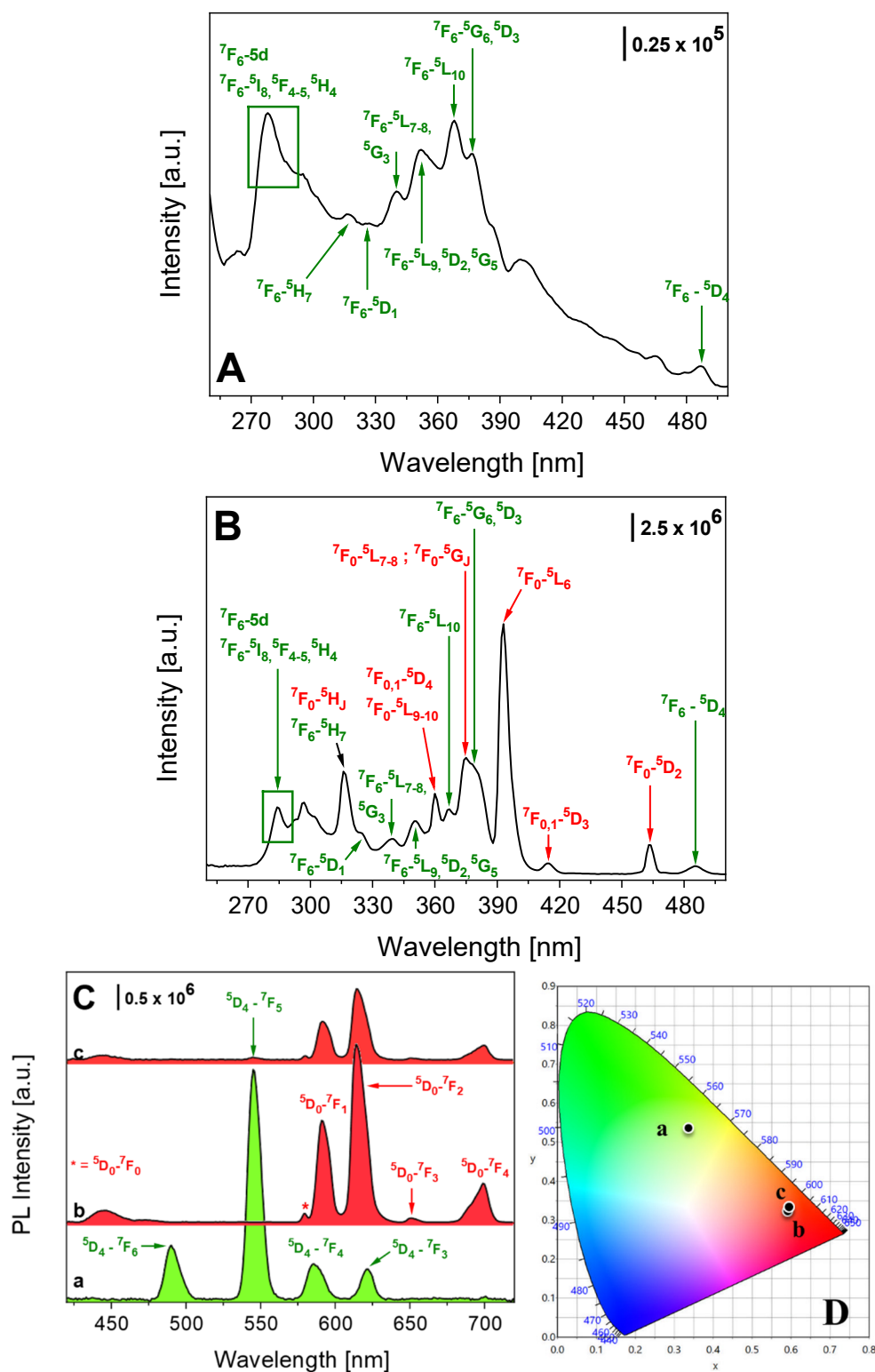
Figure 4. Excitation spectra at solid-state of TbEu-PhPOSS monitored at λ_{em} = 545 nm (**A**) and λ_{em} = 615 nm (**B**). (**C**) Emission spectra at solid-state of Tb-PhPOSS (a, λ_{exc} = 285 nm) and TbEu-PhPOSS (b, λ_{exc} = 395 nm, c, λ_{exc} = 285 nm). The electronic transitions of terbium are marked in green colour, while those assigned to europium are in red, for more clarity. (**D**) CIE 1931 xy chromaticity diagrams derived from emission spectra in frame (**C**). The colour of each emission spectrum in frame (**C**) is associated with its corresponding *xy* coordinates (frame (**D**) and Table S2).

Further confirmation of the energy transfer process was obtained by collecting the solid-state emission spectra of TbEu-PhPOSS under irradiation at the λ_{max} of Eu^{3+} at 395 nm (Figure 4C, b) and of Tb^{3+} at 285 nm (Figure 4C, c). The comparison with the photoluminescence spectrum of Tb-PhPOSS collected under excitation at 285 nm is reported in Figure 4C. The emission spectrum measured under excitation at 285 nm (Figure 4C, c) showed a very weak and broad emission peak at 545 nm, typical of Tb^{3+} ($^5D_4$-$^7F_5$) [108–110], together with the intense and characteristic emission bands of Eu^{3+} ($^5D_0$-^7F_J, $J = 0$–4), with the most intense line centred at 615 nm ($^5D_0$-$^7F_2$) [108–111]. The photoluminescence of Eu^{3+} under excitation of Tb^{3+}, coupled with a marked decrease in the intensity of the main emission band of Tb^{3+} at 545 nm, testifies to the occurrence of the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process because the two metals are in close proximity [110,112–114].

The nature of the local chemical environment around the lanthanide centres was extrapolated from the emission spectra shown in Figure 4C. First, the Eu^{3+} sites appear to be heterogeneously distributed in the TbEu-PhPOSS sample, due to the presence of two weak peaks assigned to the $^5D_0$-$^7F_0$ electronic transition at 579 and 580 nm (Figure S4). This assumption is based on the fact that the number of distinct chemical domains around Eu^{3+} can be correlated to the multiplicity of the $^5D_0$-$^7F_0$ band, since its initial and final energy states are both non-degenerated [115]. In addition, the Eu^{3+} and Tb^{3+} ions in both solids are placed in a low symmetry environment with no inversion centre, as extrapolated by the high asymmetry factor (R) values between $1.4 \div 1.8$ for europium and $1.0 \div 4.3$ for terbium (Table S1). The decrease in the R parameter from ca. 4.3 for Tb-PhPOSS (Figure 4C, a) to ca. 1.1 of TbEu-PhPOSS (Figure 4C, c), both under excitation at 285 nm, represents other evidence of the energy transfer process. The R factor was calculated from the intensity ratio of the electric-dipole $^5D_0 \rightarrow ^7F_2$ on the magnetic-dipole $^5D_0 \rightarrow ^7F_1$ for europium [116,117], while for terbium the ratio is $^5D_4 \rightarrow ^7F_5/^5D_4 \rightarrow ^7F_6$ [118].

The photometric features of the Tb-PhPOSS and TbEu-POSS solids were obtained from their respective emission spectra, calculating the *xy* chromaticity coordinates and related Hex and RGB parameters according to CIE 1931 colour spaces (Figure 4D and Table S2) [119]. The direct excitation of Eu^{3+} sites at 395 nm in TbEu-PhPOSS led to a red emission colour (point b in Figure 4D), and, after excitation at 285 nm (λ_{max} of Tb^{3+}), the bimetallic sample showed a very small blue-shift of its emission towards a slightly more orange–red colour (point c in Figure 4D). For reference, the colour associated with the emission of Tb-PhPOSS is light green (point a in Figure 4D).

The average hydration state of Tb^{3+} ions (q^{Tb}) in the Tb-PhPOSS and of Eu^{3+} ions (q^{Eu}) in the TbEu-PhPOSS were estimated by measuring, via time-resolved fluorescence spectroscopy, the experimental lifetimes (τ) associated with the transitions at 545 and 615 nm, respectively, in H_2O and D_2O under excitation at 370 nm. The q^{Ln} values for Tb^{3+} and Eu^{3+} were calculated by applying the following Equations (1) and (2) [120–123].

$$q^{Eu} = 1.20 \cdot (1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.25) \tag{1}$$

$$q^{Tb} = 4.26 \cdot (1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.06) \tag{2}$$

The photoluminescence decay curves of the $^5D_4$ excited state of Tb^{3+} (Figure S5A,B) and $^5D_0$ excited state of Eu^{3+} (Figure S5C,D), fitted with a bi-exponential function, suggest the presence of ca. five water molecules in the first coordination sphere of both lanthanide ions (Table S3). The results are consistent with the hypothetical structure of the samples described before, considering that the two lanthanide ions can easily expand their coordination sphere up to coordination number values of 8–9 [108,124].

The Tb^{3+}-Eu^{3+} energy transfer mechanism was analysed in more detail by collecting the lifetime values (τ) at solid-state of Tb-PhPOSS (donor system, D) and TbEu-PhPOSS (donor-acceptor system, DA). The intensity decay curves of $^5D_4$ excited state of Tb^{3+} were measured for both samples at λ_{em} of 545 nm, under excitation at 370 nm (Figure S6). The curves were well fitted with a bi-exponential function, and, from these, the average τ values were derived. The energy transfer efficiency (E_{EnT}) and rate (k_{EnT}) parameters were then

calculated by using the average lifetimes measured at 545 nm of the donor ion (Tb^{3+}) in the presence (τ_{DA}, Figure S6B) or absence (τ_D, Figure S6A) of the acceptor one (Eu^{3+}), by using Equations (3) and (4) [112,113,125,126].

$$k_{EnT} \left[s^{-1} \right] = \left(\frac{1}{\tau_{DA}} - \frac{1}{\tau_D} \right) \tag{3}$$

$$E_{EnT} \left(o \, \eta_{sens} \right) [\%] = \left(1 - \frac{\tau_{DA}}{\tau_D} \right) \cdot 100 \tag{4}$$

The results, reported in Table 2, showed a $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer efficiency value of ca. 62%, with a rate constant of the process equal to 4.09×10^3 s^{-1}, comparable to those observed for other inorganic materials functionalized with both Tb^{3+} and Eu^{3+} ions [110,112,114,127].

Table 2. Experimental lifetimes (τ) of Tb-PhPOSS (D) and TbEu-PhPOSS (DA), collected by monitoring the main emission of Tb^{3+} at 545 nm ($^5D_4$-$^7F_5$ electronic transition) under irradiation at 370 nm. The $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer rate (k_{EnT}) and efficiency (E_{EnT}) parameters are also reported.

τ_D [s]	τ_{DA} [s]	k_{EnT} [s^{-1}]	E_{EnT} [%]
3.88×10^{-4}	1.50×10^{-4}	4.09×10^3	61.34

4. Conclusions

In this study, novel completely condensed luminescent double-decker POSS solids functionalized with Tb^{3+} and a combination of Tb^{3+} and Eu^{3+} ions were prepared by a simple one-pot corner-capping reaction under mild conditions. The synthetic protocol adopted in this work allows for obtainment of a polycondensed POSS with the following properties: (*i*) ordered architecture of the POSS structure; (*ii*) a well-defined molar ratio of cage units and the lanthanide ions in both samples; (*iii*) each lanthanide ion is connected to different POSS cages with an expansion of the coordination state with five inner sphere water molecules; (*iv*) tunable emission properties for the bimetallic POSS and (*v*) remarkable energy transfer from the Tb^{3+} to Eu^{3+} centers in terms of efficiency and the process rate. The optical properties of both Tb-PhPOSS and TbEu-PhPOSS solids make them ideal candidates for the fabrication of novel optical thermometers and sensor devices. Further studies are currently underway to evaluate the effect of the reaction's stoichiometry on the structure and chemical composition of the final samples.

obtained from the experimental lifetimes (*t*) measured in H$_2$O and D$_2$O. The lifetimes were collected at 545 nm for terbium and 615 nm for europium, under excitation at 370 nm with a SpectraLED source.

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