

Smart grafting of lanthanides onto silica via *N,N*-dialkylcarbamato complexes

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ABSTRACT:

The grafting and the post-grafting functionalization of lanthanide ions on commercial amorphous silica have been herein carried out by using as precursor the terbium *N,N*-dibutylcarbamato derivative [Tb(O₂CNBU₂)₃]. The reaction of the complex with the surface silanols involved only a fraction of the carbamato ligands. The following protolytic substitution of the residual carbamato ligands was carried out by exploiting the Brønsted's acidity of a β-diketone, dibenzoylmethane (Hdbm), in view of the “antenna” effect of the β-diketonato groups, which are commonly used in lanthanide photoluminescence studies. The reaction proceeded at room temperature in a clean and easy way affording the introduction of the chosen functionality in the lanthanide coordination sphere.

The same procedure has been followed by using as precursor the X-ray characterized heterometallic *N,N*-dibutylcarbamato complex [NH₂BU₂]₂[Ln₄(CO₃)(O₂CNBU₂)₁₂] (Ln = Eu, Tb, Tm). In both cases, XPS evidenced the chemical implantation of the lanthanide ions on the silica surface, and photoluminescence studies pointed out the potentiality of the proposed synthetic approach in the preparation of highly luminescent materials.

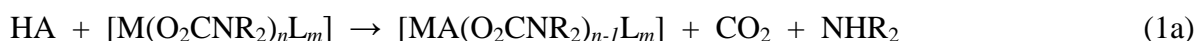
INTRODUCTION

Lanthanide ions play a relevant role in chemistry, both in fundamental and applied research,¹ and also in the advancement of new technologies, where their peculiar electronic properties are exploited, for instance, in the field of superconductors and magnetic materials,² luminescent sensors,³ contrast and shift reagents in NMR spectroscopy.⁴

The grafting of metal ions onto the surface of supports like silica, alumina, ceramics in general or resins is an important route to the preparation of materials exploiting the features of the loaded metal ions, for instance their catalytic, magnetic, and photoluminescence properties. The formation

of robust bonds between the surface atoms of the carrier and the metal ions assures a good resistance of the material against the metal release. When silica is used as the support, surface silanols easily react with metal complexes that undergo protolytic ligand substitution, allowing the formation of strong O–M bonds.⁵

In previous works we have described the grafting of a few metals (Sn, Cu, Ni, Pd, Pt, Au) onto silica or resin surfaces using *N,N*-dialkylcarbamato complexes $[M(O_2CNR_2)_nL_m]$ as precursors.⁶ The use of these derivatives, which with an appropriate choice of R groups are rather soluble in non-polar solvents, can be a convenient alternative to the methods based on organometallics,^{5,7} as they show a prompt reactivity towards molecular protic agents, $HA^{8\ 6f}$ (eq 1a), or Brønsted's acid sites on the surface of suitable materials (eq 1b).⁹

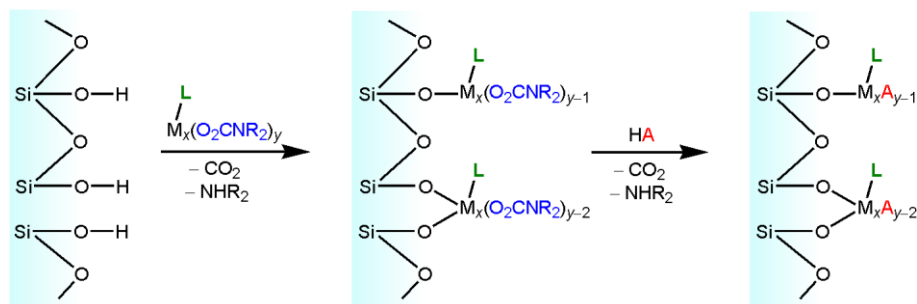


represents the deprotonated support surface

The reaction of the carbamato complexes with the surface protic functionalities produces CO_2 and NHR_2 . If a complete transfer of the metal to the carrier surface is achieved, the gas-volumetric measurement of the evolved CO_2 supplies information about the number of the support-metal bonds that have been formed and consequently, about the number of carbamato ligands that remain coordinated to the grafted metal centers. The geometry of the parent metal complex, its hindrance, its nuclearity and the silanol distribution on the silica surface play a role on the number of M–support bonds that are formed and, as a consequence, on the number of the residual carbamato ligands, as evidenced by previous studies on gold(I), $[Au(O_2CNEt_2)(PPh_3)]$,^{6f} palladium(II), $[trans-Pd(O_2CNEt_2)_2(NHEt_2)_2]$,^{6b} and tin(IV), $[Sn(O_2CN^iPr_2)_4]$ ^{6h} complexes.

The maintenance of easily displaceable ligands in the coordination sphere of the loaded metal is indeed attractive, because they can be involved in subsequent processes.^{5a}

So far, no data have been described about the exploitation of the residual carbamato ligands on the metal centers after the grafting procedure. A prompt reaction with protic agents is expected to afford the functionalization of the silica surface by a sequential approach (Scheme 1), as previously reported for metal silylamide grafting.^{5a}



Scheme 1. Grafting of a metal carbamate complex to a surface followed by further functionalization. L represents possible additional ligands.

In this paper we report the grafting of terbium ions onto the silica surface exploiting the reactivity of the terbium *N,N*-dibutylcarbamate, $[\text{Tb}(\text{O}_2\text{CNBu}_2)_3]$. This species is easily obtained by extraction of metal ions from aqueous solution into hydrocarbons containing a lipophilic secondary amine saturated with CO_2 ,¹⁰ a method recently extended to lanthanides of the first part of the rare earth series (Nd, Sm, Eu, Tb) with formation of complexes of formula $[\text{Ln}(\text{O}_2\text{CNBu}_2)_3]$, $[\text{NH}_2\text{Bu}_2]_2[\text{Ln}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{12}]$ and $[\text{Ln}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$.¹¹ Once anchored, the residual carbamate ligands have been substituted by β -diketonato ligands, able to act as sensitizer for lanthanide emission.

The reactivity here described exemplifies the possible introduction of novel functionalities on a support through a simple protolysis of the lanthanide-carbamato ligand bonds. With the aim to extend the process to the simultaneous functionalization of silica with different lanthanide ions in a known molar ratio exploiting only one grafting reaction, the tri-metallic ($\text{Eu}^{3+}/\text{Tb}^{3+}/\text{Tm}^{3+}$ in 1/1/1 molar ratio) *N,N*-dibutylcarbamato complex, $[\text{NH}_2\text{Bu}_2]_2[\text{Ln}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{12}]$, has been prepared and characterized. Its silica-grafting and the further functionalization of the material so obtained, according to the procedure carried out with the terbium derivative, are reported. The lanthanide loaded silica samples have been studied by XPS analysis and photoluminescence (PL) measurements.

EXPERIMENTAL SECTION

Materials and Instrumentation. Commercial europium, terbium and thulium oxides $[\text{Eu}_2\text{O}_3]$ (Strem Chemicals, 99.99 %); $[\text{Tb}_4\text{O}_7]$ (Strem Chemicals, 99.9 %), $[\text{Tm}_2\text{O}_3]$ (Apollo, 99.9%) were used without further purification. Aqueous solutions of the lanthanide chlorides were prepared by dissolving the appropriate metal oxide in diluted hydrochloric acid. The solution was then evaporated to dryness and the solid residue was dissolved in water. $[\text{Tb}(\text{O}_2\text{CNBu}_2)_3]$ was prepared according to the literature.¹¹ $[\text{Tm}(\text{O}_2\text{CNBu}_2)_3]$ was prepared in a similar way (see S1).

All manipulations after extraction were performed in anhydrous conditions under a dinitrogen or CO₂ atmosphere, as specified. ATR-FTIR spectra in the solid state were recorded with a Perkin-Elmer “Spectrum One” spectrometer, with ATR technique. The carbon dioxide evolution was measured by a gas volumetric apparatus substantially similar to that previously described by Cotton and Calderazzo.¹²

Volumetric analyses of the lanthanide content via EDTA complexometry were carried out on the aqueous layer discarded after extraction and on the filtrates of the grafting and functionalization processes.¹³ Commercial silica (Grace, EP 17G, surface area 325m² g⁻¹, pore volume 1.82 cm³ g⁻¹) was treated at 160 °C over P₄O₁₀ for 12 h *in vacuo* up to a constant weight and then stored in flame-sealed vials under an atmosphere of dry N₂. On the basis of our past experience this type of pre-treatment eliminates most of the hydrogen-bonded water from the surface, leaving most of the hydroxyl groups ≡Si–OH, which are chemically reactive towards the metal precursor. The total silanol content (typically, between 2.8 and 3.1 mmol g⁻¹) was estimated from the mass loss upon further heating at 850 °C.

SEM-EDX analyses were carried out on a Philips XL 30 instrument. Samples, suspended in acetone, were dispersed on a glass where, after solvent evaporation, were metalized twice with graphite.

XPS analysis was performed to assess the sample surface chemical composition. Experiments were run on a Perkin–Elmer Φ5600-ci spectrometer using non-monochromatized Al Kα radiation (1486.6 eV). The sample analysis area was 800 μm in diameter, and the working pressure was lower than 10⁻⁹ mbar. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f_{7/2} line at 83.9 eV with respect to the Fermi level. The standard deviation for the BEs values was ± 0.2 eV. Survey scans were obtained in the 0–1300 eV range. Detailed scans were recorded for the C1s, O1s, N1s, Si2p, Tm4d, Eu3d and Tb3d regions. No further element was detected. The BE shifts were corrected by assigning to the C1s peak associated with adventitious hydrocarbons a value of 284.8 eV.¹⁴ Samples were mounted on steel holders and introduced directly in the fast-entry lock system of the XPS analytical chamber. The analysis involved Shirley-type background subtraction, non-linear least-squares curve fitting adopting Gaussian–Lorentzian peak shapes, and peak area determination by integration.¹⁵ The atomic compositions were evaluated from peak areas using sensitivity factors supplied by Perkin–Elmer, taking into account the geometric configuration of the apparatus.¹⁶

The luminescence spectra were recorded on solid samples at room temperature in a front-face acquisition geometry with a spectrofluorimeter (Fluorolog-3, Horiba Jobin Yvon) equipped with double-grating monochromator in both the excitation and emission sides coupled to a R928P

Hamamatsu photomultiplier and a 450 W Xe arc lamp as the excitation source. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter supplied by the manufacturer. The excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector.

Syntheses, grafting and functionalization

Grafting of [Tb(O₂CNBu₂)₃], 1, on silica and treatment with Hdbm. A colorless solution of [Tb(O₂CNBu₂)₃], (1.91 g; 2.83 mmol) in toluene (150 mL) was reacted under dinitrogen atmosphere with SiO₂ (8.26 g; 0.34 mmol of Tb per gram of silica). The suspension was stirred for 4 h repeating vacuum/dinitrogen cycles and then was filtered. The solid was washed with toluene (2 × 20 mL) and dried *in vacuo* at RT. The product was labeled as **SIL1**. ATR-FTIR: 1517, 1434, 1380, 1323 cm⁻¹. The metal content of the colorless filtrate was under 1% of the initial metal. The product was characterized by XPS and PL measurements. The grafting procedure was repeated using 1.63 mmol of Tb per gram of silica. In this case the quantitative analysis of the metal in the filtrate corresponded to 41 % of the initial amount.

The gas-volumetric monitoring of the reaction was also carried out. A sealed glass ampoule with solid [Tb(O₂CNBu₂)₃] (0.36 g; 0.53 mmol) was introduced in a flask containing a suspension of SiO₂ (2.67 g, 0.20 mmol of Tb per gram of silica) in toluene (50 mL) saturated with carbon dioxide connected to a gas-volumetric apparatus. Once the thermal equilibrium was established, the glass ampoule was broken and carbon dioxide evolution was monitored (0.39 mmol, CO₂/Tb molar ratio 0.74).

Reaction of SIL1 with Hdbm. A sample of silica functionalized with terbium, **SIL1**, (2.03 g; *ca* 0.69 mmol of Tb) was suspended in toluene (50 mL) and reacted with Hdbm (0.45 g, 2.00 mmol). The suspension turned light-yellow with carbon dioxide evolution. After 12 h stirring, regularly repeating vacuum-dinitrogen cycles, the suspension was filtered and the solid was washed with toluene (2 × 20 mL), dried *in vacuo* at RT for 6 h and labeled as **SIL1dbm**. ATR-FTIR: 1597, 1552, 1518, 1478, 1424 cm⁻¹. The product was characterized by XPS and PL measurements. The colorless filtrate was evaporated *in vacuo* to dryness at 35 °C. The colorless residue (0.16 g; 0.71 mmol) was identified through IR spectroscopy as free Hdbm.

Synthesis of [NH₂Bu₂]₂[Eu_{4/3}Tb_{4/3}Tm_{4/3}(CO₃)(O₂CNBu₂)₁₂], 2. A solution of dibutylamine (12.6 mL, 74.8 mmol) in heptane (50 mL) was saturated with carbon dioxide and then added to 20 mL of an aqueous solution containing europium chloride (2.02 mmol) terbium chloride (1.99 mmol) and thulium chloride (2.08 mmol) at 0 °C. After the extraction procedure, the organic layer was evaporated at reduced pressure, and the colorless residue dissolved in anhydrous heptane (20 mL)

and cooled at -30°C . A crystalline compound was recovered (1.91 g; 42 % yield). Single crystal data: orthorhombic, space group *Cmca*, cell parameters $a = 32.714(4)$, $b = 17.560(2)$, $c = 28.215(4)$ Å, $V = 16208(6)$ Å³. It appears to be isotypical with the orthorhombic phases of the analogues homometallic complexes of samarium, and terbium.¹¹ ATR-FTIR (bands in the range 1700-1250 cm^{-1}): 1586, 1487, 1423, 1375, 1313. SEM-EDX analysis on several single crystals showed a molar ratio Tm/Tb/Eu of about 1:1:1. The product was characterized by XPS and PL measurements.

*Grafting of $[\text{NH}_2\text{Bu}_2]_2[\text{Eu}_{4/3}\text{Tb}_{4/3}\text{Tm}_{4/3}(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{12}]$, **2**, to silica.* A solution of **2** (0.73 g; 0.24 mmol, 0.96 mmol of Ln) in toluene (50 mL) was added to a suspension of SiO_2 (2.72 g; 0.35 mmol of Ln per gram of silica) in toluene (100 mL). The suspension was stirred for 4 h repeating vacuum/dinitrogen cycles and then was filtered. The solid was washed with toluene (2×20 mL) and dried *in vacuo* at RT. It was labeled as **SIL2**. ATR-FTIR (bands in the range 1700-1250 cm^{-1}): 1525, 1436, 1380, 1317. The colorless filtrate did not contain appreciable amounts of lanthanide. The loaded silica was characterized by XPS and PL measurements.

*Reaction of **SIL2** with Hdbm.* A sample of **SIL2** (2.00 g; *ca* 0.70 mmol of Ln) was suspended in toluene (100 mL) and reacted with Hdbm (0.36 g, 1.61 mmol). Carbon dioxide evolution from the yellow suspension was observed. After 24 h stirring, regularly repeating vacuum-dinitrogen cycles, the suspension was filtered and the solid was washed with toluene (2×20 mL) and dried *in vacuo* at RT for 6 h. The product was labeled as **SIL2dbm**. ATR-FTIR (bands in the range 1700-1250 cm^{-1}): 1599, 1553, 1520, 1480, 1457, 1406. The colorless filtrate did not contain appreciable amounts of lanthanide. **SIL2dbm** was characterized by XPS and PL measurements.

RESULTS AND DISCUSSION

Grafting of lanthanide ions onto silica surface.

The grafting of $[\text{Tb}(\text{O}_2\text{CNBu}_2)_3]$ onto silica surface have been carried out in toluene at room temperature, under dinitrogen for preparative purposes, or under CO_2 when the aim was the quantitative control of the carbon dioxide evolution. In the latter case a large excess of silica was used to assure a complete transfer of the metal ions onto silica. Moreover, the use of a large excess of silica guarantees that the released amine is blocked by the silanols, so avoiding its involvement in equilibria with CO_2 .

In our previous grafting experiences involving dialkylcarbamato complexes as precursors, we have studied the CO_2 evolution from a quantitative point of view only for mononuclear complexes. In the case of $\text{Au}(\text{O}_2\text{CNEt}_2)(\text{PPh}_3)$,^{6f} for each molecule only one carbamato group is available to react

with the protic sites of the material surface and the gas-volumetric control revealed the evolution of one mole of CO₂ per mol of precursor, as expected. Also with *trans*-Pd(O₂CNEt₂)₂(NHEt₂)₂,^{6b} in spite of the presence of two carbamato ligands per molecule, only one mole of CO₂ per mol of precursor was released, probably for the unfavorable geometrical position of the two ligands. With Sn(O₂CNⁱPr₂)₄, where the metal center is octa-coordinated (each carbamato ligand is bidentate) the evolution of about 1.5 moles of CO₂ per mol of tin was observed.^{6h} The subsequent treatment of the tin or palladium containing silicas with acetic acid led to the evolution of additional CO₂, in the amount consistent with the residual carbamato ligands. These data demonstrated that: a) more than one carbamato group per molecule can react with the silanols, probably in dependence of the precursor geometry and of the OH proximity on the support surface and, b) after grafting residual carbamato groups can be maintained in the metal coordination sphere, c) the residual carbamato ligands are able to react with protic reagents.

According to its HRMS spectrum,¹⁰ the terbium complex appears to be tetranuclear in solution, hypothesis corroborated by the X-Ray characterization of the series of isostructural derivatives [Ln₄(O₂CNⁱPr₂)₁₂].¹⁷

The terbium grafting with **1** as precursor was monitored by gas-volumetric control of the CO₂ evolution. The experiment, carried out with a silanol/terbium molar ratio of 15.1 (1 gram of silica contains about 3 mmols of silanols), showed the evolution of about 0.74 mol of CO₂ per mol of terbium. The subsequent treatment of the functionalized silica with protic agents was accompanied by effervescence due to the evolution of CO₂ from the residual carbamato ligands.

The preparation of terbium functionalized silica was performed in toluene under N₂ with silanol/lanthanide molar ratio about 9. The terbium containing silica was labeled as **SIL1**. The lanthanide transfer to the silica surface was nearly quantitative as only a negligible amount of terbium was present in the solvent after the grafting procedure. In view of both the mild conditions adopted in the process and the non-coordinating nature of the solvent, the precursor nuclearity could be preserved after grafting on the matrix surface. When the process was carried out with a silanol/lanthanide molar ratio about 2, terbium was not completely transferred to the silica, but the metal left in the filtrate was about 41 % of the one initially used, corresponding to a maximum capacity of loading of about 1 millimol of terbium per gram of silica.

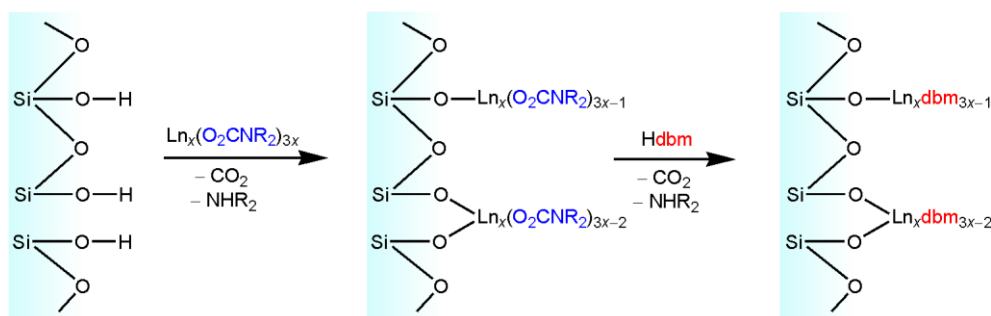
The FTIR of **SIL1**, recorded by ATR technique, showed typical absorptions in the 1600–1300 cm⁻¹ region attributable to residual carbamato ligands.

With the intent of modifying the doped silica samples through substitution of the residual carbamates with ligands functional to the photoluminescence of the metal centers, we decided to use a β-diketone as a protolytic reagent, since β-diketonate complexes have been extensively used

to enhance the luminescence of lanthanide ions.¹⁸ Although the reactivity of metal carbamato complexes towards protic reagents has been widely demonstrated;⁹ a preliminary study of the reaction between a lanthanide carbamato complex and the selected β -diketone, dibenzoylmethane, Hdbm, was carried out to confirm that the diketone, a weak protic acid ($pK_a = 8.95$), was effectively able to displace the carbamato ligands. The reaction proceeded smoothly with complete substitution of the carbamato ligands and formation of $[\text{NH}_2\text{Bu}_2][\text{Tb}(\text{dbm})_4]$, (eq 2). Further treatment of the product afforded crystals of the mononuclear complex $[\text{Tb}(\text{dbm})_3(\text{DME})]$ that was characterized by X-ray diffraction measurements (see SI).



The reaction of **SIL1** with Hdbm was carried out by using a moderate excess of Hdbm. It occurred with CO_2 evolution, so obtaining a material labeled as **SIL1dbm**. The FTIR-ATR spectra of the sample showed typical absorptions in the $1600\text{--}1400 \text{ cm}^{-1}$ region attributable to the β -diketonato ligands.



Scheme 2. Grafting of a lanthanide carbamato complex to a surface followed by reaction with Hdbm.

It is worth to note that the treatment with Hdbm did not produce leaching of the anchored lanthanide, as inferred by a control of the metal concentration in the filtrate of the reaction mixture. Moreover, at the end of the reaction the unreacted excess of Hdbm was recovered by evaporation of the filtrate and characterized by IR spectroscopy, so confirming that the β -diketone was not able to detach the metal from the silica surface.

The successful anchoring of terbium ions onto silica surface followed by modification of the metal coordination sphere urged us to try the synthesis of a multi-lanthanide species, with a defined molar ratio among the metals, with the aim to use it as precursor in the grafting process. Such a product could allow the one-pot transfer to silica of different lanthanide ions in a known molar ratio, so avoiding consecutive grafting steps of the single metal ions, quantitatively difficult to control. The

previously described procedure of lanthanide ion extraction from aqueous solution into hydrocarbons via the use of the $\text{NH}_2\text{Bu}_2/\text{CO}_2$ system^{10,11} was exploited for the preparation of a species containing Eu, Tb and Tm. With respect to the lanthanides for which successful extraction has been previously described,¹¹ thulium is characterized by a smaller ionic radius and consequently by a higher charge density that could favor hydrolysis processes. In spite of this, an experiment carried out with thulium produced $[\text{Tm}(\text{O}_2\text{CNBu}_2)_3]$ (SI), analogously to the terbium and europium cases.¹¹

By applying the protocol of lanthanide extraction to an aqueous solution containing the Eu^{3+} , Tb^{3+} and Tm^{3+} ions in molar ratio 1:1:1, crystals of $[\text{NH}_2\text{Bu}_2]_2[\text{Ln}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{12}]$, **2**, were obtained (Ln_4 approximately $\text{Eu}_{4/3}\text{Tb}_{4/3}\text{Tm}_{4/3}$). X-Ray diffraction measurements showed that the product was isotypical with the analogous homo-metal complexes of samarium and terbium that had been previously structurally characterized (Fig. 1).¹⁰

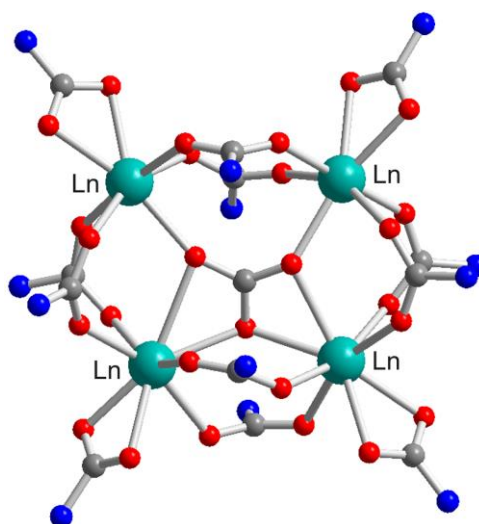


Figure 1. The bonding layout in the core of crystal structure of the anionic metallic complex. C, O and N atoms grey, red and blue, respectively. Alkyl residues on N atoms have been omitted.

Some crystals were analyzed by Energy-Dispersive X-ray Spectroscopy: the metal molar ratios in the compound correlated with those used in the synthesis. Although it was not possible to deduce if we were dealing with a mixture of homo-metal tetranuclear molecules or, most likely, with a statistical distribution of the different lanthanides in the molecules, the composition of the product appears to be dictated by the stoichiometry of the reaction.

The functionalized silica **SIL2** containing the three metals was prepared by grafting **2** to silica according to the indication of the maximum capacity of loading of our support inferred by the experiments carried out with the terbium precursor. The essentially complete transfer of the metal centres to the silica surface was evidenced by a control of the lanthanide content in the filtrate. In view of the structure of **2**, it is reasonable to suppose that some of the carbamate ligands, which are peripheral, are involved in the protolytic grafting process, rather than the central carbonate connecting the four metal centers, whose presence could favour the maintenance of the precursor nuclearity. As in the case of **SIL1**, **SIL2** was further functionalized by treatment with dibenzoylmethane (Hdbm) to afford **SIL2dbm**.

The successful grafting of **1** and **2** to the silica surface with maintenance of residual carbamate ligands displaced in a second step by reaction with Hdbm (Scheme 2) resulted also from XPS and PL measurements carried out on **SIL1**, **SIL2**, **SIL1dbm** and **SIL2dbm**.

XPS measurements.

The chemical composition of the terbium complex **1**, of **SIL1** and **SIL1dbm** silica-based materials was investigated by XPS. In Figure 2 we compare the survey spectra of $\text{Tb}(\text{O}_2\text{NBU}_2)_3$ and of silica samples after complex grafting and after ligand exchange.

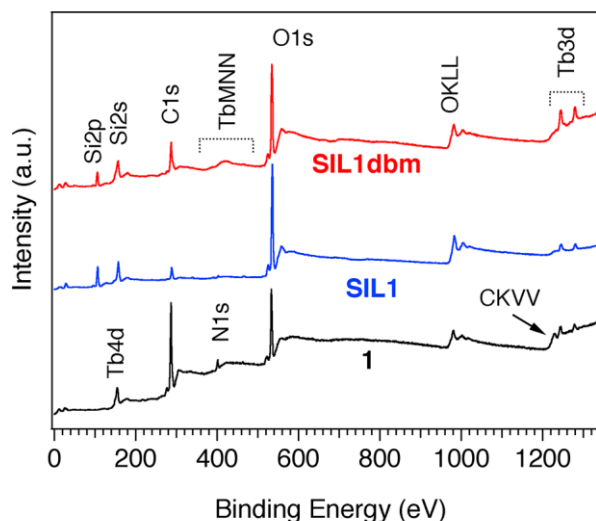


Figure 2 Survey spectra of **1**, **SIL1** and **SIL1dbm**. The principal bands are labeled in the figure.

XPS evidences the presence of C, O, N, and Tb related signals. The N1s peak is well visible for terbium carbamate **1** and its intensity clearly decreases after grafting on the silica surface. It is no longer detectable in **SIL1dbm**. This trend is in agreement with schemes 1 and 2 evidencing the loss of the carbamate moieties due to the grafting and ligand exchange reactions. It is worth noticing

that, the nitrogen loss related to the $\text{Tb}(\text{O}_2\text{NBU}_2)_3$ grafting reaction is not easily quantifiable by XPS due to the partial overlap between the nitrogen N1s peak and Tb^{3+} MNN Auger signal¹⁹ thus hampering its quantitative determination. Where present, the N1s signal is centered at 399.5 eV, a position typical for nitrogen in organic or metal organic environment.^{14,19}

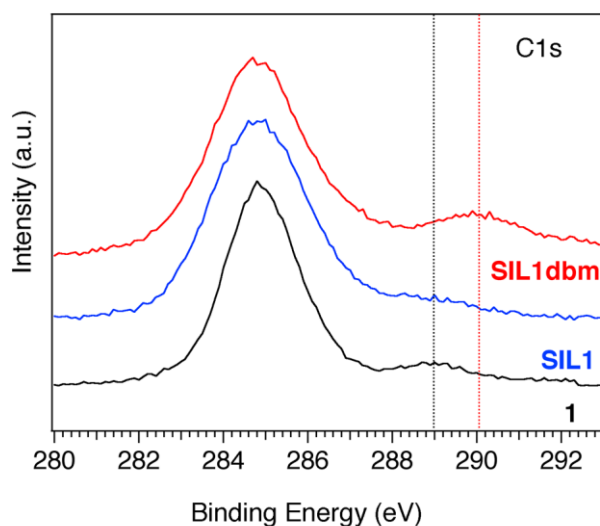


Figure 3. C1s peaks for **1**, **SIL1** and **SIL1dbm**. The two vertical dotted lines indicate the positions of the signals belonging to oxidized carbon in $\text{Tb}(\text{O}_2\text{CNBU}_2)_3$ (black line) and in the silica based materials after ligand exchange with Hdbm (red line).

Regarding carbon, more interesting is the shape variation of the C1s photoelectron peak in the different samples. In the *N,N*-dialkylcarbamato complex, the C1s signal shows two different contributions at 284.8 and 288.5 eV, attributed to aliphatic/adventitious carbon and to oxidized carbon species respectively.¹⁹ The minor component on the high BE side is correlated to the carbamato moieties of the organic ligands. The grafting reaction involves the interaction between acid sites at the silica surface with carbamato groups with release of CO_2 and NHR_2 as reaction products. In this way the content of oxidized carbon is reduced as evidenced from the decreased intensity of the high binding energy signal in the C1s (Figure 3). Finally, after ligand exchange with Hdbm, the C1s signal of the carbamato groups is no longer detectable due to the replacement with dbm units. Accordingly, a new signal is observable at higher binding energy related to the carbonyl groups of the coordinated β -diketone.

An analogous behavior has been observed for the trimetallic complex **2**, **SIL2** and **SIL2dbm** indicating a similar reactivity for the two species toward grafting on the silica surface and ligand exchange. In this samples set, in addition to the signals of C, N, O, Si and Tb, also the photoelectron peaks of Eu^{3+} and Tm^{3+} are detected.

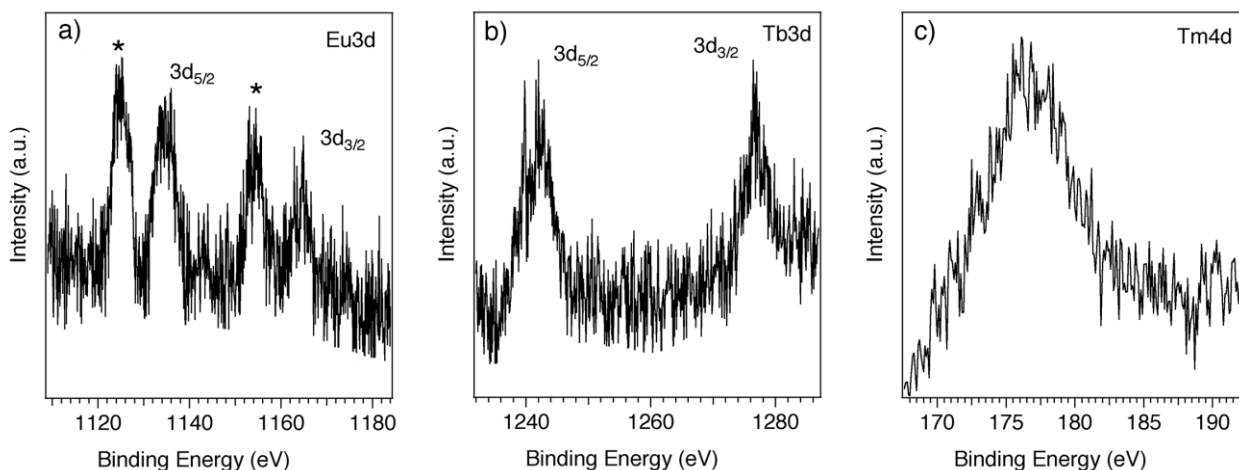


Figure 4. a) Eu3d, b) Tb3d and c) Tm4d XPS peaks of sample **SIL2dbm**. For the star labeled peaks see text

The main photoelectron peaks of Eu^{3+} , Tb^{3+} , and Tm^{3+} do not show modifications in their profile and positions in the different samples. They are reported in Figure 4. Their BE values ($\text{Tm4d} \approx 177$ eV; $\text{Tb3d} \approx 1242$ eV, $\Delta_{\text{SO}} \approx 35$ eV; $\text{Eu3d} \approx 1134$ eV, $\Delta_{\text{SO}} \approx 31$ eV) and shapes are consistent with the presence of oxygen-coordinated trivalent cations.²⁰ The Eu3d region (Figure 3d) showed four peaks in the 1110-1170 eV range. Besides the peaks due to the splitting of the Spin-Orbit (SO) $j = 5/2$ and $3/2$ components, two further peaks are present at the low binding energy side of each SO component. Core-level photoemission spectra of the light rare-earth compounds exhibit, in addition to the well-known spin-orbit multiplet splitting, a characteristic satellite structure that mainly has been attributed to final state effects and/or to charge-transfer coexcitations, principally from O_{2p} to RE_{4f} for lanthanide cations having a partially occupied 4f subshell.^{20a,21} In general, high binding energy (*shake-up*) and low binding energy (*shake-down*) satellites can be identified. In the case of Eu^{3+} compounds, the satellite structure visible in the spectra reported in Figure 3d is attributed to *shake-down* processes. The energy separation between each satellite and the main spin-orbit split component (*ca.* 10 eV) is in agreement with data reported for Eu^{3+} .^{20a,21}

Photoluminescence Studies.

The grafting and ligand exchange reactions have been investigated also by photoluminescence. In Figure 5 are reported the emission and excitation spectra of $\text{Tb}(\text{O}_2\text{CNBu}_2)_3$.

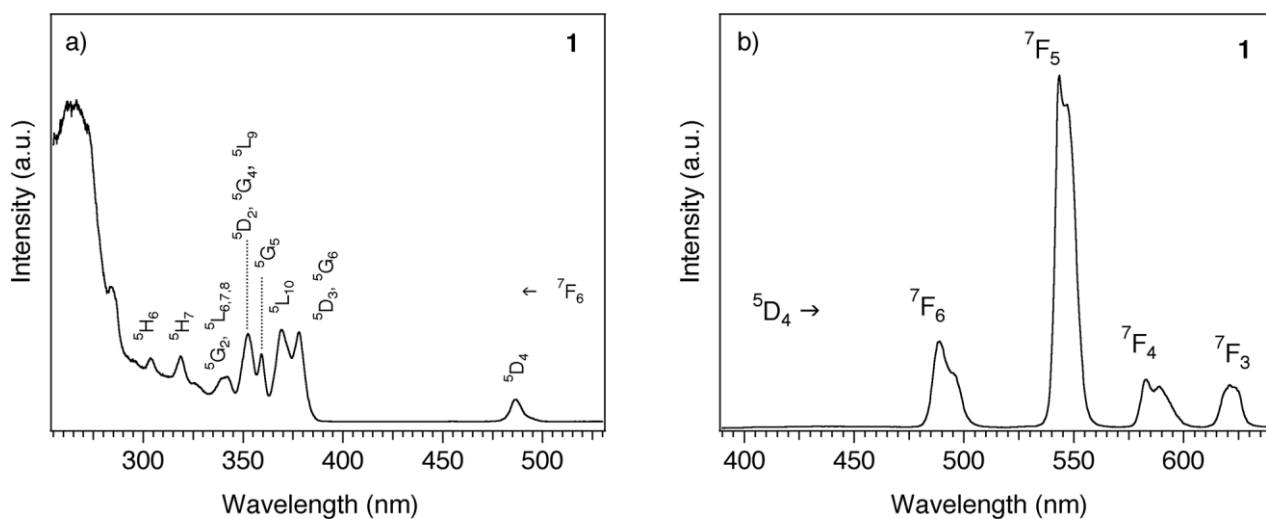


Figure 5. a) Excitation spectrum of $\text{Tb}(\text{O}_2\text{CNBu}_2)_3$, obtained by monitoring the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition at 546 nm. b) Emission spectrum of $\text{Tb}(\text{O}_2\text{CNBu}_2)_3$, obtained under excitation at 378 nm.

Concerning terbium, the excitation spectra (PLE) from **1** have been recorded by monitoring the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition at 546 nm. The spectrum is composed of several sharp lines characteristic of Tb^{3+} f–f transitions in the 300 – 500 nm wavelength range and of a broad band centered at 266 nm likely due to the presence of ligand centered excitations. Upon excitation at 378 nm, a bright green luminescence clearly appreciable by the naked eye and typical of terbium compounds is observed. The tuning of the excitation wavelength across the several bands of the PLE did not induce any appreciable variation in the emission spectra.

It is interesting to compare the terbium excitation spectra of the carbamate complex **1** with those of silica-based materials obtained after grafting (**SIL1**) and ligand exchange reactions (**SIL1dbm**). In fact, the shape and position of the excitation bands, being dependent on the coordination geometry and the nature of the ligands (polarizability, bond strength, and so forth), can be helpful in the identification of variation around the emitting center.

The grafting of $\text{Tb}(\text{O}_2\text{CNBu}_2)_3$ on the silica surface does not induce any variation in the excitation spectra whose profile is conversely modified after the reaction of **SIL1** with dibenzoylmethane.

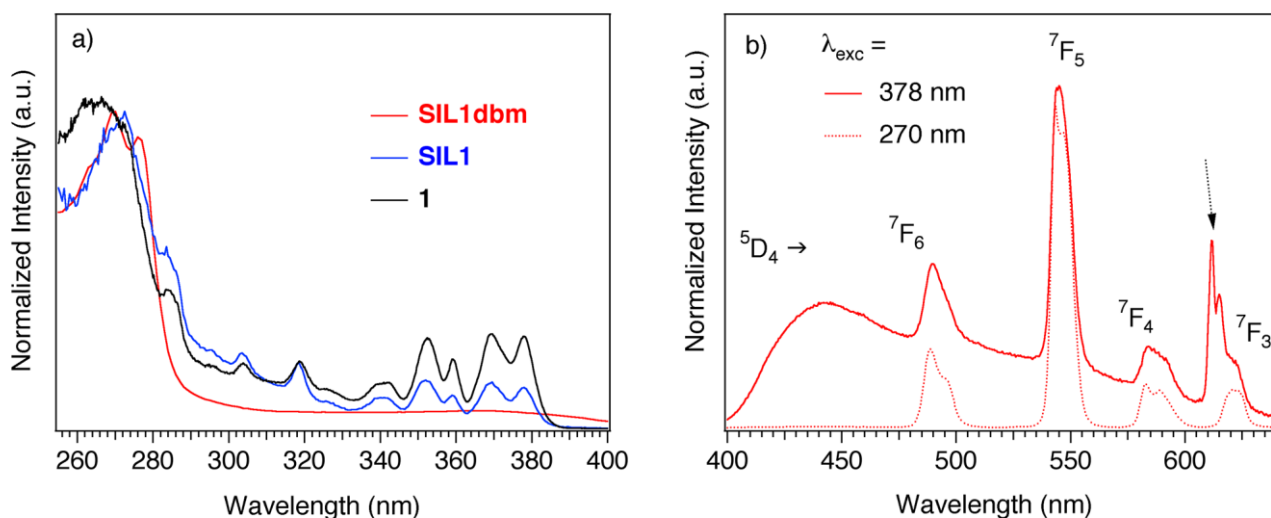


Figure 6. a) Excitation spectrum of **1** (black), **SIL1** (blue) and **SIL1dbm** (red), obtained by monitoring the $^5D_4 \rightarrow ^7F_5$ transition at 546 nm. b) Emission spectrum of **SIL1dbm** obtained under excitation at 378 nm (full line) and 270 nm (dotted line). $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} is arrowed in the figure.

In fact, while a broad band at around 260 nm is still detectable in sample **SIL1dbm**, the characteristic f-f transitions, well visible in the PLE of **1** and **SIL1**, are no longer observable (Figure 6a). Interestingly, the emission spectra of **SIL1dbm** obtained by exciting at 270 and 378 nm show different profiles (Figure 6b). In both cases, terbium bands are visible but, excited at the longer wavelength, they are overlapped with a broad signal peaked at 440 nm. Moreover, two new sharp bands appear at 611 and 615 nm thus strongly interfering with the $^5D_4 \rightarrow ^7F_3$ (621 nm) terbium transition. Dibenzoylmethane has an absorption spectra with the most intense band around 350 nm and extends in the UV with a relative maximum at 260 nm.²² It is likely that dbm units coordinated to terbium ions grafted on the silica surface could act as sensitizers for the lanthanide emission. When the sample is excited at the longer wavelength, the energy of the involved levels is not high enough to effectively induce terbium luminescence (see below) and Tb^{3+} emissions are superimposed with the ligand centered ones. The new bands in the red region (611 and 615 nm), arrowed in Figure 6b, are attributed to $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} . Since the sensitized emission of lanthanide ions is usually much stronger than the one achieved by direct excitation in the f^n-f^n multiplets, the luminescence from elements in trace can be easily detected. In this case, being dbm a good sensitizer for europium, it is able to sensitize the emission of the Eu impurity present in the terbium oxide used for the synthesis.

Conversely, upon excitation at shorter wavelength (270 nm), only terbium-related signal are observed (Figure 6b).

Concerning the emission properties of the tri-metallic derivative **2**, due to the usually extremely low value of photoluminescence quantum yields for thulium and to the tendency of luminescence quenching in its compounds, Tm-centered emissions have not been detected (Figure 7a).

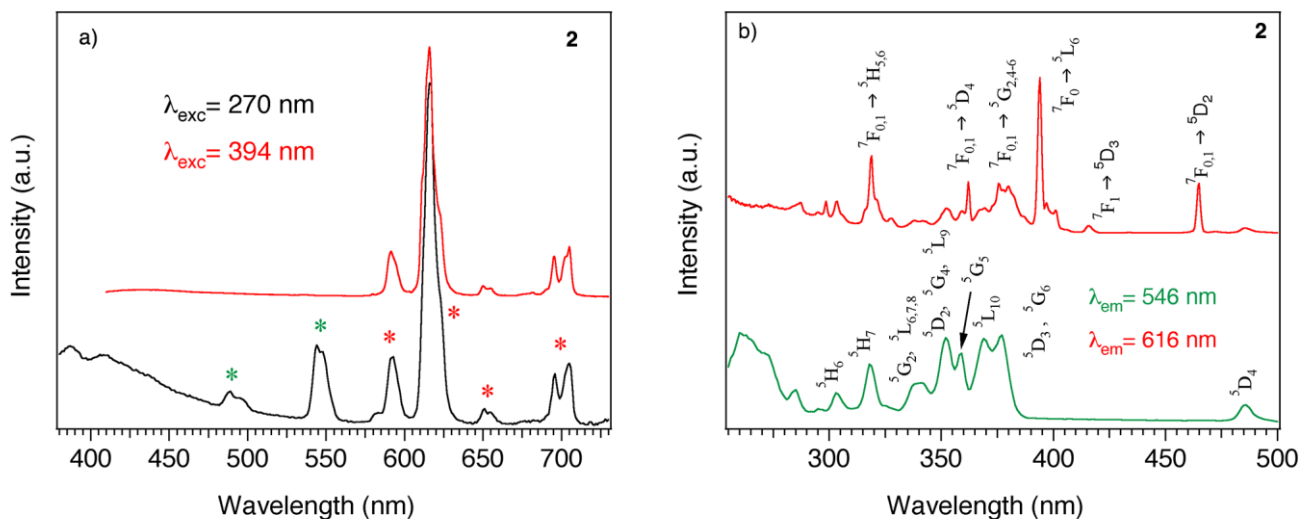


Figure 7. a) emission spectra of sample **2** excited at different wavelengths. The bands belonging to Tb³⁺ and Eu³⁺ are highlighted in the figure by green and red asterisks respectively. b) excitation spectra of **sample 2**: Tb³⁺ ($\lambda_{em} = 546$ nm) and Eu³⁺ ($\lambda_{em} = 616$ nm) centered luminescence.

The emission spectra (Figure 7a) excited at 270 nm are composed of several sharp lines characteristic of Eu³⁺ ($^5D_0 \rightarrow ^7F_J$, J= 0-4) and Tb³⁺ ($^5D_4 \rightarrow ^7F_J$, J= 6-4) f-f transitions, the latter showing an overall luminescence intensity smaller respect to the europium centered emissions. Indeed, the Tb³⁺ excitation spectra closely resemble those observed for Tb(O₂CNBU₂)₃ (Figure 5a). The *N,N*-dibutylcarbamato complex behaves like a two color yellow-red emitter in which the chromatic output can be easily tuned by changing the excitation wavelength. In fact, a strong overlap of the PLE bands at wavelength shorter than 390 nm does not allow the separation of the Eu³⁺ and Tb³⁺ emissions which is conversely readily achieved upon exciting the luminescence on the europium transitions at 394 and 465 nm free from interferences (Figure 7a).

After grafting on the silica surface (**SIL2** sample), the emission properties of the lanthanide ions are almost unaffected, in analogy to what observed for **1** and **SIL1**.

As previously reported, the reaction with dibenzoylmethane, Hdbm, modifies the coordination around Ln ions, both in solution and in the solid state. These variations strongly influence the luminescence properties of the material; in fact, the bonding of the β -diketonato ligands to Ln ions introduces a new and highly effective excitation channel for lanthanide emission.

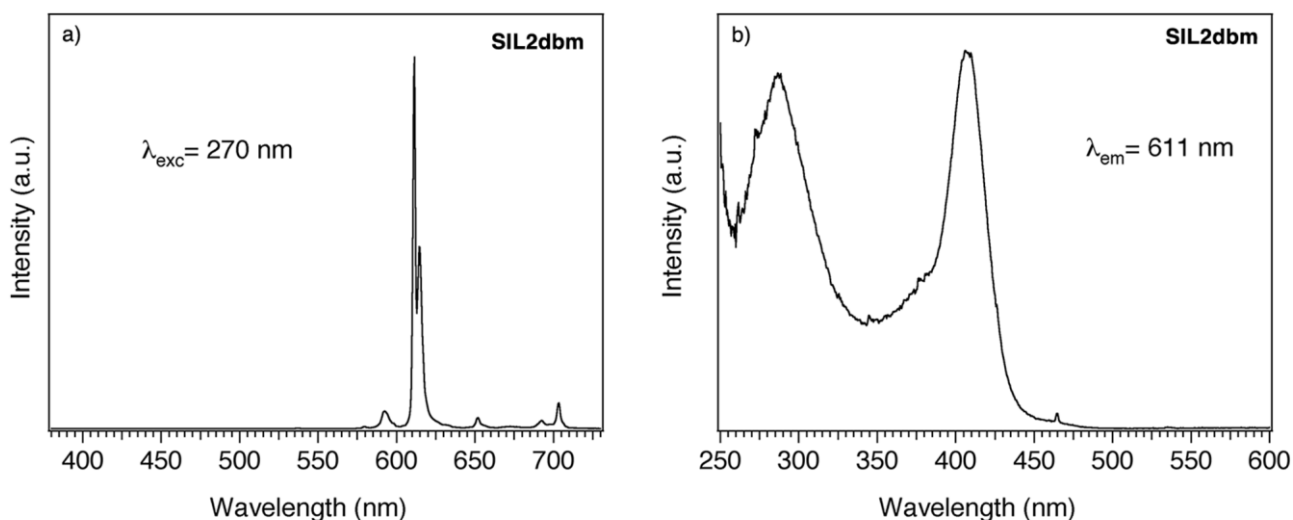


Figure 8. a) emission spectra of sample **SIL2dbm** excited at 270 nm. b) excitation spectra of Eu^{3+} -centered ($\lambda_{\text{em}} = 616 \text{ nm}$) luminescence.

Irrespective of the employed excitation wavelength, only europium emissions are detected (Figure 8a). Moreover, a strong modification in the shape of the excitation spectra is observed. Due to exchange reaction dibenzoylmethane moieties are present in the Ln coordination sphere, which can thus act as sensitizer for the Ln-based luminescence, accordingly to the following steps: (i) absorption of light, (ii) intersystem crossing (ISC) from the singlet (S) to the triplet (T) chromophore level, and (iii) energy transfer to the lanthanide cation. It is worth to be noted that the resulting metal centered (MC) luminescence can be influenced by several factors depending on both the energy of the involved excited states and external environment.^{21d} In this case, the triplet level of dibenzoylmethane is nearly resonant with $^5\text{D}_4$ emitting level (20.500 cm^{-1})²³ of Tb^{3+} leading to a scarce MC luminescence intensity. Conversely, the triplet level matches with an effective population of the Eu^{3+} excited states ($^5\text{D}_0$ 17.500 cm^{-1}) thus inducing strong europium emission.²⁴ The excitation spectra modify accordingly, and f-f transitions are no longer detectable. Only two strong bands centered at 287 and 406 nm, and attributed to ligand (dbm) centered transitions, are observed (Figure 8b). The profile of the europium emission spectra does not show any appreciable variation upon varying the excitation wavelength across the whole PLE spectrum (Figure 5b).

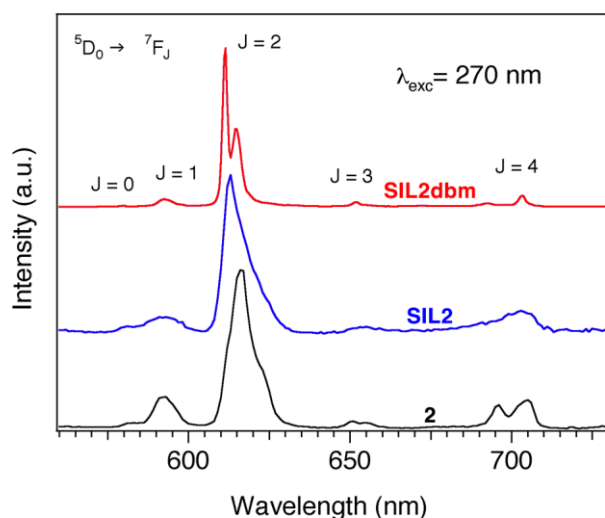


Figure 9. Emission spectra excited at 270 nm of sample **2**, **SIL2** and **SIL2dbm**.

The change in the Eu^{3+} coordination sphere^{24a, 25} as a consequence of *i*) grafting and *ii*) ligand exchange reactions is displayed by the variation in the emission spectra. Both are characterized by the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ($\lambda_{\text{max}} \approx 615$ nm) transition as the most intense band, but the relative intensity of the J components of the ${}^7\text{F}$ multiplets in the various samples is different (Figure 9).

Moreover, thanks to the great light harvesting capability of dibenzoylmethane and to the effective sensitization of europium emission, the luminescence intensity of the silica-based materials exchanged with Hdbm (**SIL2dbm**) is much stronger with respect to those exhibited both by **2** and **SIL2** samples.

CONCLUSION

The terbium carbamate complex $[\text{Tb}(\text{O}_2\text{CNBu}_2)_3]$, easily obtained by extraction of terbium(III) from aqueous solution into heptane according to a previously developed method, has been found to be a suitable precursor to graft the lanthanide ions onto commercial amorphous silica due to the protolytic displacement of a part of the carbamate ligands through reaction with the surface silanols. Moreover, after surface anchoring, the residual carbamate ligands in the metal coordination sphere can be easily substituted, in a second step, by reaction with the relatively weak Brønsted's acid Hdbm. With the aim to extend this procedure to the preparation of multi-lanthanide functionalized silicas containing the metals in a defined molar ratio, the preparation of a carbamate product containing three different lanthanides, $[\text{NH}_2\text{Bu}_2]_2[\text{Ln}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{12}]$ has been carried out by the extraction method already used for the terbium derivative, so extending the procedure to the synthesis of hetero-lanthanide carbamate species. The hetero-lanthanide complex was successfully

exploited to transfer the three different lanthanide ions to silica surface in one single step. The subsequent protolytic substitution of the residual carbamate ligands by reaction with Hdbm was observed also in this case.

The prompt availability of molecular lanthanide precursors, their facile grafting to material surfaces showing Brønsted acidity and the subsequent possibility to modify the metal coordination sphere can be widely exploited. In particular, with the present experimental choices, the sensitization of Eu^{3+} ions through the dbm unit leads to highly red luminescent materials. The effectiveness of the adopted synthetic approach can be easily extended to the preparation of multifunctional materials. In fact, by choosing appropriate exchange ligands for the lanthanide ions, or by adding additional ligands to the parent carbamate complexes, a variety of different functions can be introduced in oxide-based or polymeric materials with important fallout in several forefront application fields. Further studies are in course concerning the preparation and characterization of lanthanide derivatives and their use to anchor these ions to the surface of suitable materials.

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ASSOCIATED CONTENT

Supporting Information

S1 Experimental details of the synthesis of $[\text{Tm}(\text{O}_2\text{CNBu}_2)_3]$. **S2** Single-Crystal X-ray Structure Determination of $[\text{Tb}(\text{dbm})_3(\text{DME})]$: experimental details, discussion, Figure S3.1, Tables S3.1 and S3.2.

CCDC 1048080 contains the supplementary crystallographic data for the compounds described in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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