Highly homogeneous, transparent and luminescent SiO_2 glassy layers containing a covalently bound tetraazacyclododecane–triacetic acid–Eu(III)–acetophenone complex

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The preparation of sol–gel glasses is described wherein highly stable Eu(III) centres are anchored to the silica glass upon acidic hydrolysis and by using tetraethylorthosilicate (TEOS) as a silica source. The complex employed is **Eu·1** and is obtained from bipartite ligand **1**, which features a **DO3A** macrocycle as a hosting unit for the Eu(III) centre, a methoxy-acetophenone unit as an antenna chromophore, and an alkyl chain bearing one primary hydroxy group (**DO3A** is 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid). **Eu·1** is linked to the forming silica glass through the –OH groups and a uniform distribution of the luminescent centres is obtained, as indicated by results from secondary ion mass spectrometry in-depth profiling. The luminescent efficiency of the Eu(III) centres in the solid matrix is evaluated to be 10%, which is comparable to that of **Eu·1** in water solution and of a convenient reference complex, **Eu·2** (**2** is a ligand featuring the same hosting and antenna functionalities of **1**, wherein the –OH residue is replaced by an unreactive group, a benzoylmethyl residue). A discussion is given of the photophysical properties exhibited by the complexes in the film and in solution.

Introduction

Luminescent lanthanide complexes can find applications, among others, as diagnostic tools,[1–3] sensors,[4] optical fibre lasers and amplifiers,[5,6] and electroluminescent materials.[7] Great efforts have been devoted in order to find out chelating agents resulting in highly stable complexes and several ligand systems have been explored like polyaminocarboxylates,[8] cryptands,[9] calixarenes,[10,11] podands[12] and helicates.[13,14] Somewhat disappointingly, approaches involving direct coordination of chromophores at the 8–9 available positions of the lanthanide centre have sometimes proved not very convenient from the point of view of the stability of the resulting complexes or of their efficiency as luminophores.[9,15,16] This has stimulated alternative approaches aimed at generating highly stable and luminescent complexes. For instance, in carefully designed bipartite systems[17–24] one can exploit the tight coordination taking place at a macrocycle unit and obtain light absorption by an appended, not directly coordinated chromophore; in several cases this approach appears to yield complexes featuring both good structural and optical properties.[25]

Eu(III) complexes are regarded as convenient red-emitting phosphors, with λ_{max}^{em} = 612 nm.[25–28] However, while a wealth of studies in solutions is available for Eu(III) complexes (and of other lanthanides), in order to be useful for some of the target applications, these emitters have to be included or grafted into a solid matrix. For instance, incorporation into polymers[5,29,30] or sol–gel glasses[31–35] represents an appealing possibility. Yet, within a solid matrix, the wished statistical distribution of the chromophores is not always observed; instead changeable degrees of aggregate formation may occur.[36] Clearly, formation of aggregates can be a source of problems, because mutual interaction between spatially close luminescent centres may lead to self-quenching, a parasitic event against luminescence efficiency.

In this paper we describe the sol–gel preparation of silica-based glassy layers with a homogeneous distribution of the Eu(III)-luminophores in the solid matrix.[37,38] The employed photoactive unit is a bipartite system, **Eu·1**, comprised of a **DO3A** macrocyclic hosting unit for the lanthanide centre and a **MAP**-containing chromophore (**DO3A** is 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid, and **MAP** is 4′-methoxyacetophenone).[23] Chart 1 shows the schematic formula of **Eu·1** and of the reference complex **Eu·2**, see Experimental section. Within **Eu·1** and **Eu·2**, all the coordination positions of the lanthanide centre are fulfilled by **DO3A** but one (only one coordination site is available to solvent molecules, which is indicated by $q = 1$),[23] and these complexes are highly stable, the 1 : 1 **DO3A:Ln** association constant being $K_A > 10^{20}\ M^{-1}$.[39] **Eu·1** can be covalently linked to the forming silica glass through the –OH moieties, yielding highly homogeneous layers with luminophores tightly anchored to the host medium.

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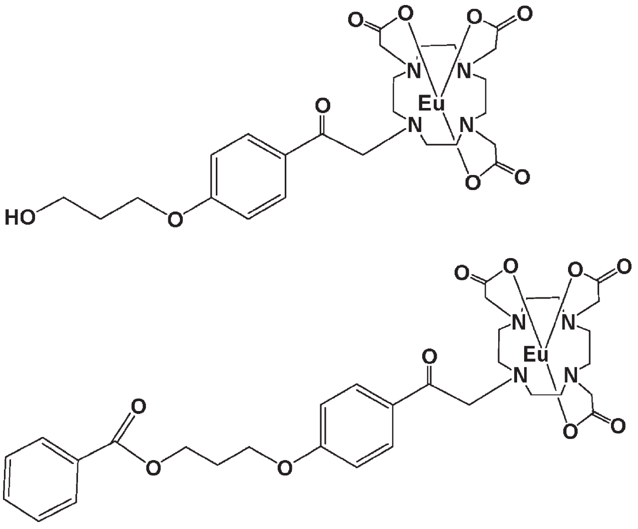


Chart 1 **Eu·1** and **Eu·2** complexes.

Chart 2 schematically depicts the binding of the Eu(III) complex to the silica glass matrix.

Results and discussion

Design and synthesis of ligands and complexes

Bipartite ligand **1** (see Scheme 1), features a 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (**DO3A**) as the coordination site for the lanthanide cation, bearing on the fourth nitrogen atom a covalently bonded functionalized acetophenone as chromophore. The choice of the chromophore, besides its high efficiency in the sensitization process, as demonstrated by Beeby, Williams and coworkers,[23] is due mainly to the easy functionalization of its 4′ position with a short alkyl chain bearing one primary hydroxyl group. As a matter of fact, –OH groups are useful for the anchoring of complexes to a forming silica network during a sol-gel process.[40]

DO3A was selected as the Ln-chelating subunit because of the high thermodynamic and kinetic stabilities which are well assessed for its lanthanide complexes.[39] Ligand **1** was synthesized according to Scheme 1. Alkylation of **DO3A** tris(tertbutyl) ester **4**,[41] with 3-[4-(2-bromoacetyl)phenoxy]propyl benzoate **5** carried out in CH_3CN at reflux in the presence of solid Na_2CO_3 as base afforded **3**, in 91% yield, after purification of the crude by column chromatography. Treatment of **3** with CF_3COOH, at room temperature, afforded the tricarboxyl derivatives **2**, in 92% yield, as a brown solid after purification through a short Amberlite XAD 1600T column.

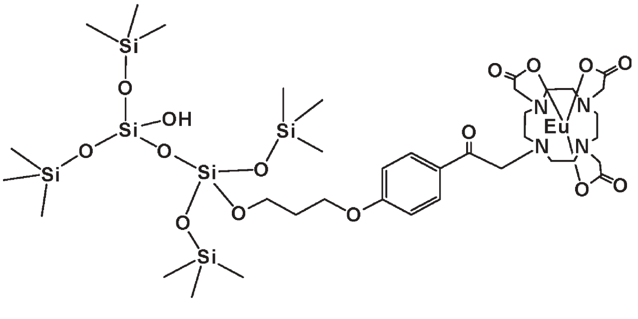


Chart 2 The binding of the Eu(III) complex to the silica glass matrix.

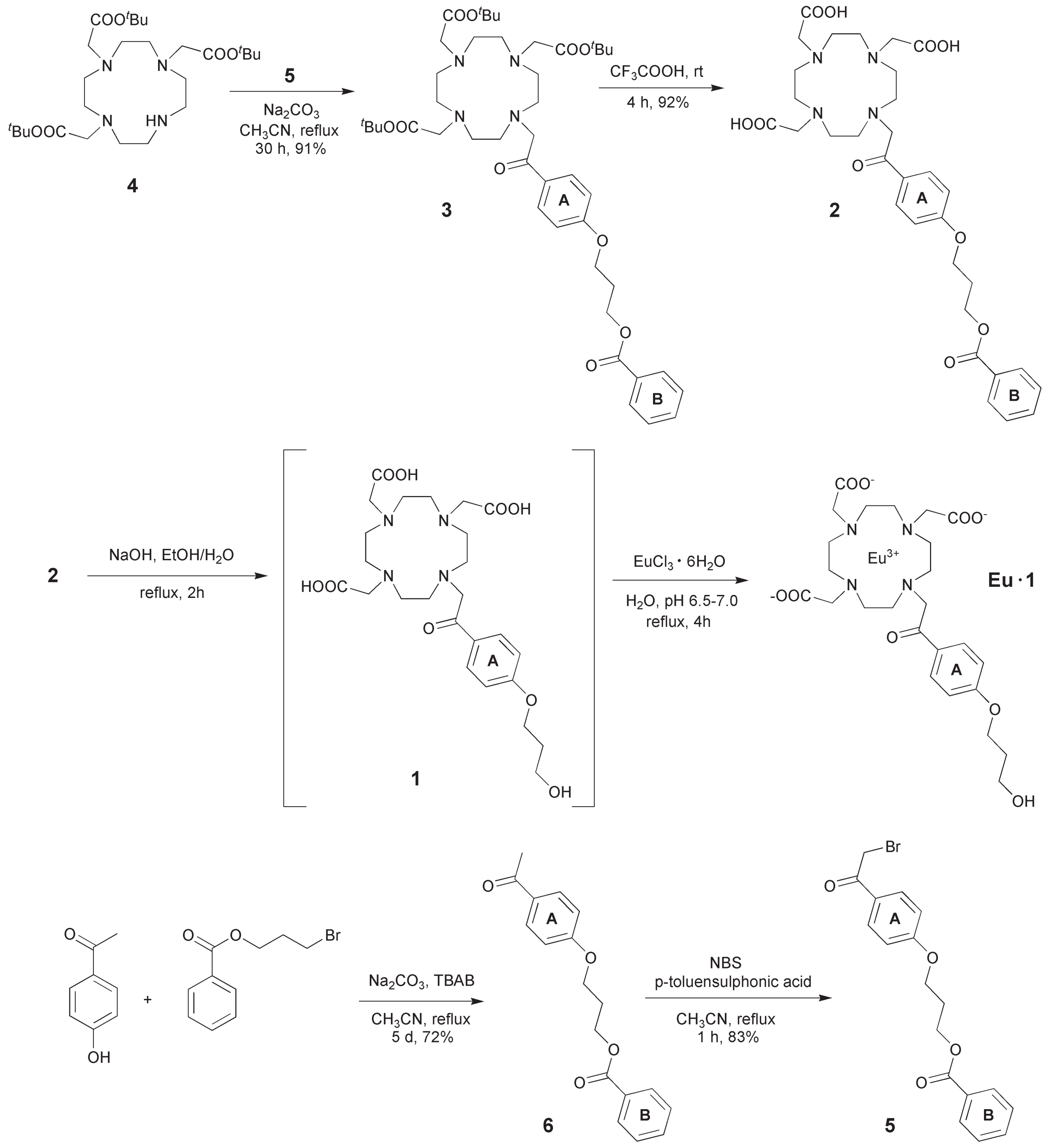
The **Eu·1** complex was prepared in a one step procedure starting from the benzoyl protected ligand **2** by saponification with aqueous NaOH-2% and subsequent complexation of the crude **1** with $EuCl_3{\cdot}6H_2O$ that was carried out at pH 6.5–7.0 in water at reflux. The product was purified by column chromatography with Amberlite XAD 1600T eluting first with water, to remove the inorganic salts, and then with water–CH_3CN 9/1 (v/v) and afforded pure complex in quantitative yield.

Functionalized acetophenone **5** was obtained in two steps: alkylation of the commercially available 4-hydroxyacetophenone with 3-bromopropyl benzoate carried out in CH_3CN and solid Na_2CO_3 as base and in the presence of 5% of tetrabutylammonium bromide (TBAB) as phase transfer catalyst; and bromination of the intermediate **6** with *N*-bromosuccinimide (NBS) and *para*-toluensulfonic acid in CH_3CN at reflux according to a literature procedure used for similar compounds.[42]

Physical and optical properties of films

The films were prepared as described in the Experimental section. The europium distribution throughout their thickness was investigated by secondary ion mass spectrometry (SIMS) depth profiling on selected **DO3A**-silica layers. In Fig. 1 is reported the SIMS in-depth distribution of Eu, C, and N as well as Si and O for an *as-prepared* sample (Fig. 1a) and for a film dried at 100 °C for 5 h (Fig. 1b). In both cases, homogeneous profiles of all elements throughout the whole film thickness are observed. Moreover, the remarkable similarity in the shape of Eu, C and N profiles suggests a common chemical origin of these species, in agreement with the presence of **DO3A** throughout the investigated depth. Estimates of film thickness yielded values around 40 nm irrespective of the thermal treatment, that at our employed conditions correspond to *ca.* 4.8 nm^3 of film volume/luminophore.

While ligand **1** is non-emissive upon irradiation at 305 nm, both **Eu·1** in water and the film incorporating this complex showed a strong red emission, Table 1 and Fig. 2. Actually, within the chromophore/luminophore associate, the **MAP** unit acts as an *antenna* for sensitisation of the lanthanide-based luminescence. This occurs according to the following sequence of events:[25] (i) absorption of UV light at 305 nm (ε_{308} = 19 300 and 24 300 M^{-1} cm^{-1} for **Eu·1** and **Eu·2**, respectively), (ii) highly efficient intersystem crossing (ISC) from the populated singlet (S) level to the triplet (T) level, lying at 25 200 cm^{-1} (ϕ_{ISC} = 1)[43,44] and (iii) transfer of excitation energy to the lanthanide cation. The last step, a **MAP** → Eu(III) energy (en) transfer, occurs with an efficiency ϕ_{en} ~ 1,[23] as expected because the acetophenone triplet exhibits a slow decay ($k_T \sim 5 \times 10^6$ s^{-1})[44,45] and the energy gap between the donor and the acceptor levels is *ca.* 7300 cm^{-1}, *i.e.*, so high as to hamper any back-transfer process.[8,25]



Scheme 1 Outline of synthetic steps.

Table 1 lists the optical properties of the film as compared to that of dilute (1×10^{-5} M) air-equilibrated water solutions of the **Eu·1** parent complex and of the related **Eu·2** complex. Fig. 2 further illustrates the absorption and emission behaviour of the film and of the **Eu·1** model in water. The absorption results indicate that inclusion of the lanthanide centre causes a shift of the absorption peak of the **MAP** unit from 282 (for the lanthanide-free ligand **1**) to 308 for both the **Eu·1** and the **Eu·2** complexes in water solution and to 310 nm for the **Eu·1** unit bound to the silica-glass. A similar perturbation effect of the electronic properties of the **MAP** ligand by the cationic Eu(III) centre was already noted for very similar complexes that were found to exhibit practically identical luminescence properties in water solution.[23] The lack of any emission for the lanthanide-free chromophore **1** is explained by the fact that the lowest-lying singlet level of **MAP** is of acetophenone origin and is depopulated with unit efficiency by the ISC step, leading to a non-emissive triplet.[23,43,44]

The luminescence spectra observed in solution and in film are quite similar to each other and appear finely resolved. The narrow peaks are due to the transitions between the $^5D_0$ excited level and the various terms of the ground level, ^7F_J, $J = 0–6$,[25,28] of which those for $J = 0–4$ are apparent in Fig. 2.

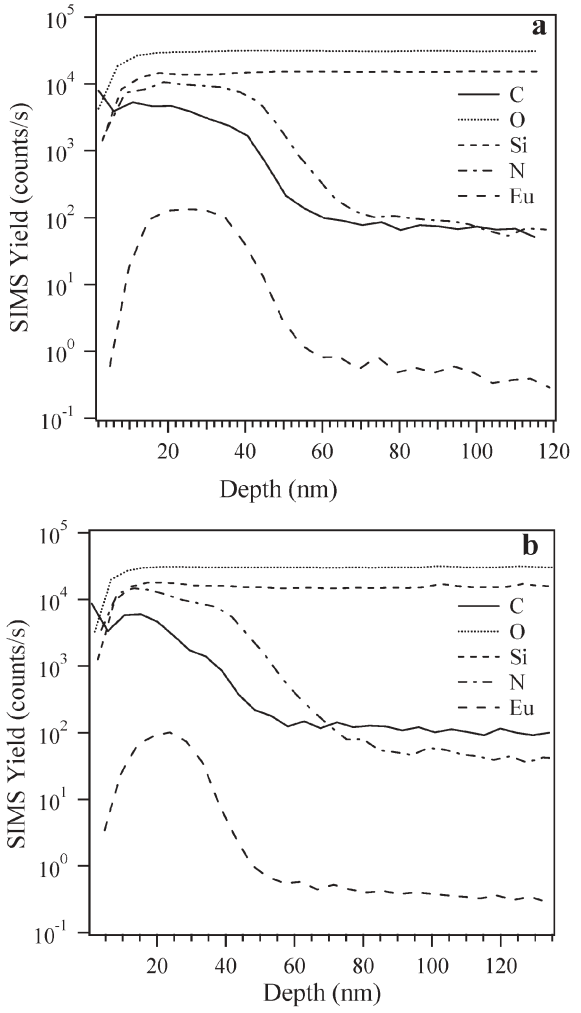


Fig. 1 SIMS depth profile for an as-prepared sample (a) and for a film dried at 100 °C for 5 h (b).

Table 1 Absorption and emission data[a]

	Absorption		Emission			
	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	ϕ_{se}	τ/ms	k_r/s^{-1} [b]
Eu·1	308	19 300	612	0.080	0.60	133
Eu·2	308	24 300	612	0.081	0.62	131
film(**Eu•1**)	310	—[c]	616	0.096[d]	0.73	132

[a] At room temperature. [b] $k_r = \phi/\tau$ [c] Extinction coefficient not determined [d] Evaluated from $\phi = \tau k_r$,[18,23,49] by taking k_r = 132 s^{-1}, and disregarding the effect of the different refraction index for water and film.[19,48]

The most intense peak occurs at 612 nm in solution (616 nm in the film), and corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition. This is the so called hypersensitive transition,[23,46,47] and the ratio between its intensity and that for the lower energy transition ($^5D_0 \rightarrow {}^7F_1$) is *ca.* 5 and 6 for the solution and the film, respectively. This suggests that the Eu-based luminophore is embedded in a similar environment for the two cases (solution and film), which in turn points to a high degree of homogeneity for the physical state of the film as pointed out by SIMS analysis.

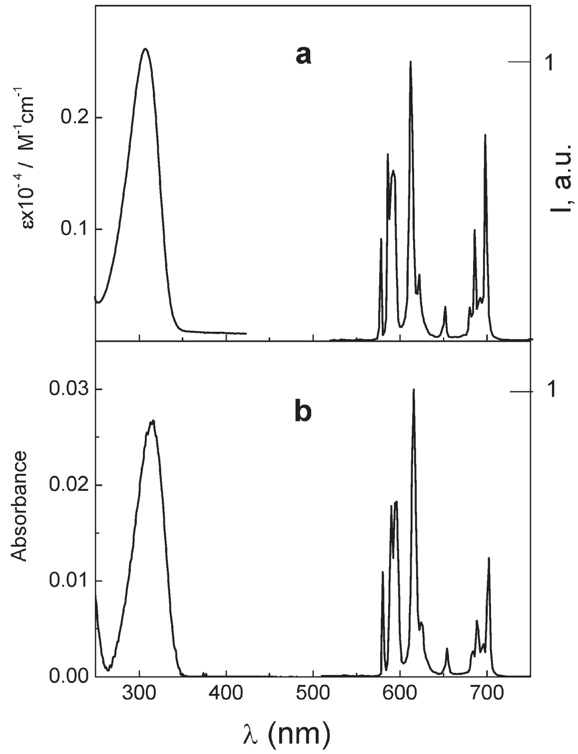


Fig. 2 Room temperature absorption spectrum (left) and emission profile (right) of the **Eu·1** complex in water (a) and of the film incorporating the **Eu·1** (b); λ_{exc} = 305 nm for both cases.

Experimental

Material and methods

All commercially available solvents and reagents were used as received. TLC was carried out on silica gel Si 60-F254. Column chromatography was carried out on silica gel Si 60 mesh size 0.040–0.063 mm (Merk, Darmstadt, Germany). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC 300 spectrometer operating at 300 MHz and 75 MHz respectively. Elemental analyses were carried out by the Departmental Service of Microanalysis (University of Milan).

Synthetic procedures. The synthetic paths are summarized in Scheme 1.

Synthesis of 3-(4-acetylphenoxy)propyl benzoate (6). A mixture of 4-hydroxyacetophenone (2.04 g, 15 mmol), 3-bromopropyl benzoate (4.0 g, 16.5 mmol) and sodium carbonate (4.77 g, 45 mmol) in 60 cm^3 of acetonitrile was heated at reflux and maintained under magnetic stirring for five days. After this time the reaction mixture was cooled at room temperature, filtered, the solvent evaporated in vacuo and the residue was purified by column chromatography (silica gel, CH_2Cl_2) to afford 6 (3.21 g, 72%) as a white solid; δ_H (400 MHz, $CDCl_3$) 2.29 (2 H, quintet, *J* 6.2, $COOCH_2CH_2CH_2O$), 2.55 (3 H, s, $COCH_3$), 4.20 (2 H, t, *J* 6.2, $COOCH_2CH_2CH_2O$), 4.53 (2 H, t, *J* 6.2, $COOCH_2$-CH_2CH_2O), 6.93 (2 H, d, *J* 8.8, Ar(A)H^2,H^6), 7.43 (2 H, bt, *J* 7.7, Ar(B)H^3,H^5), 7.56 (1 H, bt, *J* 7.7, Ar(B)H^4), 7.92 (2 H, d, *J*

8.8, Ar(A)H^3,H^5), 8.04 (2 H, d, *J* 7.4, Ar(B)H^2,H^6); δ_C (100.6 MHz, CDCl$_3$) 26.3 (COCH$_3$), 28.7 (COOCH$_2$CH$_2$CH$_2$O), 61.6 (COOCH$_2$CH$_2$CH$_2$O), 64.8 (COOCH$_2$CH$_2$CH$_2$O), 114.2 (Ar(A)C^2,C^6), 128.4 (Ar(B)C^3,C^5), 129.6 (Ar(B)C^2,C^6), 130.1 (Ar(B)C^1), 130.5 (Ar(A)C^4), 130.6 (Ar(A)C^3,C^5), 133.0 (Ar(B)C^4), 162.7 (COOCH$_2$CH$_2$CH$_2$O), 166.5 (Ar(A)C^1), 196.7 (COCH$_3$); *m*/*z* (ESI) 321.10923 (100.0%), 322.11282 (19.6%), 323.11606 (1.8%) [M + Na]$^+$ (C$_{18}$H$_{18}$O$_4$ requires 298.33).

Synthesis of 3-[4-(2-bromoacetyl)phenoxy]propyl beanzoate (5). *N*-Bromosuccinimide (0.89 g, 5 mmol) was added in two portions to a solution of **6** (1.49 g, 5 mmol) and *p*-toluensulfonic acid monohydrate (1.71 g, 9 mmol) in 100 cm^3 of acetonitrile. The reaction mixture was then heated at reflux and stirred for one hour. The solvent was evaporated *in vacuo* and the residue was dissolved in 150 cm^3 of CH$_2$Cl$_2$ and washed with 100 cm^3 of H$_2$O. The organic phase was separated, dried over MgSO$_4$ and the solvent evaporated to afford a white solid residue which was purified by column chromatography (silica gel, CH$_2$Cl$_2$) to give 5 (1.56 g, 83%) as a white solid; δ_H (400 MHz, CDCl$_3$) 2.30 (2 H, quintet, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 4.21 (2 H, t, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 4.39 (2 H, s, COCH$_2$Br), 4.53 (2 H, t, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 6.93 (2 H, d, *J* 8.9, Ar(A)H^3,H^5), 7.43 (2 H, bt, *J* 7.6, Ar(B)H^3,H^5), 7.56 (1 H, bt, *J* 7.3, Ar(B)H^4), 7.95 (2 H, d, *J* 8.9, Ar(A)H^2,H^6), 8.03 (2 H, d, *J* 7.4, Ar(B)H^2,H^6); δ_C (100.6 MHz, CDCl$_3$) 28.7 (COOCH$_2$CH$_2$CH$_2$O), 30.7 (COCH$_3$), 61.5 (COOCH$_2$CH$_2$CH$_2$O), 64.9 (COOCH$_2$CH$_2$CH$_2$O), 114.5 (Ar(A)C^3,C^5), 127.0 (Ar(A)C^4), 128.4 (Ar(B)C^3,C^5), 129.6 (Ar(B)C^2,C^6), 130.1 (Ar(B)C^1), 131.4 (Ar(A)C^2,C^6), 133.0 (Ar(B)C^4), 163.3 (COOCH$_2$CH$_2$CH$_2$O), 166.5 (Ar(A)C^1), 189.9 (COCH$_2$Br); *m*/*z* (ESI) 399.01968 (100.0%), 400.02372 (19.5%), 401.01783 (97.3%), 402.02167 (18.9%) [M + Na]$^+$ (C$_{18}$H$_{17}$BrO$_4$ requires 376.0).

Synthesis of 10-{4-[3-(benzoyloxy)propyloxy]benzoylmethyl}-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid tris(1,1-dimethylethyl) ester (3). A suspension of **5** (1.13 g, 3 mmol), 4HCl (1.65 g, 3 mmol) and sodium carbonate (3.18 g, 30 mmol) in 50 cm^3 of acetonitrile was refluxed for 30 h under magnetic stirring. The mixture was cooled at room temperature and filtered over a fritted glass and the filtrated evaporated to afford a viscous yellow oil. Purification by column chromatography (silica gel, CH$_2$Cl$_2$–MeOH 95/5) afforded **3** (2.22 g, 91%) as a white solid; δ_H (400 MHz, CDCl$_3$) 1.46 (27 H, s, C(CH$_3$)$_3$), 2.29 (2 H, quintet, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 2.09–3.90 (22 H, m, (NCH$_2$)H^2,H^3,H^5,H^6), (NCH$_2$)H^8,H^9,H^{11},H^{12}, N^{4}CH$_2$COOH, N^{1}CH$_2$COOH, N^{7}CH$_2$COOH, 4.21 (2 H, t, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 4.54 (2 H, t, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 6.94 (2 H, d, *J* 8.8, Ar(A)H^2, H^6), 7.45 (2 H, bt, *J* 7.7, Ar(B) H^3,H^5), 7.58 (1 H, bt, *J* 7.7, Ar(B)H^4), 7.88 (2 H, d, *J* 8.8, Ar(A)H^3,H^5), 8.05 (2 H, d, *J* 7.4, Ar(B)H^2,H^6); δ_C (100.6 MHz, CDCl$_3$) 28.0 (C(CH$_3$)$_3$), 28.6 (COOCH$_2$CH$_2$CH$_2$O), 55.6 and 55.8 ((NCH$_2$)C^2,C^3,C^5,C^6, (NCH$_2$)C^8,C^9,C^{11},C^{12}), 59.9 (N^{4}CH$_2$COO^{t}Bu, N^{1}CH$_2$COO^{t}Bu, N^{7}CH$_2$COO^{t}Bu), 61.6 (COOCH$_2$CH$_2$CH$_2$O), 64.8 (COOCH$_2$CH$_2$CH$_2$O), 81.9 (C(CH$_3$)$_3$), 114.3 (Ar(A)C^3,C^5), 128.4 (Ar(B)C^3,C^5), 128.9 (Ar(A)C^4), 129.5 (Ar(B)C^2,C^6), 129.9 (Ar(B)C^1), 132.6 (Ar(A)C^2,C^6), 133.1 (Ar(B)C^4), 163.1 (COOCH$_2$CH$_2$CH$_2$O), 166.5 (Ar(A)C^1), 172.8 (NCH$_2$COO^{t}Bu), 197.8 (Ar(A)COCH$_2$N^{10}); *m*/*z* (ESI) 833.46769 (100.0%), 834.47107 (47.6%), 835.47441 (11.1%) (M + Na$^+$) (C$_{44}$H$_{66}$N$_4$O$_{10}$ requires 810.48).

Synthesis of 10-{4-[3-(benzoyloxy)propyloxy]benzoylmethyl}-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (2). A solution of **3** (1.67 g, 2.06 mmol) in 30 cm^3 of trifluoroacetic acid was stirred at room temperature for 4 h. The solvent was evaporated and the viscous oil residue was heated with 30 cm^3 of diethyl ether to give 2.32 g of a brown clear solid. This product was dissolved in 5 cm^3 of water and adsorbed on a short Amberlite XAD 1600T column which was eluted with water until the pH was neutral and then with water–acetonitrile 1/1 (v/v) to recover 2 (1.21 g, 92%) as a brown solid; δ_H (400 MHz, CDCl$_3$) 2.27 (2 H, quintet, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 3.09 (8 H, bs, (NCH$_2$)H^2,H^3,H^5,H^6), 3.45 (8 H, bs, (NCH$_2$)H^8,H^9,H^{11},H^{12}), 3.69 (2 H, s, (N^{4}CH$_2$COOH)), 3.77 (4 H, s, (N^{1}CH$_2$COOH, N^{7}CH$_2$COOH)), 4.23 (2 H, t, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 4.51 (2 H, t, *J* 6.2, COOCH$_2$CH$_2$CH$_2$O), 6.99 (2 H, d, *J* 8.8, Ar(A)H^2, H^6), 7.48 (2 H, bt, *J* 7.7, Ar(B) H^3,H^5), 7.60 (1 H, bt, *J* 7.7, Ar(B)H^4), 7.95 (2 H, d, *J* 8.8, Ar(A)H^3,H^5), 8.02 (2 H, d, *J* 7.4, Ar(B)H^2,H^6); δ_C(100.6 MHz, CDCl$_3$) 28.3 (COOCH$_2$CH$_2$CH$_2$O), 48.5 and 48.8 ((NCH$_2$)C^2,C^3,C^5,C^6), 50.8 and 50.9 ((NCH$_2$)C^8,C^9,C^{11},C^{12}), 53.5 (N^{4}CH$_2$COOH), 56.2 (N^{1}CH$_2$COOH, N^{7}CH$_2$COOH)), 61.6 (COOCH$_2$CH$_2$CH$_2$O), 64.8 (COOCH$_2$CH$_2$CH$_2$O), 114.0 (Ar(A)C^3,C^5), 128.4 (Ar(B)C^3,C^5), 128.6 (Ar(A)C^4). 129.1 (Ar(B)C^2,C^6), 130.0 (Ar(B)C^1), 130.2 (Ar(A)C^2,C^6), 132.9 (Ar(B)C^4), 163.3 (COOCH$_2$CH$_2$CH$_2$O), 166.6 (Ar(A)C^1), 169.2 (NCH$_2$COOH), 172.9 (Ar(A)COCH$_2$N^{10}); *m*/*z* (ESI) 665.27906 (100.0%), 666.28282 (34.6%), 667.28755 (5.9%), [M + Na]$^+$ (C$_{32}$H$_{42}$N$_4$O$_{10}$ requires 642.29).

Synthesis of 10-[4-(3-hydroxypropoxy)benzoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid europium(III) complex (Eu·1). A solution of **2** (321 mg, 0.5 mmol) and sodium hydroxide (200 mg, 5 mmol) in 50 cm^3 of ethanol–water 95/5 was heated at reflux and stirred for two hours. The solvent was evaporated *in vacuo*; the residue was taken up in 50 cm^3 of water and the pH was adjusted at 6.5 by addition of 5% aqueous chlorydric acid. A solution of EuCl$_3$·6H$_2$O (201 mg, 0.55 mmol) in 5 cm^3 of water was slowly added to the previously prepared solution containing the ligand keeping the pH at 6.5–7.0 by contemporary addition of 5% aqueous sodium hydroxide. The reaction mixture was then heated at reflux for four hours, cooled at room temperature and concentrated to 5 cm^3 by evaporation of the solvent under reduced pressure. The product was purified by column chromatography with Amberlite XAD 1600T, eluiting first with water to remove all inorganic salts and then with water–acetonitrile 9/1 to afford **Eu·1** (365 mg, quantitative yield) as a light brown solid (Found: C, 39.13; H, 5.87; N, 6.92. C$_{25}$H$_{35}$EuN$_4$O$_9$·5H$_2$O requires C, 38.60; H, 5.84; N, 7.20); *m*/*z* (ESI) 711.15193 (100.0%), 709.14954 (89.7%), 712.15509 (28.0%), 710.15331 (25.9%), [M+Na]$^+$ (C$_{25}$H$_{35}$EuN$_4$O$_9$ requires 688.16).

10-{4-[3-(benzoyloxy)propyloxy]benzoylmethyl}-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid europium(III) complex (Eu·2). The pH of a solution of **2** (321 mg, 0.5 mmol) in water (50 cm^3) was adjusted at 6.5 by addition of 2% aqueous sodium hydroxide. A solution of $EuCl_3 \cdot 6H_2O$ (201 mg, 0.55 mmol) in 5 cm^3 of water was slowly added to the previously prepared solution containing the ligand keeping the pH at 6.5–7.0 by contemporary addition of 2% aqueous sodium hydroxide. The reaction mixture was then heated at reflux for three hours, cooled at room temperature and concentrated to 5 cm^3 by evaporation of the solvent under reduced pressure. The product was purified by column chromatography with Amberlite XAD 1600T, eluting first with water to remove all inorganic salts and then with water–acetonitrile 8/2 to afford **Eu·2** (313 mg, 79%) as a light brown solid (Found: C, 45.39; H, 5.30; N, 6.59. $C_{32}H_{39}EuN_4O_{10} \cdot 3H_2O$ requires C, 45.45; H, 5.36; N, 6.63); *m/z* (ESI) 815.17798 (100.0%), 813.17613 (91.6%), 816.18020 (34.6%), 814.17914 (31.7%), $[M + Na]^+$ ($C_{32}H_{39}EuN_4O_{10}$ requires 792.19).

Preparation of the film. The sol–gel starting solution was prepared using tetraethylorthosilicate $Si(OC_2H_5)_4$ (TEOS), as silica source. The europium complex **Eu·1** was first dissolved in ethanol at room temperature and subsequently TEOS, water and hydrochloric acid were added. The molar composition of the resulting solution was: 1TEOS : 15EtOH : 0.1HCl : $3H_2O$ while the Si/DO3A molar ratio was 440. Before film deposition, the transparent and clear solution was aged at room temperature under stirring for 24 h.

Silica based thin films were obtained by the dip-coating procedure using Herasil® silica slides (Heraeus, Quarzschmelze, Hanau, Germany) as a substrate. Film deposition was carried out in air at room temperature with a controlled withdrawal speed of about 10 cm min^{-1}. Coatings were obtained by means of a multi-dipping process, up to 3 depositions, without any thermal treatment between them. The *as-prepared* samples containing the **Eu·1** luminescent component resulted homogeneous, well-adherent to the substrates, transparent, and crack free.

The obtained layers were subsequently used in the luminescence experiments both *as-prepared* and dried at 100 and 200 °C for 5 h. Higher treatment temperatures were disregarded in order to avoid the degradation of the europium complex occurring at $T > 250$ °C, as evidenced from thermal analysis performed in the same conditions (in air, 10 °C min^{-1} heating rate) adopted for film annealing.

Equipment. Secondary ion mass spectrometry (SIMS) depth profiles were obtained by an IMS 4f mass spectrometer using a 14.5 keV Cs$^+$ primary beam (10 nA) and negative secondary ion detection. Beam blanking mode was used to improve the depth resolution. The charge compensation was achieved by means of an electron gun. For each sample the erosion speed was evaluated at various depths measuring the corresponding crater by means of a Tencor Alpha Step profiler. The dependence of the sputtering rate on the material composition was therefore taken into account in the film thickness determination.

Absorption spectra of water solutions of **Eu·1**, **Eu·2** (see Chart 1) and of films on glass substrate containing **Eu·1** were measured at room temperature with a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer. The absorption profile for both solutions and films is ascribed to the methoxy-acetophenone unit,[23] with subsequent energy transfer to the lanthanide center resulting in the observed luminescence, Fig. 2. For the steady state luminescence experiments performed at room temperature, slightly different geometries were employed for the cases of solutions or films. For the water solutions, 1 cm cuvettes were used with a 90° arrangement between the excitation light and the detector. For the films, the glass plane was at 30° to the incident light in order to ensure detection of luminescence and avoid scattered light from the source. The selected excitation wavelength was 305 nm in all cases, which is close to the peak maximum of the lowest-energy absorption band, *vide infra*. For both solution and film cases, the absorbance of the samples was lower than 0.05, thus ensuring transmittance of more than 90% of the incident light. The luminescence spectra were registered with a Spex Fluorolog II spectrofluorimeter equipped with Hamamatsu R928 phototube or with an Edinburgh FLS920 spectrometer equipped with Hamamatsu R5509-72 supercooled photomultiplier tube (193 K), and a TM300 emission monochromator with NIR grating blazed at 1000 nm; 150 and 450 W Xenon arc lamps were used, respectively as light sources. Corrected luminescence spectra in the range 500–820 nm were then obtained by taking care of the known wavelength dependence of the phototube response. The excitation spectra taken at 612 or 616 nm, for solution and film cases, respectively, were found to correspond to the absorption spectra of the complexes.

Luminescence efficiencies for lanthanide-based sensitized emission (ϕ_{se}) were evaluated either by comparison of relative intensities,[48] or by exploiting known photophysical parameters for the Eu(III)-based emission.[49] In the former case, one compares the wavelength integrated area of the lanthanide luminescence with that of isoabsorbing samples of $[Ru(bpy)_3]Cl_2$ as a luminescence standard ($\phi = 0.028$ in air-equilibrated water[50]). The latter approach is based on the fact that the luminescence lifetime of an emitter is governed by radiative (r) and non-radiative (nr) processes, $\tau = 1/(k_r + k_{nr})$, and that for a Eu(III) centre the intrinsic radiative rate constant is moderately affected by the environment, $k_r = 90/170\ s^{-1}$.[19,23,49] This allows evaluation of k_r and k_{nr} from the observed value of τ, and the luminescence efficiency is in turn evaluated on the basis of $\phi = k_r/(k_r + k_{nr})$.[23] Luminescence lifetimes on the ms time scale were obtained with a Perkin-Elmer LS50B luminescence spectrometer; all decays were single exponentials, both for solutions (1 cm cuvettes, 90° between the excitation light and the detector) and films (30° between the excitation light and the plane of the film). The experimental uncertainty on the absorption and luminescence maxima is 2 and 1 nm, respectively, that for the ϕ and τ values is 20 and 10%, respectively.

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