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Highly Photoluminescent Silica Layers Doped with Efficient Eu(III) and Tb(III) Antenna Complexes

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Eu(III) and Tb(III) antenna complexes employing different units—phenanthroline and acetophenone derivatives—for light absorption and sensitization of the lanthanide (Ln) emitting states, have been synthesized and successively anchored in silica layers by the sol—gel technique. The luminescence properties of the complexes, preliminarily studied in H_2O and D_2O solutions, were improved in the oxide host matrix, showing the effectiveness of the employed synthesis route for the preparation of efficient molecular-based light-emitting materials. All the prepared films were highly transparent and homogeneous and displayed a bright red (Eu^{3+}) or green (Tb^{3+}) luminescence notwithstanding the low luminophore content (Ln/Si = 1/400 or 1/100 molar ratios) and limited film thickness ($\leq$140 nm). It is worth highlighting that the silica layers containing the Tb^{3+} complex bearing an acetophenone derivative as an antenna are characterized by photoluminescence quantum yields as high as 45%.

1. Introduction

During the last decades, solid-state lighting has attracted a great attention because the opportunity to attain more efficient, color tunable, and multiform light sources.[1−3] To this, the research activity on materials employed in luminescent devices produced a variety of solutions involving luminescent metal complexes, organic polymers, charge transporting or blocking units, and organic/inorganic hosting materials.[4] Nevertheless, limitations and technical problems in the fabrication process of devices, such as the tedious and time-consuming multistrate deposition largely used in the production of white-light-emitting OLED, are not completely overcome. To this purpose, alternative approaches voted to simplify the architecture of the emitting layers and to improve their efficiency and lifetime have been pursued.[5−12] For instance, the sol—gel technique,[13] because of its mild synthesis conditions, suitably allows the dispersion of highly luminescent molecular species into stable and optically transparent oxide-based inorganic hosts. Nowadays, the incorporation of light-emitting lanthanide complexes in solid matrices with controlled structural organization is of widespread interest in materials science as it affords functional materials with a variety of optical properties. In this framework, exhaustive reviews on different strategies toward lanthanide-doped hybrid materials[5,8] have been recently reported in the literature. Both class I and II hybrid materials have been prepared following different synthetic strategies involving the insertion of lanthanide complexes (β-diketonates, aromatic carboxylic acids,

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heterocyclic ligands, etc.) into different matrices by means of both simple embedding of the complexes and anchoring of the metal center to specific functional groups or ligands bonded to the host framework.[5,8]

Among Ln elements, Eu(III) and Tb(III) rightly match with that aim because of their exclusive luminescence features and well-known properties as red (λ_{em}^{max} = 614 nm) and green (λ_{em}^{max} = 544 nm) emitters. In general, the luminescence from trivalent lanthanide ions is only slightly affected by the ligand environment, because of their shielded internal ($f-f$) transitions.[14] On the other hand, to fully exploit the luminescence potential of these ions, they must be coordinated by properly selected ligands able to both saturate the 8−9 coordinating positions and act as an antenna for light absorption and sensitization of the emitting states.[15] An interesting and elegant possibility to develop highly luminescent materials is given by the use of a macrocycle as Ln coordinating moiety, bearing an appended light harvesting unit that in turn can be covalently linked to an optically transparent matrix, like SiO_2.[16] In this case, properly designed lanthanide antenna complexes can be successfully embedded as preformed and stable systems within the growing host matrix. To this aim, the modification of the ligands through the introduction of suitable grafting groups (i.e., hydroxyl moieties) is a necessary requisite. Such an approach allows the covalent insertion of the chromophores within the decided matrix and the homogeneous dispersion of the emissive components. As a matter of fact, inhomogeneous distribution could result in the partial loss of luminescence because of undesired interactions of the complexes with the environment, involving the relatively long-lived emitting centers and the excited states of the sensitizer units. On the other hand, this strategy results convenient if simple synthetic procedures to functionalize the emitting compounds are readily available.

In this paper, we report the synthesis and the photophysical properties of 10-[(4,7-diphenyl-9-methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid europium(III) and terbium(III), $Eu^{3+}\subset$**1** and $Tb^{3+}\subset$**1**, respectively, in water and D_2O solutions (Figure 1, Scheme 1).

Successively, the highly luminescent $Eu^{3+}\subset$**1** has been incorporated into sol−gel silica films, yielding transparent glassy layers. The solid-state photoluminescence has been investigated and correlated to the emitting properties obtained in aqueous solutions. In order to get insight on the role played by the nature of the chromophore, $Ln^{3+}\subset$**8** and $Ln^{3+}\subset$**9a** complexes (Ln = Eu, Tb), involving a 9-methylphenanthroline and a 10-[(4-methoxybenzoyl)-methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid units as chromophore,[17] respectively, were comparatively embedded by sol−gel into silica thin films.

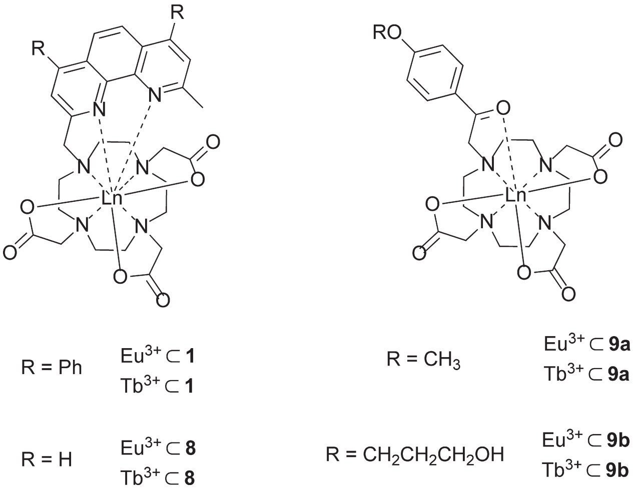

Figure 1. Structures of synthesized complexes.

This study results particularly appealing for the possibility to rationalize the chemical design of emissive materials based on the embedding of luminescent molecular components into transparent host matrices, mostly when the synthesis of emissive species suitably functionalized for the covalent linking to the host medium is very difficult or almost impossible to be achieved. Furthermore, the influence of some parameters that could contribute to the luminescence quenching in the solid state, such as the vibronic coupling due to residual silanol groups and/or water molecules coordinated to the metal center, and the distribution homogeneity of the emitting species within the silica films, which can be severely compromized when the lanthanide complexes are simply dispersed within the matrix, have also been investigated.

2. Experimental Section

Materials and Methods. Solvents were purified by using standard methods and dried when necessary. All commercially available reagents were used as received: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline 96%, europium(III) trichloride hexahydrate 99.9%, and terbium(III) trichloride hexahydrate 99.999% have been purchased from Sigma Aldrich. 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). ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer operating at 400 and 100.6 MHz, respectively. ^1H and APT spectra were referenced to residual solvent proton and carbon resonances. Melting points (uncorrected) were determined with a Buchi B-540 capillary melting point apparatus. Elemental analyses were carried out by the Department Service of Microanalysis (University of Milan).

2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline-*N*-oxide Dihydrate (5). A solution of bathocuproine monohydrate (200 mg, 0.55 mmol) in 5 cm^3 of trifluoroacetic acid and 1.5 cm^3 of 35% aqueous hydrogen peroxide was heated at 60−65 °C and maintained under magnetic stirring for 5 h. After this time the solvent was evaporated in vacuo and the residue, dissolved in 50 cm^3 of CH_2Cl_2, was washed with saturated aqueous solution of $NaHCO_3$ (2 × 10 cm^3) and H_2O (10 cm^3). The organic phase was separated and dried under $MgSO_4$; the solvent was evaporated and the

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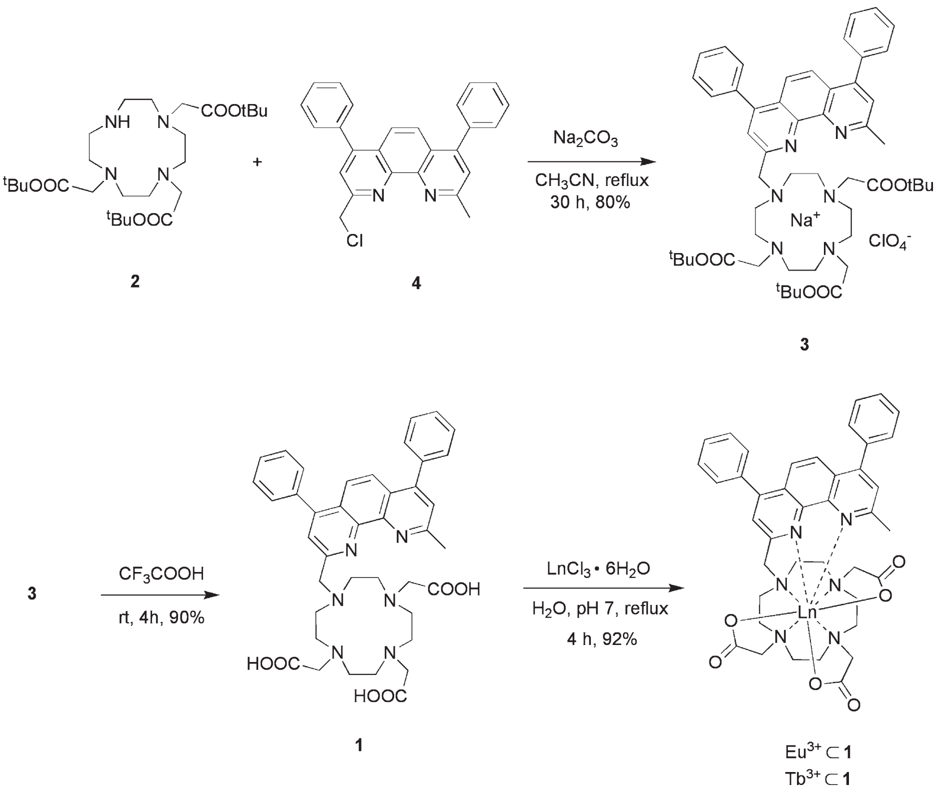
Scheme 1. Synthesis of Complexes $Eu^{3+}\subset 1$ and $Tb^{3+}\subset 1$



residue was purified by column chromatography (silica-gel, CH_2Cl_2/MeOH 95/5 v/v) to afford **5** (190 mg, 92%) as a white solid. Found: C, 82.93; H, 5.37; N, 7.46. $C_{26}H_{20}N_2O$ requires: C, 82.95; H, 5.35; N, 7.44. Mp = 220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (s, 3H, phen2-CH_3), 3.01 (s, 3H, phen9-CH_3), 7.45−7.55 (m, 12H, phen3-H, phen8-H and Ph-H), 7.70 (d, 1H, J = 9.4, phen5-H), 7.79 (d, 1H, J = 9.4, phen6-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 19.5 (phen2-CH_3), 25.7 (phen9-CH_3), 123.9 (phen5-C), 124.5 (phen3-C), 125.2, 125.4 (phen6-C and phen8-C), 128.5 (Ph-C), 128.7 (Ph-C), 128.8 (Ph-C), 129.4, 129.7 (Ph-C), 129.8 (Ph-C), 137.5, 137.8, 149.5 (phen2-C), 157.1 (phen9-C). ESI-MS (m/z): 377.3 $[M + H]^+$ ($C_{26}H_{20}N_2O$ requires 376.45).

2-(Acethoxymethyl)-4,7-diphenyl-9-methyl-1,10-phenanthroline (6). Acetic anhydride (4 cm^3) was added to a solution of **5** (1 g, 2.65 mmol) in CH_2Cl_2 (30 cm^3), the CH_2Cl_2 was removed in vacuo and the solution was refluxed for 1 h. The mixture was concentrated; the residue was dissolved in $CHCl_3$ (60 cm^3) and washed with saturated aqueous Na_2CO_3 (2 × 30 cm^3); and the organic phase, dried with $MgSO_4$, was again concentrated in vacuo. The residue was purified by column chromatography (silica-gel, CH_2Cl_2 followed by CH_2Cl_2/MeOH 95/5) to afford **6** (950 mg, 85%) as yellow solid. Found: C, 80.33; H, 5.32; N, 6.65. $C_{28}H_{22}N_2O_2$ requires: C, 80.36; H, 5.30; N, 6.69). Mp = 55.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H, phen2-$CH_2OOCC\mathit{H}_3$), 3.06 (s, 3H, phen9-CH_3), 5.73 (s, 2H, phen2-$C\mathit{H}_2OOCCH_3$), 7.52−7.55 (m, 11 H, phen8-H and Ph-H), 7.65 (s, 1H, phen3-H), 7.79 (d, 1H, J = 9.6, phen6-H), 7.84 (d, 1H, J = 9.6, phen5-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 21.0 (phen2-$CH_2OOC\mathit{C}H_3$), 25.5 (phen9-CH_3), 67.8 (phen2-$\mathit{C}H_2OOCCH_3$), 121.6 (phen3-C), 123.2 (phen6-C), 124.0 (phen5-C), 124.5 (phen8-C), 125.0, 126.1, 128.7 (Ph-C), 129.6 (Ph-C), 130.0 (Ph-C), 137.8, 137.9, 149.5, 156.1 (phen9-C), 158.9 (phen2-C), 170.7 (phen2-$CH_2OO\mathit{C}CH_3$). m/z (ESI-MS) 419.3 $[M + H]^+$; 441.3 $[M + Na]^+$ ($C_{28}H_{22}N_2O_2$ requires 418.17).

2-(Hydroxymethyl)-4,7-diphenyl-9-methyl-1,10-phenanthroline (7). A suspension of **6** (500 mg, 1.2 mmol) and anhydrous K_2CO_3 (284 mg, 2.03 mmol) in anhydrous EtOH (10 cm^3) was stirred at room temperature for 4 h. The mixture was concentrated in vacuo, the residue was triturated with CH_2Cl_2 and the solid was filtered off. The filtrate was concentrated in vacuo to afford **7** (450 mg, quantitative yield) as a light brown solid. Found: C, 82.91; H, 5.32; N, 7.40. $C_{26}H_{20}N_2O$ requires: C, 82.95; H, 5.35; N, 7.44. Mp = 245.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.04 (s, 3H, phen9-CH_3), 5.18 (s, 2H, phen2-$C\mathit{H}_2OH$), 7.50−7.57 (m, 14H, phen3-H, phen8-H and Ph-H), 7.82 (s, 2H, phen5-H and phen6-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 25.2 (phen9-CH_3), 65.5 (phen2-$\mathit{C}H_2OH$), 121.1 (phen3-C), 123.4 (phen6-C), 123.6 (phen5-C), 124.4 (phen8-C), 124.98, 125.97, 128.6 (Ph-C), 129.62 (Ph-C), 137.7, 137.8, 149.5, 149.6, 158.7 (phen9-C), 159.8 (phen2-C). m/z (ESI-MS) 377.4 $[M + H]^+$; 399.3 $[M + Na]^+$ ($C_{26}H_{20}N_2O$ requires 376.16).

2-(Chloromethyl)-4,7-diphenyl-9-methyl-1,10-phenanthroline (4). To a stirred solution of **7** (200 mg, 0.53 mmol) in $CHCl_3$ (10 cm^3) was added PCl_3 (1 cm^3) in $CHCl_3$ (5 cm^3). The mixture was refluxed for 1 h and then concentrated in vacuo to afford a viscous oil that was carefully neutralized with aqueous 10% Na_2CO_3. The light yellow precipitate was filtered, washed with cold water, and dried under a vacuum to afford **4** (120 mg, 57%) as an ivory solid. Found: C, 78.99; H, 4.80; N, 7.05. $C_{26}H_{19}ClN_2$ requires: C, 79.08; H, 4.85; N, 7.09. Mp = 203.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.01 (s, 3H, phen9-CH_3), 5.17 (s, 2H, phen2-CH_2Cl), 7.49−7.56 (m, 11H, phen8-H and Ph-H), 7.80 (d, 1H, J 9.6, phen6-H), 7.84 (d, 1H, J 9.6, phen5-H), 7.88 (s, 1H, phen3-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 26.0 (phen9-CH_3), 47.8 (phen2-CH_2Cl), 122.6 (phen3-C), 122.9 (phen6-C), 124.3 (phen8-C), 124.4 (phen5-C), 124.97, 126.03, 128.6 (Ph-C), 129.7 (Ph-C), 137.9, 138.0, 145.4, 146.0, 148.8, 149.8, 156.6 (phen9-C), 159.1 (phen2-C). m/z (ESI-MS) 395.4 $[M + H]^+$ ($C_{26}H_{19}ClN_2$ requires 394.12).

10-[(4,7-Diphenyl-9-methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic Acid Tris(1,1-dimethylethyl) Ester Sodium Perchlorate Complex (3). A suspension of **4** (784 mg, 1.99 mmol), DO3A tris (*tert* butyl) ester **2** (1.0 g, 1,81 mmol), and Na_2CO_3 (385 mg, 3.63 mmol) in acetonitrile (80 cm^3) was refluxed for 24 h under magnetic stirring. The mixture was cooled to room temperature and filtered on a fritted glass, and the filtrate was evaporated to afford a viscous oil residue. This product was dissolved in CH_2Cl_2 (100 cm^3) and washed with water (2×50 cm^3) and then with 30% aqueous $NaClO_4$ (3×50 cm^3). The solvent was removed under reduced pressure and the product was purified by column chromatography (silica-gel, CH_2Cl_2 followed by CH_2Cl_2/MeOH 95/5) to afford **3** (1.42 g, 80%) as a yellow solid. Found: C, 62.69; H, 6.92; N, 8.40. $C_{52}H_{68}ClN_6NaO_{10}$ requires: C, 62.73; H, 6.88; N, 8.44. Mp = 185.2 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.05 [bs, 18H, N1-$CH_2COOC(C\mathit{H}_3)_3$ and N7-$CH_2COOC(C\mathit{H}_3)_3$], 1.36 [s, 9H, N4-$CH_2COOC(C\mathit{H}_3)_3$], 1.76 [bs, 2H, N4−$C\mathit{H}_2COOC(CH_3)_3$], 2.29−3.49 [bs, 23H, N1−$C\mathit{H}_2COOC(CH_3)_3$, N7−$C\mathit{H}_2COOC(CH_3)_3$, NCH_2CH_2N and phen9-CH_3], 4.00 (bs, 2H, N10-CH_2phen), 7.46−7.54 (m, 11H, phen8-H and Ph-H), 7.71 (s, 1H, phen3-H), 7.76 (d, 1H, *J* 9.4, phen6-H), 7.79 (d, 1H, *J* 9.4, phen5-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 25.9 (phen9-CH_3), 27.8 [N4-CH_2COOC-$(\mathit{C}H_3)_3$], 28.1 [N1-$CH_2COOC(\mathit{C}H_3)_3$ and N7-$CH_2COOC(\mathit{C}H_3)_3$], 51.6 ($\mathit{C}H_2$−N10-$\mathit{C}H_2$), 56.2 ($NCH_2CH_2N$), 56.3 ($NCH_2CH_2N$), 60.1 (N10-$\mathit{C}H_2$phen), 81.9 [N1-$CH_2COO\mathit{C}(CH_3)_3$ and N7-CH_2-$COO\mathit{C}(CH_3)_3$], 82.1 [N4-$CH_2COO\mathit{C}(CH_3)_3$], 123.0 (phen6-C), 123.9 (phen5-C), 124.1 (phen8-C), 124.4 (phen3-C), 124.89, 125.54, 128.6 (Ph-C), 128.7 (Ph-C), 129.5 (Ph-C), 129.7 (Ph-C), 137.8, 137.9, 145.94, 148.8, 149.4, 158.0 (phen9-C), 158.4 (phen2-C), 172.4 [N4-$CH_2\mathit{C}OOC(CH_3)_3$], 172.9 [N1-$CH_2\mathit{C}OOC(CH_3)_3$ and N7-$CH_2\mathit{C}OOC(CH_3)_3$]. *m*/*z* (ESI-MS) 895.5 $[M + Na]^+$, 873.4 $[M + H]^+$ ($C_{52}H_{68}N_6O_6Na^+$ requires 895.51).

10-[(4,7-Diphenyl-9-methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (1). A solution of **3** (1.3 g, 1.31 mmol) in trifluoroacetic acid (40 cm^3) was stirred at room temperature for 4 h. The solvent was evaporated to afford a viscous oil residue that was triturated with diethyl ether to yield a white solid. The solvent was separated and the solid, dissolved in H_2O (2 cm^3), was adsorbed on a short Amberlite XAD 1600T column that was eluted with water until the pH was neutral and then with water/acetonitrile 9/1 (v/v) to recover **1** (0.82 g, 90%) as a white solid. Found: C, 68.12; H, 6.31; N, 11.89. $C_{40}H_{44}N_6O_6$ requires C, 68.16; H, 6.29; N, 11.92. Mp = 214.5 °C; ^1H NMR (CD_3OD, 400 MHz): δ 3.10 (s, 3H, phen9-CH_3), 3.24−3.32 (m, 12H, NCH_2CH_2N), 3.50 (m, 8H, N1−$C\mathit{H}_2COOH$, N7−$C\mathit{H}_2COOH$ and $C\mathit{H}_2$−N10-$C\mathit{H}_2$), 3.67 (bs, 2H, N4−$C\mathit{H}_2COOH$), 4.49 (bs, 2H, N10-CH_2phen), 7.46−7.60 (m, 10H, Ph-H), 7.76 (s, 1H, phen8-H), 7.83 (d, 1H, *J* 9.6, phen6-H), 7.86 (d, 1H, *J* 9.6, phen5-H), 7.88 (s, 1H, phen3-H); ^{13}C NMR (CD_3OD, 100.6 MHz): δ 24.0 (phen9-CH_3), 49.0 (NCH_2CH_2N), 49.2 (NCH_2CH_2N), 50.6 (NCH_2CH_2N), 51.1 (NCH_2CH_2N), 54.3 (N4-$\mathit{C}H_2COOH$), 56.1 (N1−$\mathit{C}H_2COOH$ and N7−$\mathit{C}H_2COOH$), 58.4 (N10-$\mathit{C}H_2$phen), 123.6 (phen6-C), 124.1 (phen5-C), 125.3, 125.5 (phen8-C), 125.7 (phen3-C), 126.1, 128.5 (Ph-C), 128.6 (Ph-C), 129.15 (Ph-C), 129.5 (Ph-C), 129.7 (Ph-C), 136.6, 136.9, 141.99, 143.18, 150.14, 152.92, 155.0 (phen9-C), 158.0 (phen2-C), 169.4 (N4-$CH_2\mathit{C}OOH$), 172.2 (N1- $CH_2\mathit{C}OOH$ and N7-$CH_2\mathit{C}OOH$); *m*/*z* ESI-MS: 705.4 $[M + H]^+$ ($C_{40}H_{44}N_6O_6$ requires 704.33).

10-[(4,7-Diphenyl-9-methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic Acid Europium(III) Complex ($Eu^{3+}\subset$1). A solution of $EuCl_3 \cdot 6H_2O$ (142 mg, 0.39 mmol) in H_2O (2 cm^3) was slowly added to a magnetically stirred solution of **1** (250 mg, 0.36 mmol) in H_2O (20 cm^3) at room temperature. During this addition, the pH of the reaction solution was maintained at 6.5−7.0 by contemporary addition of a 2% NaOH aqueous solution. The reaction mixture was then heated to reflux for 4 h, 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 6/4 to afford $Eu^{3+}\subset$**1** (280 mg, 92%) as a white solid. Found: C, 56.22; H, 4.79; N, 9.80. $C_{40}H_{41}EuN_6O_6$ requires C, 56.27; H, 4.84; N, 9.84. Mp = 328.9 °C. *m*/*z* ESI-MS: 875.21594 (81.95%); 876.22038 (38.24%); 877.21701 (100%); 878.22132 (41.53%); 879.22727 (8.06%) $[M + Na]^+$ [$C_{40}H_{41}N_6O_6EuNa$ requires 875.21782 (83%); 876.22092 (38%); 877.21966 (100%); 878.22246 (43.54%); 879.22525 (10.79%)].

10-[(4,7-Diphenyl-9-methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid terbium(III) Complex ($Tb^{3+}\subset$1). This compound was prepared as described for $Eu^{3+}\subset$1 starting from 1 (250 mg, 0.36 mmol) and $TbCl_3 \cdot 6H_2O$ (146 mg, 0.39 mmol). Purification of the crude with Amberlite XAD 1600T afforded $Tb^{3+}\subset$**1** (280 mg, 92%) as a light yellow solid (Found: C, 55.78; H, 4.78; N, 9.68. $C_{40}H_{41}N_6O_6Tb$ requires C, 55.82; H, 4.80; N, 9.76); mp = 363.0 °C; *m*/*z* ESI-MS: 883.22205 (100%); 884.22735 (42.18%); 885.23255 (7.63%) $[M + Na]^+$ [$C_{40}H_{41}N_6O_6TbNa$ requires 883.22331 (100%); 884.22642 (46%); 885.22929 (11.65%)].

10-[(4-Methoxybenzoyl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic Acid Europium(III) Complex ($Eu^{3+}\subset$9a). This compound was prepared as described for $Eu^{3+}\subset$1 starting from **9a** (250 mg, 0.51 mmol) and $EuCl_3 \cdot 6H_2O$ (204 mg, 0.56 mmol). Purification of the crude with Amberlite XAD 1600T afforded $Eu^{3+}\subset$**9a** (301 mg, 92%) as a light yellow solid. Found: C, 42.89; H, 4.79; N, 8.68. $C_{23}H_{31}EuN_4O_8$ requires: C, 42.93; H, 4.86; N, 8.71. *m*/*z* ESI-MS: 665.12222 (91.45%); 666.12803 (24.17); 667.12376 (100%); 668.12906 (23.06%); 669.13354 (3.07%) $[M + Na]^+$ [$C_{23}H_{31}N_4O_8EuNa$ requires 665.12328 (87.52%); 666.12630 (23.61%); 667.12483 (100%); 668.12776 (26.41%); 669.13023 (5.0%)].

10-[(4-Methoxybenzoyl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic Acid Terbium(III) Complex ($Tb^{3+}\subset$9a). This compound was prepared as described for $Eu^{3+}\subset$1 starting from **9a** (250 mg, 0.51 mmol) and $TbCl_3 \cdot 6H_2O$ (207 mg, 0.56 mmol). Purification of the crude with Amberlite XAD 1600T afforded $Tb^{3+}\subset$**9a** (301 mg, 92%) as a light yellow solid. Found: C, 42.44; H, 4.76; N, 8.58. $C_{23}H_{31}N_4O_8Tb$ requires: C, 42.47; H, 4.80; N, 8.61. *m*/*z* ESI-MS: 673.12859 (100%); 674,13308 (23.67%); 675.13777 (3.51%) $[M + Na]^+$ [($C_{23}H_{31}N_4O_8TbNa$ requires 673.12875 (100%); 674.13182 (26,98%); 675.13427 (5.15%)].

Preparation of the Sol−Gel Films. Silica-based thin films embedding Eu(III) and Tb(III) complexes were obtained by sol−gel dip-coating using TEOS [$Si(OC_2H_5)_4$] as the silica source under acidic conditions following a well-established procedure.[12,16] The solutions containing the single lanthanide complexes were prepared employing a Eu:Si = Tb:Si = 1: 400 (or 100) molar ratio. Herasil silica slides (2×1 cm^2) were used as the substrate. Regardless of the employed antenna and complex concentration, as-prepared samples resulted homogeneous and well-adherent to the substrates, transparent, and crack free. The obtained layers were subsequently used in the photoluminescence experiments both as-prepared and annealed at 200 °C for 5 h. After thermal treatment ca. 140 nm thick layers were obtained.

Spectroscopic Measurements. Absorption spectra were recorded with a Perkin-Elmer Lambda9 spectrophotometer.

For luminescence experiments, the samples were placed in fluorimetric 1 cm path cuvettes and, when necessary, purged from oxygen by bubbling with argon. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplayer tube (185−850 nm). Corrected spectra were obtained via a calibration curve supplied with the instrument. Luminescence quantum yields (Φ_{em}) in solution obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas and Crosby[18] using air-equilibrated $[Ru(bpy)_3]Cl_2$ in water solution [Φ_{em} = 0.028][19] as standard. The luminescence lifetimes in the microsecond-millisecond scales were measured by using a Perkin-Elmer LS-50 spectrofluorimeter equipped with a pulsed xenon lamp with a variable-repetition rate and elaborated with standard software fitting procedures. To record the 77 K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz dewar, filled up with liquid nitrogen. For solid samples, Φ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulfate coated integrating sphere (6 in.), a 5mW He−Cd laser (λ_{exc} = 325 nm) or a 450W Xe lamp (λ_{exc} = tunable by a monochromator supplied with the instrument) as light source, and a R928 photomultiplayer tube as signal detector, following the procedure described by De Mello et al.[20] Experimental uncertainties are estimated to be ±8% for lifetime determinations, ±20% for emission quantum yields, and ±2 and ±5 nm for absorption and emission peaks, respectively.

Chemical Characterization of Thin Films. Secondary ion mass spectrometry (SIMS) was exploited to measure the elemental in-depth profiles of chemical species in the lanthanide-doped silica films. SIMS measurements were carried out by means of a IMS 4f mass spectrometer (Cameca, Padova, Italy) using a 14.5 keV Cs^+ primary beam and by negative secondary ion detection. The charge build up while profiling the insulating samples was compensated by an electron gun without any need to cover the surface with a metal film. The SIMS spectra were carried out at a primary beam intensity (10 nA, stability 0.4%) rastering over a 150 × 150 μm^2 area and detecting secondary ions from a sub region close to 10 × 10 μm^2 to avoid crater effects. The signals were detected in beam blanking mode (i.e., interrupting the sputtering process during magnet stabilization periods) in order to improve the in-depth resolution. The erosion speed was then evaluated by measuring the depth of the erosion crater at the end of each analysis by means of a Tencor Alpha Step profilometer with a maximum uncertainty of few nanometers. The measurements were performed in high mass resolution configuration to avoid mass interference artifacts.

X-ray photoelectron spectroscopy (XPS) analysis was exploited to measure the actual Ln/Si atomic ratio in the lanthanide-doped silica films. XPS measurements were performed on a Perkin-Elmer Φ 5600ci spectrometer using a monochromatized Al Kα radiation (1486.6 eV), at a working pressure lower than 1×10^{-9} mbar. The specimens, mounted on steel sample holders, were introduced directly into the XPS analytical chamber by a fast entry lock system. The Binding Energies (BEs, standard deviation = ±0.2 eV) were corrected for charging effects assigning to the adventitious C1s line a BE of 284.8 eV. The atomic composition of the samples was calculated by peak integration, using sensitivity factors provided by the spectrometer manufacturer (Φ V5.4A software) and taking into account the geometric configuration of the apparatus.

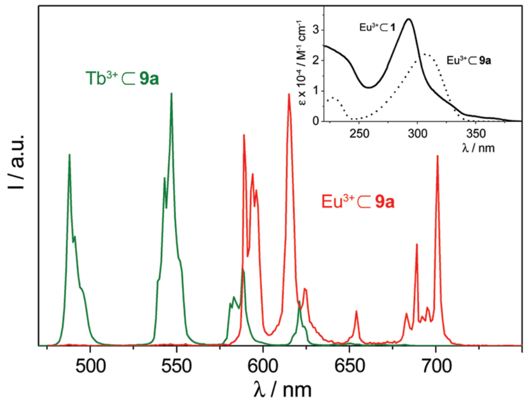


Figure 2. Normalized emission spectra in water solution of $Eu^{3+} \subset$**9a** (red line) and $Tb^{3+} \subset$**9a** (green line) (Room temperature, O.D. = 0.2, $\lambda_{exc} = \lambda_{max}$). Inset: absorption spectra in water solution of $Eu^{3+} \subset$**1** (solid line) and $Eu^{3+} \subset$**9a** (dotted line).

3. Results and Discussion

Design and Synthesis of Ligands and Complexes. Bipartite ligand **1** features a bathocuproine group, as the light absorbing chromophore, covalently connected through one methylene spacer to a 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A) unit as the lanthanide (III) coordination site.

The polyazapolycarboxylate heptadentate ligand DO3A was selected as the chelating site because of its well-known capability to form neutral lanthanide complexes characterized by a very high thermodynamic stability and kinetic inertness.[21] The Eu(III) complex of a bathocuproine derivative, namely, 4,7-bis(chlorosulfonylphenyl)-1,10-phenanthroline-2,9-dicarboxylic acid (BCPDA), has been largely used for time-resolved fluoro immunoassays (TR-FIA) in the CyberFluor system.[22] In this system, the BCPDA is covalently linked to the immunoreactant and behaves as an efficient Eu(III) chelator and sensitizer.[23] The choice of bathocuproine as antenna, besides the high sensitization efficiency that we expected to be similar to that of phenanthroline,[15,17,24] is related to its red-shifted electronic absorption profile (Figure 2) relative to that of phenanthroline, which allows the use of longer excitation wavelenghts. Ligand **1** was synthesized according to Scheme 1.

Alkylation of DO3A tris(*tert*-butyl)ester **2**[25] with 2-chloromethyl-4,7-diphenyl-9-methyl-1,10-phenanthroline **4** carried out in acetonitrile at reflux in the presence of solid Na_2CO_3 as base, and subsequent treatment of the crude, dissolved in CH_2Cl_2, with aqueous $NaClO_4$ afforded the complex **3** isolated in 80% yield after column chromatography.

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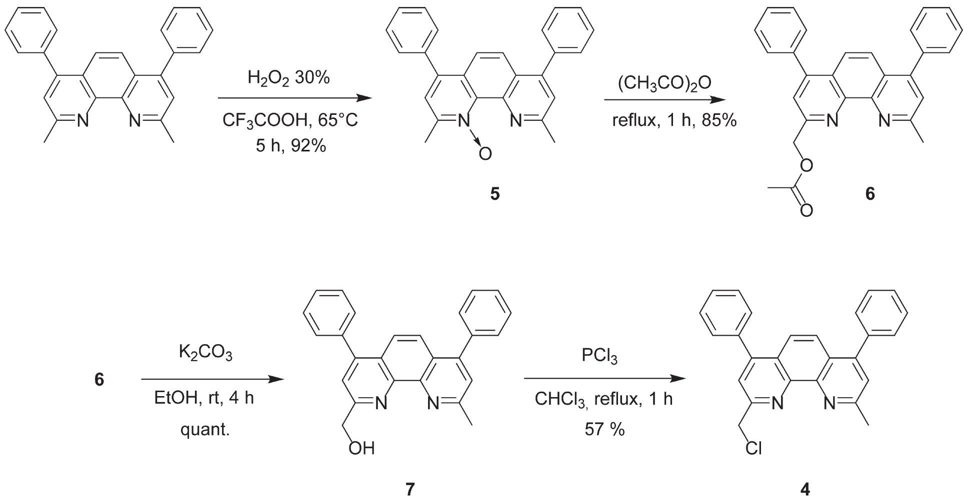
Scheme 2. Synthesis of Compound 4



The preparation of **3** is necessary in order to simplify the chromatographic purification and allows higher yields of isolated product. Treatment of **3** with CF_3COOH at room temperature afforded the tris-carboxyl derivative **1**, as white solid, in quantitative yield after purification through an Amberlite XAD 1600T resin.

Complexes $Eu^{3+}\subset$**1** and $Tb^{3+}\subset$**1** were prepared by addition of an aqueous solution of $EuCl_3\cdot 6H_2O$ or $TbCl_3\cdot 6H_2O$ respectively, to an aqueous solution of free ligand **1** and maintaining the pH at 6.5−7.0 by contemporary addition of diluted NaOH. These complexes were obtained in quantitative yields after purification through a Amberlite XAD 1600T column that allows to remove all the inorganic salts.

The preparation of the chloromethylbathocuproine **4** (Scheme 2) was achieved according to the four steps procedure already reported by Newkome and co-workers for the preparation of the 2-chloromethyl-9-methyl-1,10-phenanthroline.[26] However differently from the Newkome's procedure, the mono-N-oxide **5** was readily obtained by oxidation of the commercially available bathocuproine with 35% hydrogen peroxide in trifluoroacetic acid and afforded **5** in 92% yield.[17] All the other steps from **5** to **4** were carried out using reagents and the reaction conditions described.[26]

Ligand **9a** (Scheme 3) bearing a 4-methoxyacetophenone covalently linked to the secondary nitrogen atom of the DO3A has been prepared following the procedure reported by Beeby et al.[27] Complexation of **9a** with Eu(III) and Tb(III) was carried out as described above for ligand **1** and afforded $Eu^{3+}\subset$**9a** and $Tb^{3+}\subset$**9a** complexes in high yields after purification through Amberlite XAD 1600T column.

Photophysical Properties. The employed chromophores differ basically in the coordination features at the Ln cations (acetophenone vs phenanthroline derivatives), and in the energy of the triplet state of their antennas, which affects the efficiency of energy transfer to the Ln^{3+} emitting states. A further point to consider in luminescent materials is the nature of host−guest interactions: clustering and aggregation of the emitting centers should be avoided in order to minimize concentration quenching effects, hence the dispersion of the functional molecules in the matrix represents an important aspect. To compare the role played by the nature of the chromophore incorporation, i.e., covalent linking vs blending of the emissive components, on the photoluminescence (PL) performances of the final materials, we compare the results here presented for silica layers embedding the $Ln^{3+}\subset$**9a** antenna complexes with our previous results,[12,16] where the structurally similar complexes $Ln^{3+}\subset$**9b** were bonded to the silica matrix through a propyl-hydroxy group, properly introduced in the antenna unit. The absorption spectra of $Eu^{3+}\subset$**1** and $Eu^{3+}\subset$**9a** in water solution, reported in Figure 2 (those of related Tb(III) complexes showed identical profiles), can be attributed to the ligand-centered (LC) electronic transitions[28] and are confined in the UV spectral region.

The chelating chromophores (bathocuproine and acetophenone) play as antennas for the sensitization of the lanthanide-based luminescence, accordingly to the following steps: (i) absorption of light, (ii) highly efficient intersystem crossing (ISC) from the populated singlet (S) level to the triplet (T) level, and (iii) transfer of excitation energy to the lanthanide cation. Nevertheless, the resulting metal centered (MC) luminescence (Figure 2) can be influenced by several factors depending on both the energy of the involved excited states and external environment.[29]

For instance, in the case of $Eu^{3+}\subset$**9a** and $Tb^{3+}\subset$**9a**, the suitable energy gap between Eu(III) and Tb(III) emissive states ($^5D_0 \sim 17.500$ and $^5D_4 \sim 20.500$ cm^{-1}, respectively) and the acetophenone triplet level (25.200 cm^{-1})[16] leads to an efficient sensitization step, avoiding any back

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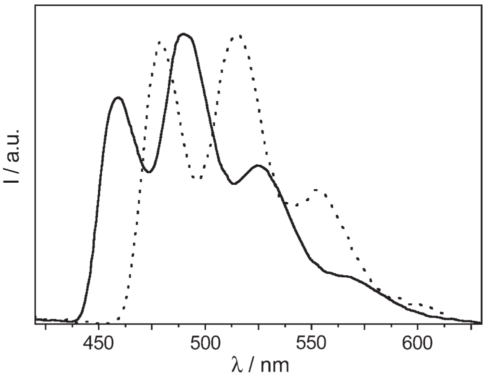

Figure 3. Normalized phosphorescence spectra of phenanthroline (solid line) and bathocuproine (dotted line) obtained at 77 K in ethylene iodide rigid matrix in order to enhance the singlet−triplet intersystem crossing (ISC) due to heavy atom effect, λ_{exc} = 264 and 274 nm, respectively. From the highest energy vibrational feature of the phosphorescence bands, the zero−zero energy of the lowest ligand-centered triplet state can be evaluated.[28]

Scheme 3. Complexation of Ligand 9a

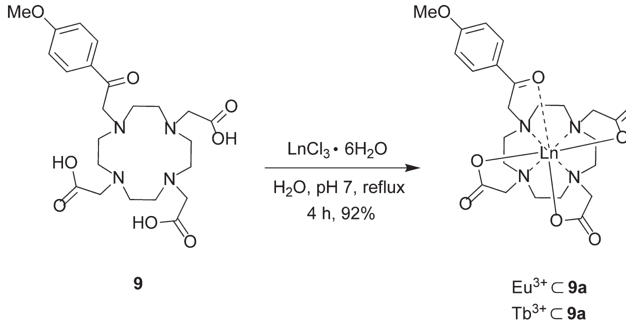

Table 1. Room-Temperature Luminescence Data in Solution and in the Solid Silica Films (Ln/Si = 1/400).

	H_2O^a		D_2O^a		SiO_2 matrix^{a,g}	
	ϕ_{se}	τ (ms)	ϕ_{se}	τ (ms)	$\phi_{se}{}^b$	τ (ms)
$Eu^{3+}\subset$**1**	0.18	1.25	0.31	1.82	0.25	1.2
$Tb^{3+}\subset$**1**	< 0.001^c	^{d}	< 0.001	^{d}	< 0.001	^{d}
$Eu^{3+}\subset$**8**	0.21^e	1.24^e	0.30^f	1.77^f	0.19	1.25
$Tb^{3+}\subset$**8**	0.11^e (0.55)^e	0.31^e (1.51)^e	0.12	0.32	0.15	1.1
$Eu^{3+}\subset$**9a**	0.07	0.6	0.25	2.2	0.12	0.7
$Tb^{3+}\subset$**9a**	0.34	1.7	0.54	2.5	0.45	1.5

[a] $\lambda_{exc} = \lambda_{max}$. [b] Average values obtained with three measurements. [c] Negligible improvements have been recorded by removing oxygen upon bubbling with argon for 10 min. [d] Not reported due to the weakness of the signal. [e] From ref 17. [f] From ref 24. [g] A 450W Xe lamp was used as light source for the excitation of the glassy samples (see ref 30 for details). In brackets () = degassed sample.

energy transfer process. The triplet level of the bathocuproine (20.900 cm^{-1}, as calculated by low-temperature emission profile reported by Figure 3, see caption) matches with an effective population of the Eu(III) excited states, but it is unsuitable for the higher-energy Tb(III) emitting level, leading to a scarce MC luminescence intensity (Table 1).

On the contrary, as previously reported,[17] the phenanthroline unit effectively acts as antenna for both $Eu^{3+}\subset$**8** and, to a lesser extent, $Tb^{3+}\subset$**8**. In fact, in the latter case, a larger energy gap between the sensitizer and emitting levels would further improve the PL performances.

Another contribution to the MC luminescence quenching is given by the vibronic coupling between the metal ion emitting states and the oscillator levels (−OH is the most efficient, although −CH and −NH show significant abilities).[31] This effect can be limited by replacing the −OH groups with −OD ones upon using deuterated solvents (D_2O in the present case). This allows a decrease in the overlap between involved orbitals, leading to a drastic cut of the oscillators quenching power.[28] As a result, the emission efficiencies of $Eu^{3+}\subset$**9a** and $Tb^{3+}\subset$**9a** are enhanced by ~3.6 and ~1.6 times, respectively (Table 1). The related decays show similar behavior confirming the close relationship between intensity and lifetime of lanthanide (III) radiative transitions. A similar trend has also been followed by complexes involving **1** and **8** as chelating units (Table 1).

The number of coordinated solvent molecules (q, uncertainty ± 0.5) at the metal centers can be estimated on the basis of the following eq[32,33]

$$q^{Eu} = 1.2(1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.25) \qquad (1a)$$

$$q^{Tb} = 4.2(1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.06) \qquad (1b)$$

For $Eu^{3+}\subset$**9a** and $Tb^{3+}\subset$**9a**, only one water molecule in the first coordination sphere of the metal ($q = 1.1 \pm 0.5$ and 0.6 ± 0.5, respectively) has been calculated, whereas $Eu^{3+}\subset$**1** shows a very small value ($q \approx 0.0007$) (in the case of $Tb^{3+}\subset$**1**, the weakness of the signal forbids the estimation of the coordinating solvent molecules, although a value of q similar to that of $Eu^{3+}\subset$**1** could be expected). This result indicates that, as has been demonstrated in the case of $Eu^{3+}\subset$**8**,[24] both the nitrogen atoms of the bathocuproine are coordinated to the metal center leading to a saturation of the lanthanide cation coordination sites. This excludes the presence of water molecules in the first metal ion coordination sphere, resulting in a higher overall luminescence of $Eu^{3+}\subset$**1** and $Eu^{3+}\subset$**8** with respect to $Eu^{3+}\subset$**9a**, as showed in Table 1 (to be noted that the PL performances of terbium(III) complexes are affected by energetic issues, see above).

In the solid state, the Ln(III) complexes showed remarkable luminescence intensities, with quantum yields up to 45% for $Tb^{3+}\subset$**9a** (see Table 1); an exception is observed for $Tb^{3+}\subset$**1**, in which the sensitization process is not successful because of the unfavorable energy gap between its donor and acceptor levels (see above). Literature values of luminescence quantum yields for both classes I and II

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(30) The use of laser as an excitation source to measure the thin film (tens of nanometers) quantum yields may be unsuitable because the high energy power and the reduced size of the spot generate a partial deterioration of the sample during the measurement, leading to an underestimation of the emission efficiency. On the contrary, less energetic arc lamps (i.e., Xe lamp) avoid such a problem.

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hybrid materials mostly containing Eu^{3+} β-diketonate complexes fall within the 20−35% range.[5,34,35] Conversely, a few papers have been found in the literature concerning Tb^{3+} complexes. Moreover, to the best of our knowledge, quantum yields data for Tb^{3+} derivatives in solid matrices have not been reported in literature up to date.

Basically, the luminescent complexes showed a similar PL trend both in solution and in the SiO_2 glassy layers, indicating that the phenanthroline derivatives (**1** and **8**) and the acetophenone-based units (**9a**) resulted in being the most efficient antenna systems for the Eu(III) and Tb(III) luminescence, respectively, regardless of the chromophore amount and thermal annealing. All the samples, when irradiated with a black light (λ = 254 and 365 nm, 4W tubes), presented a bright red (Eu^{3+}) or green (Tb^{3+}) luminescence clearly visible to the naked eye. Furthermore, whereas the luminescence quantum yield and lifetime are not influenced by the different conditions, the difference in the emission intensities between diluted ($1Ln^{3+}$: 400Si) and concentrated ($1Ln^{3+}$: 100Si) solid samples was clearly appreciated at the macroscopic level. As for the thermal treatment, no variation in the macroscopic appearance of the specimen was observed. The observation that both as-deposited and annealed silica layers show a comparable emissive behavior suggests that the glassy matrix can be structurally strenghtened through suitable thermal treatments while maintaining unaltered the luminophores efficiency and the high degree of homogeneity for the physical state of the films.

Furthermore, such antenna complexes, simply dispersed via sol−gel and not covalently linked to the SiO_2 matrix (see section on film preparation), showed a uniform distribution inside the glassy layers, similarly to that found for the covalently linked complexes previously investigated.[12,16] In this regard, in Figure 4, the SIMS depth profiles for the silica thin films embedding $Eu^{3+}\subset$**1** and $Eu^{3+}\subset$**9a** in two different concentrations (see section on film preparation) are reported.

Regardless of the structural difference of the employed chromophores and their concentration in the sol−gel silica matrices, similar in-depth distribution features are displayed from the SIMS profiles. In particular, all the films are characterized by the homogeneous presence of C, N, and Eu throughout the whole layer thickness and no segregation peaks can be detected. As concerns the actual Ln/Si atomic ratio in the silica layers, it was determined through XPS analysis and compared to the nominal value in the precursor solution. Interestingly, the XPS analysis of the concentrated $Eu^{3+}\subset$**1**/SiO_2 specimen revealed the presence of Si (19.2 at %), O (56.8 at %), C (22.8 at %), and N (1.2 at %) on the film surface. Eu signals could not be detected because of the low amount of the lanthanide in the silica matrix. Considering that for the preparation of the concentrated sol−gel solutions a Si/Eu ratio of 100 has been employed (see Experimental Section) and that each $Eu^{3+}\subset$**1** molecule contains 6 nitrogen atoms whose source is the only lanthanide compounds, a nominal Si/N = 16.7 ratio can be easily calculated. The experimental Si/N value of 16 is thus in good agreement with the nominal one pointing out, together with the SIMS results, the efficacy of the employed synthesis method for the realization of highly dispersed host−guest systems with tailored composition.

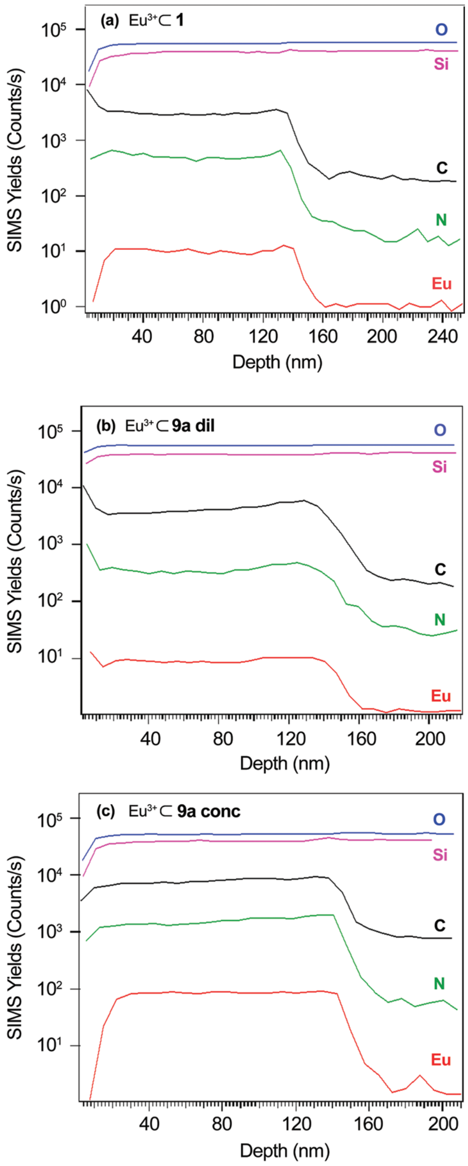

Figure 4. SIMS depth profiles of (a) $Eu^{3+}\subset$**1**/SiO_2 and (b, c) $Eu^{3+}\subset$**9a**/SiO_2 layers annealed at 200 °C for 5 h at different lanthanide complex concentrations.

It is worth noticing that the overall luminescence quantum yields of the films were high and only slightly affected by the nature of the host−guest chemical interactions between the matrix and the chromophores (see Table 1). Consequently, whenever the synthesis of antenna complexes suitably functionalized for the covalent linking to the host medium is very demanding or almost impossible to be achieved, comparable luminescence efficiencies can be obtained by embedding the proper luminescent molecular components into transparent host matrices. Hence, for solid-state lighting purposes, the choice between covalent

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grafting vs embedding of the complexes will be driven, once we have identified the better sensitizer, by the possibility of an easy functionalization procedure for the antenna unit.

Considering that this kind of materials is also studied for applications in clinical diagnostics (such as fluoroimmunoassay[23−25]), it is important to consider their behavior in contact with liquid media, in order to achieve the better performance in the more convenient way. To this purpose, two different SiO_2 films containing the covalently linked $Eu^{3+}\subset$**9b** and the simply dispersed $Eu^{3+}\subset$**9a** complexes were prepared and dipped in water for 12 h. After that period, the resulting solutions were irradiated with a UV source and only in the latter case was a pale red emission detected, indicating a partial leaching of the luminophore from the solid to the solution phase when the antenna complexes are simply embedded in the host matrix. In this case, the design of the antenna complexes and materials synthesis will be driven by the need of originating highly amplified optical signals in the silica layers, avoiding the release of the active species.

4. Conclusion

The data here reported indicate that the correct design of the ligand is of paramount importance to achieve highly luminescent lanthanide(III) antenna complexes. The most relevant aspects that should be considered are as follows: (i) the ligand should contain a number of properly organized binding sites providing the complete saturation of the Ln^{3+} sphere coordination sites, in order to minimize the nonradiative deactivation by vibronic quenchers; and (ii) the energy gap between the triplet state of the chromophore and the emissive levels of the Ln^{3+} cation should be large to avoid possible back energy transfer deactivation processes. The noncovalent incorporation of highly luminescent Eu(III) and Tb(III) complexes into silica thin films by sol−gel technique proved to be a valuable and easy procedure for the preparation of efficient visible emitters. Indeed, the materials here described are homogeneous and transparent and show very high overall sensitization quantum yields, up to 45%. A partial leaching of the emissive species is observed under particular conditions (e.g., by immersion of the material in water) thus representing a limitation for the use of these materials in applications that require aqueous media. Finally, the procedure here reported is particularly appealing when the synthesis of suitable functionalized emissive species for the covalent linking to the silica network is very difficult or almost impossible to be achieved. These aspects are particularly important to rationalize the chemical design and the preparations of highly efficient light-emitting materials.

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Note Added after ASAP Publication. In the version of this paper published online May 19, 2009, there were incorrect symbols in the Photophysical Properties section of the Results. The corrected version was published to the Web on May 21, 2009.