Photophysical properties and tunable colour changes of silica single layers doped with lanthanide(III) complexes†

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Received (in Cambridge, UK) 12th February 2007, Accepted 9th March 2007
First published as an Advance Article on the web 23rd March 2007
DOI: 10.1039/b702238g

Highly stable Eu(III) and Tb(III) complexes, emitting in the red and green visible regions, respectively, have been anchored onto a single SiO_2 transparent layer, yielding *ca.* 40 nm thick films; this allows high loading of tailored proportions of the red and green emitters within the films and results in highly uniform and easily colour-tunable luminescent layers.

The sol–gel technique,[1,2] due to mild synthesis conditions, represents a suitable route to create hybrid materials that are conveniently designed by combining highly luminescent lanthanide antenna complexes with stable and transparent inorganic hosts.[3–6] The hybrids can show attractive properties from both the mechanical and chemical viewpoints and doping with lanthanide complexes emitting in the visible range represents a promising way to fabricate luminescent devices.[7,8] Europium(III) and terbium(III) centres are well-known red and green emitters (λ_{em}^{max} = 614 and 544 nm, respectively) and as such have been widely employed in several fields.[9–14] In order to exploit their luminescence potential, these ions must be coordinated by a properly selected ligand capable to both saturate the 8–9 coordinating positions of the Eu(III) and Tb(III) centres and to act as an antenna for light absorption and sensitisation of the lanthanide luminescence.[15,16] To these purposes, an interesting possibility is to use a macrocycle as a coordinating unit with an appended chromophore as the light harvesting functionality.[17–24] Simple incorporation of lanthanide complexes within silica matrices can, however, result in an inhomogeneous dispersion of the dopant. Thus, there can be practical limitations in the lanthanide loading of the glasses because of undesired interactions involving the relatively long-lived emitting centres, causing loss in luminescence features.

A successful alternative approach to obtain luminescent hybrids is to covalently bind the complexes to the silica matrix. Along these lines, we have previously reported on red-emitting sol–gel glassy layers exhibiting an overall Eu(III)-based luminescence efficiency of 10%.[25] These were obtained upon acidic hydrolysis and condensation involving the alkoxide group of tetraethyl orthosilicate (TEOS) and the primary hydroxy group of an alkyl chain inserted into the Eu(III) complex structure, where the coordinating unit of the ligand is 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A, $K_A > 10^{20}$ M^{-1} in water)[21,22] which is covalently bonded through a methylene spacer to a 4-(3-hydroxypropoxy)-acetophenone antenna,[17] Chart 1.

This procedure yielded highly homogeneous, transparent, and red-luminescent SiO_2 films. These are 40 nm thick, undergo thermal processing up to 200 °C for hours with no appreciable consequences, and exhibit a distributed high loading of the emitters (4.8 nm^3 of film volume per chromophore).[25]

For applicative reasons, it is of relevant interest to gain control over tunability of colour.[26,27] To this goal, we show here the potential of a two-colour approach based on the use of different and controlled combinations of the Eu(III)- and Tb(III)-based propenyloxyacetophenone–DO3A complexes covalently linked to SiO_2 substrates. This fabrication approach is based on a statistical distribution of the different emitting centres within the same substrate and not on the tedious and time consuming multistrate arrangement technique largely used, for instance, in fabrication of white light emitting OLED devices.[28]

The synthesis of the complexes has been carried out by following a procedure previously reported.[25] Silica-based 40 nm thick films embedded with Eu(III) and Tb(III) complexes, **Eu** and **Tb** respectively, were obtained by sol–gel dip-coating using TEOS [$Si(OC_2H_5)_4$] as the silica source under acidic conditions.[25] The solutions containing the single lanthanide complexes were prepared employing a Eu : Si = Tb : Si = 1 : 400 molar ratio. The same procedure afforded the mixed systems reported here,

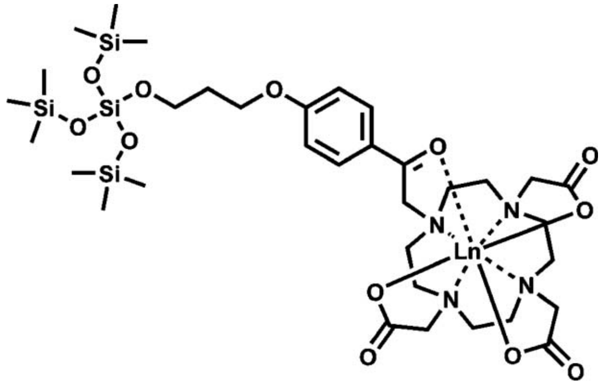

Chart 1 Chemical structure of the trivalent lanthanide complexes linked to the silica matrix.

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† Electronic supplementary information (ESI) available: Details of film preparation and spectroscopic measurements. See DOI: 10.1039/b702238g

with Tb/Eu molar ratios of 0.4, 1.0 and 2.2, yielding **Eu$_2$–Tb$_1$, Eu$_1$–Tb$_1$** and **Eu$_1$–Tb$_2$** films, respectively. Before film deposition, the transparent and clear solutions were aged at room temperature with stirring for 24 h. The obtained layers were subsequently used in the luminescence experiments both as-prepared and after drying at 100 or 200 °C for 5 h. Since the thermal treatment does not influence the photophysical properties of the different specimens, the following discussion will be focused on the samples annealed at 200 °C.

The absorption and emission (PL) spectra of the **Eu$_1$–Tb$_1$**, **Eu$_2$–Tb$_1$** and **Eu$_1$–Tb$_2$** films, as obtained at room temperature, are reported in Fig. 1. The absorption profile was identical for all samples and the peak, around 300 nm, is ascribed to the substituted acetophenone unit, as the sole light collector.[17] Regarding the emission properties,[29,30] the change in relative intensities between the Eu(III) and Tb(III) bands (Fig. 1) appears to be related to the molar ratios of the metal complexes and, in turn, to the colour output as illustrated by Fig. 2. The PL efficiencies (ϕ_{se}), measured by an integrating sphere apparatus[31,32] upon excitation with a He–Cd laser source (λ_{exc} = 325 nm), revealed comparable values for the **Tb** and **Eu** films (ϕ_{se}^{Tb} = 0.09 and ϕ_{se}^{Eu} = 0.10, Table 1). This is consistent with the luminescent output of the mixed **Eu$_1$–Tb$_1$**, **Eu$_2$–Tb$_1$** and **Eu$_1$–Tb$_2$** layers, see inset of Fig. 2. Furthermore, the luminescence decays from the Eu(III) (τ = 0.7 ms, as detected at λ = 614 nm) and Tb(III) (τ = 1.1 ms at λ = 544 nm) centres are nearly the same for all glassy samples, indicating that chromophore interactions do not take place significantly, Table 1. The soluble Eu(III)- and Tb(III)-based hydroxypropenyloxyacetophenone–DO3A complexes have also been studied in water solutions and the results are collected in Table 1. In the case of Eu(III), no remarkable differences between the PL properties in the solid and liquid phases (ϕ_{se} = 0.08) were registered. In contrast, the Tb(III) complex showed notably higher PL quantum yield and longer lifetime in solution than in film (ϕ_{se} = 0.31 and 0.09, respectively). This behaviour could be related to a partial Tb → Eu energy transfer in the solid state, although no concomitant increase in the Eu lifetime has been revealed. Predictably, the equimolar solution of both lanthanide complexes, **Eu$_1$–Tb$_1$** (Table 1), showed an intermediate value of PL efficiency, ϕ_{se} = 0.19.

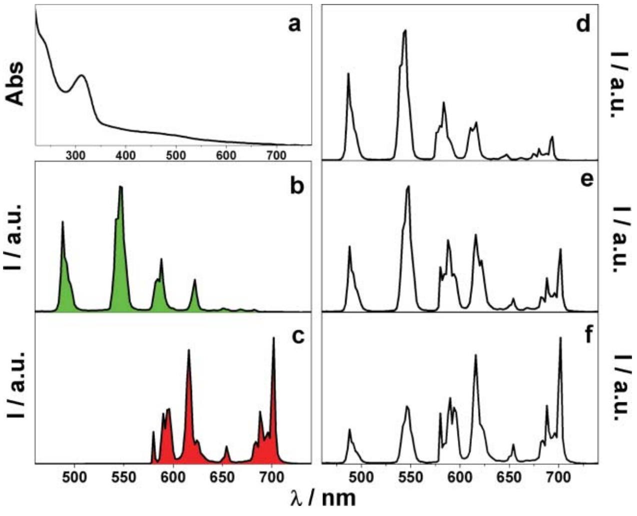

Fig. 1 Absorption (a, **Tb$_1$–Eu$_1$**) and corrected emission spectra (λ_{exc} = 300 nm) of (b) **Tb**, (c) **Eu**, (d) **Tb$_2$–Eu$_1$**, (e) **Tb$_1$–Eu$_1$** and (f) **Tb$_1$–Eu$_2$** in SiO$_2$ matrices.

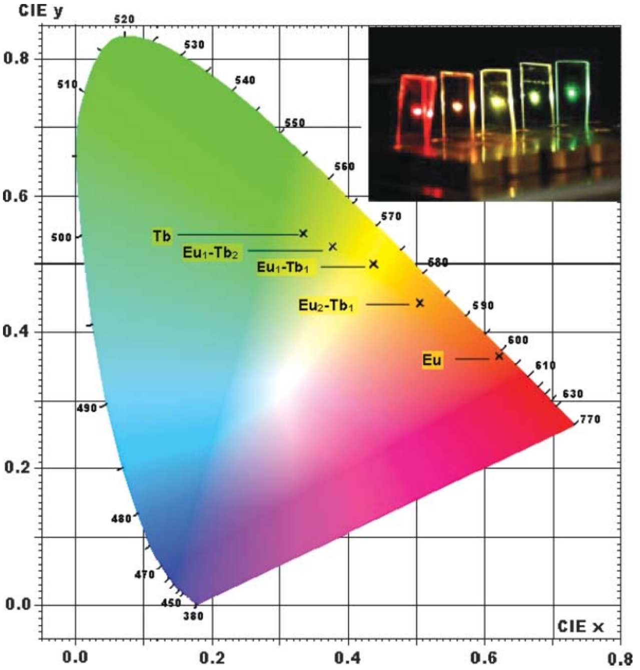

Fig. 2 Main window: Commission Internationale de l'Eclairage (CIE) coordinates, of **Tb** (0.338, 0.544), **Eu$_1$–Tb$_2$** (0.382, 0.525), **Eu$_1$–Tb$_1$** (0.442, 0.498), **Eu$_2$–Tb$_1$** (0.510, 0.441) and **Eu** (0.628, 0.363). Inset: emission behaviour (from left to right) of **Eu**, **Eu$_2$–Tb$_1$**, **Eu$_1$–Tb$_1$**, **Eu$_1$–Tb$_2$** and **Tb** irradiated at 325 nm by a He–Cd continuum laser source.

Table 1 Luminescence data in H$_2$O and SiO$_2$ matrices at RT

	H$_2$O[a]		SiO$_2$ matrix[b]	
	ϕ_{se}	τ/ms	ϕ_{se}	τ/ms
Eu	0.08	0.6	0.10	0.7
Eu$_2$–Tb$_1$	—	—	0.10	0.6[c] 1.1[d]
Eu$_1$–Tb$_1$	0.19	0.7[c] 1.7[d]	0.09	0.6[c] 1.0[d]
Eu$_1$–Tb$_2$	—	—	0.09	0.7[c] 1.0[d]
Tb	0.31	1.6	0.09	1.1

[a] In all cases [Eu] = [Tb] = 10^{-5} M. [b] See text for molar ratio details. [c] Eu(III)-centred emission. [d] Tb(III)-centred emission.

The obtained spectroscopic data are consistent with a homogeneous dispersion of the chromophores within the matrix, which likely results from the identical topology of the two Eu(III)- and Tb(III)-based complexes, whose geometries are determined almost entirely by the ligand characteristics. Consistent with this, upon changing the ratio between the metal complexes within the SiO$_2$ layer, the resulting colour changes from red (**Eu**), to intermediate colours (**Eu$_2$–Tb$_1$**, **Eu$_1$–Tb$_1$** and **Eu$_1$–Tb$_2$**), and finally to green (**Tb**), without eye-appreciable colour heterogeneity, Fig. 2 and inset.

In conclusion, an easy way to prepare silica-based light emitting layers featuring wide colour variation has been found. The colour outputs from the SiO$_2$ films are optically homogeneous and easily tuneable, reflecting the statistical and homogeneous composition of the red and green emitters. Along these lines, these results suggest that use of further blue-greenish emitters could afford white light emitting single layers, obtained through easy-manageable synthesis of the photoactive material and simple fabrication processes.

This work was financed by the CNR and MIUR (Contract FIRB RBNE019H9K, Molecular Manipulation for Nanometric Machines and RBNE033KMA Molecular compounds and hybrid nanostructured materials with resonant and non-resonant optical properties for photonic devices). Thanks are due to Prof. E. Tondello for encouragement and helpful discussion.

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