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PAPER

Synthesis and photophysical characterization of highly luminescent silica films doped with substituted 2-hydroxyphthalamide (IAM) terbium complexes

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Innovative Tb^{3+} antenna complexes employing two different substituted 2-hydroxyphthalamide ligands (**HxOH-IAM** and **bis-HxOH-IAM**) acting simultaneously as coordinating sites and light collector units have been synthesized and successively anchored in silica layers by the sol–gel technique. The complexes show remarkable photoluminescence (PL) quantum yields in methanol solution, as high as 0.30 and 0.40 for (**HxOH-IAM**)₄ \subset **Tb**³⁺ and (**bis-HxOH-IAM**)₂ \subset **Tb**³⁺, respectively. The grafting of the Tb³⁺ complexes in silica single layers accomplished by exploiting the terminal hydroxyl groups of the IAM chains results in highly transparent and homogeneous films displaying bright green emission and PL efficiencies of up to 0.40. The silica layers containing the (**bis-HxOH-IAM**)₂ \subset **Tb**³⁺ show remarkable photostability even under prolonged and continuous irradiation (up to 3.5 h). The nature of the IAM ligands allows the photoexcitation of the complexes at wavelengths even longer than 350 nm, which is a spectral window suitable to develop luminescent lanthanide probes dedicated to bioanalyses and bioimaging applications.

Introduction

The peculiar spectroscopic (optical and magnetic) characteristics¹⁻⁴ of lanthanide ions have fuelled intense research activities owing to a wide range of potential applications in different areas such as biomedicine,⁵⁻⁷ sensing,^{8,9} imaging,^{2,10,11} lighting,^{2,12-21} and telecommunications.^{20,22-25} The progress of many lanthanide-based technologies²⁶⁻²⁸ may greatly benefit from the use of luminescent complexes providing sharp, intense and long lived emission lines upon light irradiation.

In order to design highly luminescent lanthanide complexes, suitable metal core sensitization strategies are needed to overcome the extremely low molar absorption coefficients (often in the range 0.1–1 M^{-1} cm⁻¹) of the Laporte forbidden f-f transitions.

In the last few years, we have developed several lanthanide complexes, mainly Eu³⁺ and Tb³⁺, and studied their photophysical behaviour either in solution or incorporated into silica glassy films obtained through the sol–gel technique.²⁹⁻³⁵ In this regard, we have proved that the coupling between very bright luminescent Eu³⁺ and Tb³⁺ antenna complexes with the transparency and the stability of silica is well suited for technological applications. In general, the luminescence performances of the complexes improve in the oxide host matrix, pointing out the effectiveness of such a strategy for the preparation of efficient and colour tunable molecular-based photoluminescent materials.^{21,29,36}

Till now we have employed ligands suitably designed by synergically coupling the coordination unit with properly appended chromophores acting as sensitizers for Ln³⁺ emission (*antenna effect*) through the induced fit approach. The mutual adaptation of the ligand and metal cation has provided Ln³⁺ complexes characterized by high emission quantum yields, remarkable thermodynamic stability and kinetic inertness.^{32,34} The use of lightharvesting units that also contain binding sites for the metal core is another interesting approach in the design of efficient Ln³⁺ ligands.

Although this method has been applied to the synthesis of a large number of chromophores with different coordinating groups and topologies, in most cases unstable Ln^{3+} complexes in aqueous media have been obtained, thus preventing their use in biological environment and/or showing low luminescence quantum yields.

These shortcomings have been overcome, among others,³⁷ by Raymond and co-workers who developed new classes of multidentate ligands containing two or more substituted 2-hydroxyphthalamide (IAM) or 1-hydroxypyridin-2-one

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(1,2-HOPO) groups that cooperate in the coordination of the Ln³⁺ cation thus affording kinetically inert complexes that are stable in aqueous media.³⁸⁻⁴³ Either the IAM or the 1,2-HOPO groups behave as bidentate ligands for Ln³⁺, the binding sites being the oxygen atom of the phenolate or the deprotonated hydroxypyridine, and one carboxamide or ketone group, respectively. The remaining amide group is involved in a hydrogen bond with the phenolate in order to stabilize the overall complex structure.44 Furthermore, thanks to their electronic and structural features. both IAM and 1,2-HOPO act as good sensitizers for most of the Ln³⁺ ions emitting in the visible region (Sm³⁺, Eu³⁺, Tb³⁺ and Dy³⁺).³⁹ While 1,2-HOPO is an excellent antenna for Eu³⁺,⁴⁰ IAM proved to be particularly effective for Tb³⁺ giving rise to structures with an overall emission quantum yield as high as 60% in aqueous solution at physiological pH.³⁹ According to our previous works,^{29-31,33,35} we explored the possibility to prepare light emitting silica layers using Tb³⁺ complexes of ligands containing the 2hydroxyphtalamide IAM group, that operate either as ligands and sensitizers to Tb³⁺ emission, and suitably functionalized for their covalent linking into the inorganic glass via soft solution procedures. To this aim we report the synthesis, and chemical and photophysical characterization of a bidentate (HxOH-IAM, 5) and a tetradentate (bis-HxOH-IAM, 8) 2-hydroxyphthalamide ligand bearing one or two 6-hydroxyhexylamide chains in the N^1 position, respectively. These ligands are used in the preparation of Tb³⁺ complexes with metal to ligand stoichiometries 1 to 4 in the case of (HxOH-IAM)₄ \subset Tb³⁺ and 1 to 2 in the case of (bis- $HxOH-IAM_{2} \subset Tb^{3+}$. Both complexes show one negative charge that is likely saturated by a sodium cation (Fig. 1).

The two complexes are highly stable, as evidenced by the photophysical studies carried out in methanol solution. By exploiting the terminal hydroxyl groups of the lateral hydroxyhexylamide chains, both complexes have been grafted into silica films *via* a sol–gel procedure. The photophysical properties of the obtained hybrid layer materials were studied and compared with those obtained in solution.

It is worth highlighting that these complexes can be excited at longer wavelengths (even higher than 350 nm) with respect to other lanthanide complexes studied and incorporated by us in similar thin layers systems ($\lambda_{exc} = 305 \text{ nm}$).^{30,31,33,34} This represents one of the challenges in the design of luminescent lanthanide probes dedicated to bioanalyses and bioimaging applications. Indeed, the near UV or visible spectral regions are preferred and targeted (especially when $\lambda_{exc} \ge 350 \text{ nm}$) to avoid damage of biomolecules/biopolymers (*e.g.* DNA) by short- or mediumwave UV light and tissue autofluorescence (usually below 320 nm) interference.⁴⁵

Results and discussion

Synthesis

The 2-hydroxy- N^1 -(hexan-6-ol)-3-(N^3 -methylbenzene)-1,3-dicarbamide (**HxOH-IAM**, 5) ligand was synthesized according to Scheme 1. The bis-thiazolide derivative 2 was prepared in 95% yield starting from the commercially available 2methoxyisophthalic acid 1 through the bis-acyl chloride obtained by reacting 1 with SOCl₂ in dioxane at reflux by using a few drops of DMF as catalyst and subsequent treatment with 2-



Fig. 1 Structure of ligands and of their corresponding Tb^{3+} complexes evidencing the binding mode of the 2-hydroxyphthalamide (IAM) moiety.

mercaptothiazoline in CH_2Cl_2 , in the presence of triethylamine as base. The monomethylamide derivative **3** was selectively obtained by adding very slowly, in 8 h *via* a syringe-pump, a dilute solution of 40% aqueous methylamine in 95:5 (v/v) of CH_2Cl_2 : MeOH into a magnetically stirred solution of **2** in CH_2Cl_2 .⁴³ Compound **3** was reacted with 6-hydroxyhexylamine in CH_2Cl_2 at room temperature to afford **4** in an almost quantitative yield. The methyl protecting group of this last compound was removed by using BBr₃ in CH_2Cl_2 to give the ligand **HxOH-IAM** (**5**) in 81% yield after purification by column chromatography.

The Tb³⁺ complex was obtained by reacting four molar equivalents of **5** with one molar equivalent of TbCl₃·6H₂O in methanol as the solvent and in the presence of an excess of pyridine as base. The pure complex (**HxOH-IAM**)₄ \subset **Tb**³⁺ precipitated out as a white solid by addition of diethylether to the reaction mixture, and the product was easily isolated by filtration and dried under vacuum. The stoichiometry of the complex was confirmed by high resolution ESI mass spectrometry. The preparation of *N*¹,*N*^{1/-}(pentane-1,5-diyl)bis[2-hydroxy-*N*³-(6-hydroxyhexyl)isophthalamide] (**bis-HxOH-IAM**, **8**), was achieved starting from the bis-thiazolide derivative **2** according to Scheme 2.

Reaction of 2 with 6-hydroxyhexylamine was carried out under the same conditions used in the preparation of the monomethylamide derivative 3 (Scheme 1) and afforded 6 in 54% yield after



Scheme 1 Synthesis of the bidentate ligand HxOH-IAM and of the corresponding Tb^{3+} complex.

purification by column chromatography. The very slow addition of a solution of 1,5-pentandiamine in CH₂Cl₂ in 24 h via a syringepump to a CH_2Cl_2 solution of **6** afforded **7** in satisfactory yield. The deprotection of the methyl groups of 7 was carried out by using an excess of BBr₃ in CH₂Cl₂ at -30 °C for 24 h and afforded the bis-HxOH-IAM (8) in 31% yield, as a yellow thick oil, after purification by column chromatography. All attempts to improve the yield of 8 failed. Indeed the use of a large excess of BBr₃ or higher temperatures, in this last reaction, afforded significant amounts of side products, derived from the substitution of the terminal hydroxyl group by bromine which makes the purification of 8 very difficult. The complex (bis-HxOH-IAM)₂ \subset Tb³⁺ was obtained by reacting two molar equivalents of 8 with one molar equivalent of TbCl₃·6H₂O in methanol as the solvent and in the presence of an excess of pyridine as the base. The pure complex (bis-HxOH-IAM)₂⊂Tb³⁺ was precipitated as a white solid by addition of diethylether to the reaction mixture, and the product was easily isolated by filtration and dried under vacuum. The stoichiometry of the complex was confirmed by high resolution ESI mass spectrometry. The terbium complexes were studied by thermogravimetric analysis (TGA) in order to investigate their stability under heating in air. The determination of the structural integrity upon thermal treatment is important in view of the preparation of the doped-silica films, with the aim to define the maximum annealing temperature for the materials. The variation of weight loss as a function of the heating temperature for (HxOH- $IAM)_4 \subset Tb^{3+}$ and (bis-HxOH-IAM)₂ $\subset Tb^{3+}$ is reported in Fig. 2.

For both compounds significant weight losses start at temperatures higher than 300 °C, mainly because of the decomposition of the organic ligand cage. Based on these evidences, the hybrid silica films (*vide infra*), prepared as described in the Experimental Section, were annealed at 200 °C. In fact, at this temperature ther-



Fig. 2 Thermogravimetric curves for $(HxOH-IAM)_4 \subset Tb^{3+}$ and $(bis-HxOH-IAM)_2 \subset Tb^{3+}$. Experiments were conducted in air at a heating rate of 10 °C min⁻¹.

mally induced decomposition processes of the terbium complexes do not occur.

Photophysical characterization

The absorption and emission spectra of $(HxOH-IAM)_4 \subset Tb^{3+}$ complex in methanol solution are reported in Fig. 3.

As well established for Ln³⁺ complexes, the absorption profile is attributed to ligand centred (LC) transitions.^{42,43} In the present case (Fig. 3, left) the absorption spectrum at $\lambda \ge 250$ nm is dominated by an intense single and broad band ($\varepsilon = 1.6 \times 10^4$ M⁻¹ cm⁻¹ at $\lambda = 350$ nm) associated with π - π * transitions of the IAM chromophore.^{42,43}

The photoexcitation of the ligand unit and the subsequent photoinduced energy transfer processes result in the metal centred emission (Fig. 3, left) which displays the typical Tb^{3+} bands



Scheme 2 Synthesis of the tetradentate ligand **bis-HxOH-IAM** and of the corresponding Tb^{3+} complex.

due to transitions from the ${}^{5}D_{4}$ excited state. The remarkable photoluminescence efficiencies of the complex in both deuterated (CH₃OD, $\phi = 0.40$) and non-deuterated methanol (CH₃OH, $\phi =$ 0.29) confirm the effectiveness of the employed ligands to act simultaneously as light harvesting units and binding sites for the metal cation. The corresponding luminescence lifetimes were monitored at 544 nm (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$) and match with a singleexponential decay yielding 1.35 ms and 1.56 ms in CH₃OH and CH₃OD, respectively. By means of a well-established approach, ^{46–48} we estimated the number of coordinated solvent molecules (q, uncertainty ± 0.5) at the metal centre on the basis of the following equation,

$$q^{\rm Tb} = 4.2 \left(1/\tau_{\rm CH_3OH} - 1/\tau_{\rm CH_3OD} - 0.06 \right) \tag{1}$$

We calculated that in the first metal ion coordination sphere, q is approximately zero (0.17). This indicates a good ligand shielding efficiency which prevents the occurrence of detrimental interactions with the surroundings that would lead to luminescence quenching processes *via* vibronic coupling with high frequency oscillators such as OH, NH and, to a lower extent, CH.^{1,29}

Along our previous lines,^{30,33} the light emitting sol–gel glasses were obtained upon hydrolysis involving the alkoxide groups of tetraethylorthosilicate (see Experimental Section) and the four primary hydroxy groups of the alkyl chains appended to the IAM or bis-IAM units of the Tb³⁺ complexes (see Scheme 1 and 2). This procedure yielded highly homogeneous, transparent and green luminescent SiO₂ films, as depicted in Fig. 4.

In the silica films, the (HxOH-IAM)₄ \subset Tb³⁺ complex shows photophysical properties similar to those in solution with a PL quantum efficiency and a lifetime of 0.19 and 1.29 ms, respectively. The bright green luminescence of the layers irradiated at 350 nm, clearly visible to the naked eye, was evaluated over time and was almost unaffected by aging at ambient conditions. In fact, the emission profile. PLOY and lifetime values acquired at increasing ageing times (up to 6 months) were unchanged compared to those of the freshly prepared films. Since the stability of the luminescent hybrid materials under continuous irradiation is a key factor for most applications such as sensing, bio-probing, lighting, etc.,49 and high resistance towards photoinduced damages is required to improve the service life of devices, we evaluated the photostability of the (HxOH-IAM)₄ CTb³⁺-based hybrids,³¹ under continuous irradiation at $\lambda = 330$ nm, *i.e.* at the maximum of the absorption band (Fig. 3). The integrated intensity of the ${}^{5}D_{4} \rightarrow {}^{7}F_{6-3}$ transitions was monitored as a function of the exposure time (Fig. 5). The emission intensity decreases to ca. 50% of the initial value after 3.5 h, evidencing a moderate stability toward photobleaching of the $(HxOH-IAM)_4 \subset Tb^{3+}$ chromophore anchored in the SiO₂ matrix. It should be noted that the degradation of lanthanide complexes under UV irradiation involves a series of complicated processes, often attributed to photobleaching or photon-induced chemical damage, and it has not been yet completely elucidated.⁵⁰⁻⁵³

The absorption ($\varepsilon = 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 350 \text{ nm}$) and emission spectra in methanol solutions of the corresponding (**bis-HxOH-IAM**)₂ \subset **Tb**³⁺ complex are reported in Fig. 6. The (**bis-HxOH-IAM**)₂ \subset **Tb**³⁺ complex emits very bright green light in methanol solution when excited at $\lambda = 350 \text{ nm}$ due to the strong intensity of Tb³⁺⁵D₄ \rightarrow ⁷F₆₋₃ transitions in the 480–650 nm range. Absolute quantum yields for these complexes are as high as 0.38 (0.49 in CH₃OD), in agreement with the value reported in the literature for similar compounds.^{42,43} The corresponding PL lifetimes (Fig. 6, right) for the ⁵D₄ \rightarrow ⁷F₅ transition were fitted with a singleexponential decay yielding τ values of 1.20 ms (CH₃OH) and 1.33 ms (CH₃OD), which are consistent with a number of solvent molecules close to zero (q = 0.09) in the metal ion surrounding.

The slight difference between the luminescence decays recorded for $(HxOH-IAM)_4 \subset Tb^{3+}$ and $(bis-HxOH-IAM)_2 \subset Tb^{3+}$ could be addressed by the different arrangements of the corresponding



Fig. 3 *Left*: Absorption profile (black) in CH₃OH and emission spectra ($\lambda_{exc} = 350 \text{ nm}$) in CH₃OH (green) and CH₃OD (blue) of (**HxOH-IAM**)₄ \subset **Tb**³⁺. *Right*: Corresponding luminescence decays ($\lambda_{exc} = 350 \text{ nm}$, $\lambda_{em} = 544 \text{ nm}$). The number of the solvent molecules involved in the first metal coordinating sphere has been calculated according to eqn (1) (see text).





Fig. 5 Photodecomposition profiles for (**HxOH-IAM**)₄⊂**Tb**³⁺-based hybrids as-prepared (blue circles) and after thermal treatment (red circles).

decreasing trend by passing from the as-prepared to the thermally treated glass sample (1.48 ms and 1.22 ms, respectively). Upon continuous irradiation at 330 nm, the **(bis-HxOH-IAM)**₂ \subset **Tb**³⁺ doped-SiO₂ films showed a modest PL intensity variation over the time (Fig. 7) suggesting a remarkable photostability of the terbium complex embedded in the glassy layer. We observe that after a initial quick intensity decrease (~20% of the initial amount in 30 min), the integrated light output is reduced a further 10% over the subsequent 3 h.

As already largely debated,^{50–53} the origin of photodecomposition processes of lanthanide complexes in solid matrices has not been yet completely clarified. Therefore, the interpretation of the slightly different behaviour of (**bis-HxOH-IAM**)₂ \subset **Tb**³⁺ with respect to (**HxOH-IAM**)₄ \subset **Tb**³⁺ is not straightforward. In this framework, the response of the hybrid luminescent materials to continuous UV irradiation should be considered as a *figure of merit*, helpful in the choice of a particular material for a target application. As a whole, luminescent silica glassy layers employing (**bis-HxOH-IAM**)₂ \subset **Tb**³⁺ as a luminophore present superior stability and performances (PLQY) compared to their (**HxOH-IAM**)₄ \subset **Tb**³⁺ analogues. On the other hand, the facile

Fig. 4 Schematic representation of a SiO_2 film functionalized with the green luminescent (bis-HxOH-IAM)₂ \subset Tb³⁺metal complex.

light-harvesting units around the metal centre. In fact, the two hydroxyphthalamide residues in **bis-HxOH-IAM**, linked by a – $(CH_2)_5$ spacer through the nitrogen atoms of the amide groups, may be responsible for a different topology of the resulting complex compared to that of (HxOH-IAM)₄ ⊂Tb³⁺ for which such structural constriction does not occur. The covalent incorporation of (bis-HxOH-IAM)₂ CTb³⁺ into the silica thin films does not induce any appreciable variation for both the shape and position of the terbium emission profiles (not reported), and PLQYs up to $\phi = 0.40$ have been detected for as-prepared layers. Instead, the annealed thin film (200 °C for 5 h) revealed an emission intensity loss down to $\phi \sim 0.30$, although the adopted thermal treatment was not as high as to cause decomposition of the organic ligands, as evidenced by TGA analysis on the neat complexes (see Fig. 2 and text). Accordingly, the corresponding lifetimes, obtained by exciting the thin films at 350 nm, followed the same



Fig. 6 Left: Absorption profile (black) in CH₃OH and emission spectra ($\lambda_{exc} = 350 \text{ nm}$) in CH₃OH (green) and CH₃OD (blue) of (**bis-HxOH-IAM**)₂C^T**b**³⁺. Right: Corresponding luminescence decays ($\lambda_{exc} = 350 \text{ nm}$, $\lambda_{em} = 544 \text{ nm}$). The number of the solvent molecules involved in the first metal coordinating sphere has been calculated according to eqn (1) (see text).



Fig. 7 Photodecomposition profiles for $(bis-HxOH-IAM)_2 \subset Tb^{3+}$ -based hybrids as-prepared (blue circles) and after thermal treatment (red circles).

synthesis of the **HxOH-IAM** derivative, combined with its good luminescent performances in SiO₂ films (PL efficiencies up to 0.20), should also be considered to rationalize the chemical design and the preparations of highly efficient light-emitting materials in the more convenient way.

Conclusions

Efficient Tb^{3+} antenna complexes, employing two innovative 2-hydroxyphthalamide IAM ligands (HxOH-IAM, 2-hydroxy- N^1 -(hexan-6-ol)-3-(N^3 -methylbenzene)-1,3-dicarbamide and **bis-HxOH-IAM**, N^1,N^1 -(pentane-1,5-diyl)bis[2-hydroxy- N^3 -(6-hydroxyhexyl)isophthalamide]) acting simultaneously as light harvesting units and binding sites for the metal cation, were synthesized. Both Tb^{3+} complexes, (HxOH-IAM)₄ \subset Tb³⁺ and (**bis-HxOH-IAM**)₂ \subset Tb³⁺, were stable in methanol solution and showed remarkable luminescence quantum yields, *ca*. 0.30 and 0.40, respectively. By exploiting the terminal hydroxyl groups properly inserted in the substituted IAM ligands, the Tb^{3+} complexes were successively grafted in silica single layers *via* a solgel procedure resulting in highly transparent and homogeneous films, endowed with intense bright green photoluminescence.

The SiO₂-(bis-HxOH-IAM)₂ \subset Tb³⁺ films showed considerable photostability under prolonged irradiation time (up to 3.5 h). Due to the nature of the designed IAM ligands, the Tb³⁺ complexes were efficiently excited at longer wavelengths with respect to other lanthanide systems studied and incorporated by our team in thin silica layers. This represents a major aspect in the design of luminescent lanthanide probes dedicated to bioanalyses and bioimaging applications, since photoexcitation in near UV or visible spectral regions avoids damage of biomolecules and interference due to tissue autofluorescence.

Experimental section

General procedures and materials

All available chemicals were purchased from commercial sources and were used without any further purification unless otherwise noted. Solvents were purified by using standard methods and dried if necessary. Air- and moisture-sensitive reactions were performed under a nitrogen atmosphere. Thin layer chromatography (TLC) was conducted on plates precoated with silica gel Si 60-F254 (Merck, Darmstadt, Germany). Column chromatography was carried out by using silica gel Si 60, 230-400 mesh, 0.040-0.063 mm (Merck, Darmstadt, Germany). ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 (400 and 100.6 MHz, respectively). Chemical shifts are indicated in parts per million downfield from SiMe4, using the residual proton $(CHCl_3 = 7.26 \text{ ppm})$ and carbon $(CDCl_3 = 77.0 \text{ ppm})$ solvent resonances as internal reference. The coupling constants J are given in Hz. Proton and carbon atom assignments were determined performing COSY and HSQC correlation experiments. ESI mass spectra were obtained on an ICR Mass Spectrometer APEX II & Xmann software (Bruker Daltonics) - 4.7 T Magnet (Magnex).

(2-Methoxy-1,3-phenylene)bis[(2-thioxothiazolidin-3yl)methanone] (2)

To a solution of 2-methoxyisophthalic acid 1 (2 g, 10.2 mmol) in 20 ml of dry dioxane was added 2.6 ml (35.7 mmol) of thionyl

chloride and two drops of DMF. The mixture was heated to reflux and stirred overnight under N2. The volatiles were removed under vacuum. The crude acid chloride was dissolved in 25 mL of CH₂Cl₂, and a solution of 2-thiazoline-2-thiol (2.7 g, 22.4 mmol) and NEt₃ (2.8 mL) in 35 ml of CH₂Cl₂ was added dropwise at -78 °C, then the reaction mixture was warmed to room temperature and stirred overnight. The resulting yellow reaction mixture was washed with brine (50 mL), 10% aqueous HCl (50 mL), and 10% aqueous NaOH (2×50 mL) successively. The organic phase was dried over MgSO4 and evaporated to dryness in vacuo. The residue was purified by column chromatography (silica gel, CH₂Cl₂/n-hexane 8:2 v/v) to afford pure 2 (3.88 g, 95%) as a bright yellow solid. $\delta_{\rm H}$ (400 MHz, CDCl₃) 7.43 (2H, d, 4-H and 6-H, J = 7.7), 7.13 (1H, t, 5-H, J = 7.7), 4.60 (4H, t, $J = 7.3 \text{ NCH}_2\text{CH}_2\text{S}$), 3.90 (3H, s, OCH₃), 3.41 (4H, t, J =7.3, NCH₂CH₂S). $\delta_{\rm C}$ (100.6 MHz, CDCl₃) 200.71, 155.54, 167.30, 132.11, 128.24, 123.31, 63.04, 55.70, 29.28. m/z (HRMS ESI⁺) $421.0 [M + Na]^+ (C_{15}H_{14}N_2O_3S_4 \text{ requires } 397.99)$. Found: C, 45.28; H, 3.55; N, 7.05. Calc. for C₁₅H₁₄N₂O₃S₄: C, 45.20; H, 3.54; N, 7.03%.

2-Methoxy-*N*-methyl-3-(2-thioxothiazolidine-3carbonyl)benzamide (3)

A solution of methylamine (34 mg, 1.1 mmol, 85 µl of a 40% aqueous solution) in 95:5 CH₂Cl₂/MeOH (20 mL) was added via syringe-pump in 8 h to a solution of 2 (860 mg, 2.2 mmol) in 2 mL of CH₂Cl₂ maintained under magnetic stirring and at room temperature. The solvents were removed under reduced pressure. The residue was redissolved in 100 mL of CH₂Cl₂ and washed with 50 mL of 1 M KOH aqueous solution. The solvent was evaporated to dryness and the residue purified by silica gel column chromatography eluting with pure CH₂Cl₂ to recover unreacted starting material, and then CH₂Cl₂/EtOAc 8:2 v/v to obtain the desired product 3 (320 mg, 94%) as a thick yellow oil. $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.13 (1H, dd, 4-H or 6-H, J = 7.6, J 1.8), 7.41 (2H, br s and dd overlapping, 4-H or 6-H and $CONHCH_3$, J = 7.6, J =1.8), 7.23 (1H, t, 5-H, J = 7.6), 4.67 (2H, t, NCH₂CH₂S, J =7.3), 3.86 (3H, s, OCH₃), 3.44 (2H, t, NCH₂CH₂S, J = 7.3), 3.01 (3H, d, CONHCH₃, J = 4.8). $\delta_{\rm C}$ (100.6 MHz, CDCl₃) 201.22, 167.42, 165.38, 155.58, 134.27, 131.91, 129.24, 127.35, 124.49, 63.13, 55.62, 29.03, 26.69. m/z (HRMS ESI⁺) 333.10 [M + Na]⁺ (C₁₃H₁₄N₂O₃S₂ requires 310.04). Found: C, 50.28; H, 4.56; N, 9.05. Calc. for C₁₃H₁₄N₂O₃S₂: C, 50.30; H, 4.55; N, 9.03%.

N^{1} -(6-Hydroxyhexyl)-2-methoxy- N^{3} -methylisophthalamide (4)

A solution of 6-amino-1-hexanol (154 mg, 1.3 mmol) in 20 mL of CH₂Cl₂was added dropwise over 10 min to a solution of **3** (340 mg, 1 mmol) in 10 mL of CH₂Cl₂ and the resulting reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, 5% MeOH in CH₂Cl₂) to afford pure **4** (300 mg, 97%) as a white solid. $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.07 (2H, d, 4-H and 6-H, J = 7.7), 7.31 (3H, br s and t overlapping, 5-H, CON¹HCH₂ and CON³HCH₂, J = 7.7), 3.86 (3H, s, OCH₃), 3.66 (2H, t, CH₂OH, J = 6.4), 3.49 (2H, dt, CON¹HCH₂, J = 7.0, J = 5.8), 3.05 (3H, d, CON³HCH₃, J = 4.9), 1.58–1.66 (4H, m, CH₂), 1.43–1.47 (4H, m, CH₂). $\delta_{\rm C}$ (100.6 MHz, CDCl₃) 165.72, 164.99,

 $\begin{array}{l} 155.75,\,134.39,\,134.31,\,128.02,\,127.91,\,125.27,\,63.44,\,62.69,\,39.78,\\ 32.56,\,29.60,\,26.80,\,26.74,\,25.36.\ {\it m/z}\ ({\rm HRMS}\ ESI^+)\ 309.18071\\ [M\ +\ H]^+,\,\,331.16240\ [M\ +\ Na]^+(C_{16}H_{24}N_2O_4\ requires\ 308.17).\\ Found:\ C,\,62.25;\ H,\,7.80;\ N,\,9.07.\ Calc.\ for\ C_{16}H_{24}N_2O_4:\ C,\,62.32;\\ H,\,7.84;\ N,\,9.08\%. \end{array}$

2-Hydroxy-*N*¹-(6-hydroxyhexyl)-*N*³-methylisophthalamide (5, HxOH-IAM)

A sample of 2.0 mL (2 mmol) of 1 M BBr₃ solution in CH₂Cl₂ was added via syringe to a stirred solution of 4 (300 mg, 1 mmol) in 30 mL of CH_2Cl_2 cooled at -78 °C with an acetone/dry ice bath. The reaction mixture was then warmed to room temperature and stirred for a further 24 h. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, 5% MeOH in CH₂Cl₂) to afford pure 5 (285 mg, 81%) as a yellow oil. $\delta_{\rm H}$ (400 MHz, CD₃OD) 7.96 (1H, dd, 4-H or 6-H, J = 7.8, J = 1.7), 7.93 (1H, dd, 4-H or 6-H, J = 7.8, J =1.7), 6.92 (1H, t, 5-H, J = 7.8), 3.53 (2H, t, CH_2OH , J = 6.6), 3.38 (2H, t, $CON^{1}HCH_{2}$, J = 7.1), 2.92 (3H, s, $CON^{3}HCH_{3}$), 1.61 (2H, br quint, N¹HCH₂CH₂, J = 7.1), 1.53 (2H, br quint, CH_2CH_2OH , J = 6.6), 1.37–1.42 (4H, m, CH_2). δ_C (100.6 MHz, CD₃OD) 168.68, 167.90, 160.00, 132.60, 132.39, 118.10, 118.02, 117.70, 61.51, 39.43, 32.18, 29.00, 26.55, 25.41, 25.28. m/z (HRMS ESI⁺) 317.14679 [M + Na]⁺ ($C_{15}H_{22}N_2O_4$ requires 294.16). Found: C, 61.32; H, 7.54; N, 9.54. Calc. for C₁₅H₂₂N₂O₄: C, 61.21; H, 7.53; N, 9.52%.

N-(6-Hydroxyhexyl)-2-methoxy-3-(2-thioxothiazolidine-3-carbonyl)benzamide (6)

To a solution of 2 (1 g, 2.5 mmol) in 3 ml of CH₂Cl₂ was added 6-amino-1-hexanol (294 mg, 2.5 mmol) in 95:5 CH₂Cl₂/MeOH (20 ml total) via syringe-pump in 8 h. The solvents were removed under vacuum and the reaction mixture was dissolved in 100 ml of CH₂Cl₂ and washed with 50 ml of 1 M KOH. The reaction mixture was evaporated to dryness and applied to a silica column. Unreacted starting material was eluted with 5% AcOEt in CH₂Cl₂, and the desired product 6 (540 mg, 54%), a thick yellow oil, was eluted with 20% EtOAc in CH₂Cl₂. $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.12 (1H, dd, 4-H or 6-H, J = 8.0, J = 1.8), 7.41 (2H, br s and dd overlapping, 4-H or 6-H and $CONHCH_2$, J = 8.0, J = 1.8), 7.22 (1H, t, 5-H, J = 8.0), 4.68 (2H, t, NCH₂CH₂S, J = 7.3), 3.87 $(3H, s, OCH_3)$, 3.65 (2H, t, CH₂OH, J = 6.5), 3.43–3.49 (4H, m, NCH₂CH₂S and CONHCH₂), 1.56-1.65 (4H, m, $-CH_2CH_2$ -), 1.41-1.45 (4H, m, -CH₂CH₂-). δ_c (100.6 MHz, CDCl₃) 201.23, 167.45, 164.71, 155.57, 134.35, 131.85, 129.27, 127.61, 124.53, 63.13, 62.70, 55.63, 39.71, 32.57, 29.52, 29.01, 26.69, 25.31. m/z (HRMS ESI⁺) 419.10654 [M + Na]⁺ ($C_{18}H_{24}N_2O_4S_2$ requires 396.12). Found: C, 54.46; H, 6.11; N, 7.08. Calc. for C₁₈H₂₄N₂O₄S₂: C, 54.52; H, 6.10; N, 7.06%.

Synthesis of (HxOH-IAM)₄⊂Tb³⁺ complex

To a solution of ligand **5** (HxOH-IAM) (420 mg, 1.43 mmol) in 30 ml of MeOH was added 133 mg (0.36 mmol) of TbCl₃·6H₂O. A sample of 290 μ L of pyridine was added and the reaction mixture was stirred at reflux for a further 24 h. The solvents were removed *in vacuo*, the resulting off-white solid residue was redissolved in a minimal amount of MeOH and the product was precipitated by

addition of Et₂O. The precipitate was separated by filtration and dried to afford the pure complex (**HxOH-IAM**)₄ \subset **Tb**³⁺ (370 mg, 77%) as a white solid. *m/z* (HRMS ESI⁻) (C₆₀H₈₄N₈NaO₁₆Tb requires 1354.52) 1331.53125 (100%), 1332.53348 (68.2), 1333.53674 (22.7), 1334.53473 (9.1) [M - Na]⁻. Found: C 47.10, H 6.50, N 7.20; Calcd for C₆₀H₈₄N₈NaO₁₆Tb·NaCl·6H₂O·CH₃OH: C 47.15, H 6.49, N 7.21%.

N^{1} , $N^{1'}$ -(Pentane-1,5-diyl)bis[N^{3} -(6-hydroxyhexyl)-2-methoxyisophthalamide] (7)

To a solution of 2 (1 g, 2.5 mmol) in 20 ml of CH₂Cl₂ was added 1,5diaminopentane (129 mg, 1.3 mmol) in 15 ml of CH₂Cl₂ dropwise via syringe-pump in 24 h. The solution was stirred overnight. The solvent was removed under vacuum and the resulting residue was applied to a silica gel column. The product, a white solid (710 mg, 83%) was eluted with 2% MeOH in CH₂Cl₂. $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.01 (2H, dd, 4-H or 6-H, J = 7.7, J = 1.9), 7.96 (2H, dd, 4-H or 6-H, J = 7.7, J = 1.9), 7.44 (2H, br t, CONHCH₂, J = 5.7), 7.33 (2H, br t, CONHCH₂Hex, J = 5.7), 7.25 (2H, t, 5-H, J =7.7), 3.83 (6H, s, OCH₃), 3.62 (4H, t, CH₂OH, J = 6.4), 3.44– 3.52 (8H, m, CONHCH₂), 1.89 (2H, s, CH₂OH), 1.51-1.73 (14H, m, -CH₂CH₂-), 1.41-1.44 (8H, m, -CH₂CH₂-). δ_c (100.6 MHz, CDCl₃) 165.25, 165.07, 155.68, 134.22, 134.05, 128.24, 127.98, 125.17, 63.39, 62.56, 39.79, 39.64, 32.54, 29.52, 29.19, 26.73, 25.38, 24.29. m/z (HRMS ESI⁺) 679.36593 [M + Na]⁺ (C₃₅H₅₂N₄O₈ requires 656.38). Found: C, 64.02; H, 8.00; N, 8.51. Calc. for C₃₅H₅₂N₄O₈: C, 64.00; H, 7.98; N, 8.53%.

N^1 , N^{\prime} -(Pentane-1,5-diyl)bis[2-hydroxy- N^3 -(6-hydroxyhexyl)isophthalamide] (8)

To a solution of 7 (400 mg, 0.61 mmol) in 50 ml of CH2Cl2 dry cooled in an acetone/dry ice bath (-30 °C) was added 3 ml (3 mmol, 5 mol. equiv.) of BBr₃ in 1 M CH₂Cl₂ solution with a syringe while stirring under N₂. The reaction mixture was preserved at -30 °C and was stirred for 24 h. When the reaction was complete, it was quenched by 10 ml of MeOH, diluted with 30 ml of H₂O and heated at reflux for 4 h. The organic solution was separated, dried over MgSO₄ and applied to a silica gel column. The product, a yellow thick oil, was eluted with 5% MeOH in AcOEt (120 mg, 31%). $\delta_{\rm H}$ (400 MHz, CD₃OD) 7.95 (4H, d, 4-H and 6-H, J = 7.8), 6.92 (2H, t, 5-H, J = 7.8), 3.54 (4H, t, $CH_2OH, J = 6.5$, 3.39–3.43 (8H, m, CONHC H_2), 1.48–1.70 (14H, m, -CH₂CH₂-), 1.38–1.41 (8H, m, -CH₂CH₂-). $\delta_{\rm C}$ (100.6 MHz, CD₃OD) 168.09, 167.92, 160.04, 132.48, 118.09, 117.94, 61.49, 39.29, 39.07, 32.17, 28.99, 28.66, 26.53, 25.25, 23.89. m/z (HRMS ESI⁻) 627.33784 [M – H]⁻, 649.32081 [M – 2H + Na]⁻, 313.16593 $[M - 2H]^{2-}$ (C₃₃H₄₈N₄O₈ requires 628.35). Found: C, 63.02; H, 7.70; N, 8.93. Calc. for C₃₃H₄₈N₄O₈: C, 63.04; H, 7.69; N, 8.91%.

Synthesis of (bis-HxOH-IAM)₂⊂Tb³⁺ complex

A solution of TbCl₃·6H₂O (187 mg, 0.5 mmol) in 2 ml of MeOH was added to a stirred solution of ligand **8** (126 mg, 0.2 mmol) in 40 ml of MeOH. Sym-collidine (42 μ l) were added while stirring and the reaction mixture was heated to reflux for 24 h. The solvents were removed under reduced pressure and the solid residue was redissolved in a minimal amount of MeOH. The product was precipitated with Et₂O, separated and

dried to afford pure (bis-HxOH-IAM)₂ \subset Tb³⁺ (140 mg, 95%) as a white solid. *m/z* (HRMS ESI⁻) (C₆₆H₉₂N₈NaO₁₆Tb requires 1434.5782) 1411.58924 (100%), 1412.59354 (74.7), 1413.59680 (28.7), 1414.60410 (9.6) [M – Na]⁻. Found: C 47.97, H 6.88, N 6.57. Calc. for C₆₆H₉₂N₈NaO₁₆Tb·NaCl·8H₂O·2CH₃OH: C 47.99, H 6.87, N 6.58%.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the terbium complexes was performed in air on SDT 2960 TA Instruments equipment in the 20–800 °C temperature range. The powder samples were placed in an alumina crucible and heated at 10 °C min⁻¹ under a 110 cm³ min⁻¹ flow rate.

Preparation of luminescent silica films

Silica single layers embedding (HxOH-IAM)₄⊂Tb³⁺ or (bis-HxOH-IAM)₂⊂Tb³⁺ complexes were obtained by sol-gel dipcoating using TEOS [Si(OC₂H₅)₄], Sigma Aldrich[®], 99.999%] as the silica source. The terbium complexes were first dissolved in ethanol (Fluka, \geq 99.8%) at room temperature and subsequently TEOS and deionized water were added (the molar composition of the solution employed was 1 TEOS: 15 EtOH: 3 H₂O) while the Si/Tb molar ratio was 440. Before deposition, sol-gel solutions were aged at room temperature under vigorous stirring for 72 h. Herasil[®] silica slides $(2 \times 1 \text{ cm}^2)$ were used as the substrates. Film deposition was carried out in air at room temperature with a controlled withdrawal speed of about 10 cm min⁻¹. The obtained layers were used in the luminescence experiments both as-prepared and after thermal treatment at 200 °C for 5 h. Higher treatment temperatures were not considered in order to avoid complex degradation, as evidenced from the thermal analysis. All as-prepared and annealed samples were homogeneous and well adherent to the substrates, transparent, and crack free.

Spectroscopic measurements

Absorption spectra were recorded with a Perkin-Elmer Lambda950 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 photomultiplier 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 Crosby⁵⁴ using air-equilibrated $[Ru(bpy)_3]Cl_2$ in water solution $[\phi_{em} = 0.028]^{55}$ 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 variable repetition rate and elaborated with standard software fitting procedures. The quality parameters (χ^2) for all the fittings were ~1. For solid samples, ϕ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulphate coated integrating sphere (4 inches), a 450 W Xe lamp (λ_{exc} tunable by a monochromator supplied with the instrument) as the light source and a R928 photomultiplayer tube as the signal detector, following the procedure described by De Mello *et al.*⁵⁶ Experimental uncertainties are estimated to be ±8% for lifetime determinations, ±20% for emission quantum yields, ±2 nm and ±5 nm for absorption and emission peaks, respectively. Photostability tests were performed on a home built apparatus employing a 100 W Hg lamp as light source. The samples were kept under continuous irradiation, for up to 5 h, with a constant power of ≈100 μ W cm⁻² at 330 nm by means of light intensity attenuators.

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