

Near-Infrared and Visible Luminescence from Terphenyl-Based Lanthanide(III) Complexes Bearing Amido and Sulfonamido Pendant Arms

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A series of *m*-terphenyl-based ligands bearing three coordinating oxyacetate and two amido or two sulfonamido groups, (**1a–b**)H₃ and (**2**)H₃, respectively, have been synthesized and characterized. The structures of the corresponding neutral complexes have been studied using ¹H-NMR spectroscopy and luminescence experiments. The photophysical properties of the (**1a–b**)Eu, (**2**)Eu, (**1a**)Tb, and (**2**)Tb complexes have been studied to determine the structure of the first coordination sphere in methanol. The first coordination sphere consists of eight donor atoms provided by the ligand (three chelating oxyacetate groups and two amide or sulfonamide oxygens), and one methanol molecule. The (**1a**)Dy and (**1a**)Sm

complexes exhibited sensitized luminescence in the visible spectral region, but the luminescence intensity was very sensitive to quenching by C–H groups. The near-infrared emitting (**1a**)Ln and (**2**)Ln complexes exhibited sensitized luminescence at wavelengths (at 880, 1060, and 1330 nm for Nd³⁺, at 980 nm for Yb³⁺, and at 1550 nm for Er³⁺) of interest for applications in optical telecommunication devices. The luminescence lifetimes of these complexes in DMSO and [D₆]DMSO are in the range of microseconds. The luminescent state of the NIR emitting lanthanide ions is very efficiently quenched by high frequency oscillators (such as C–H groups) in the solvent and the ligand.

Introduction

There is a worldwide interest in complexes of the trivalent rare earth or lanthanide cations for applications in fluoro-immuno-assays,^[1] laser systems,^[2] and optical amplification.^[3] The unique luminescence properties of these rare earth cations and their wide range of emission bands (500–1550 nm)^[4] make them very interesting for such purposes. The lanthanide ions have narrow emission bands and relatively long luminescence lifetimes as a result of optical transitions within the 4f shell, which are, in principle, parity-forbidden. Encapsulating ligands can enhance the luminescence properties by shielding the ion from quenchers such as the hydroxyl groups of the solvent. Luminescent complexes of the lanthanide ions Eu³⁺ and Tb³⁺ are the most widely studied, and these particular complexes are used, for example, as long-lived luminescent probes in fluoroimmuno-assays.^[5] These complexes show lumines-

cence in the visible spectral region with relatively long luminescence lifetimes in the range of ms.^[6,7] Recently, there has been an increasing interest in complexes of the near-infrared emitting lanthanide ions Yb³⁺, Nd³⁺, and Er³⁺, which have emission bands ranging from 880 to 1550 nm. The Nd³⁺ and Yb³⁺ complexes are promising probes for fluoroimmuno-assays and in vivo applications, because human tissue is relatively transparent to near-infrared light around 1000 nm. In optical telecommunication networks Er³⁺-doped silica fiber amplifiers (EDFAs) are currently used for amplification of light with a wavelength of about 1550 nm,^[8] which corresponds to an optical transition of Er³⁺ (⁴I_{13/2}→⁴I_{15/2} transition). Recently, a polymeric waveguide doped with the neodymium chloride salt has been shown to amplify light of 1060 nm.^[9]

This work is part of our research that is concerned with the development of a polymer-based optical amplifier in which lanthanide complexes bearing antenna-chromophores are incorporated in planar polymeric waveguides.^[3,10] By varying the lanthanide ion in the complex, various emission wavelengths become accessible, and hence optical signals of a range of wavelengths can be amplified. The polymer-based amplifiers can be integrated in existing polymeric optical components such as splitters, switches, and multiplexers.^[11] The main advantage of polymer-based components lies in their ease of processing, which enables low-cost manufacturing technologies to be applied. Polymer-based amplifiers can be monolithically integrated with other polymer-based functionalities. Essential for our research is the development of lanthanide complexes that: (i) allow efficient excitation by means of an antenna chromophore; (ii) have high luminescence quantum yields; and (iii)

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are soluble in organic solvents and the polymer matrix. Previously, we have reported the synthesis of oxyacetate-functionalized *m*-terphenyl derivatives which form overall neutral complexes with various lanthanide cations, such as Eu^{3+} , Yb^{3+} , Nd^{3+} , and Er^{3+} .^[3,12,13,14] It was particularly demonstrated that partial deuteration of the ligand enhances the luminescence lifetime of the complexed lanthanide ion.^[12] In search of suitable sensitizers for Yb^{3+} , Nd^{3+} , and Er^{3+} luminescence, we^[15] and others^[16] have found that fluorescein is an efficient antenna-chromophore for sensitized emission of these lanthanide ions. Examples of other reported ligand systems for lanthanide complexation are cryptand-type ligands containing 2,2'-bipyridine,^[7,17] DOTA derivatives,^[18] and calix[4]arene-based ionophores.^[6,19]

In this article we report the synthesis and photophysical properties of *m*-terphenyl-based lanthanide complexes bearing amido and sulfonamido functionalities. The *m*-terphenyl-based ligands have been designed to shield the lanthanide ion efficiently from the solvent and the resulting neutral complexes exhibit an enhanced solubility in organic solvents.^[12] The influence of the metal-coordinating functionalities on the photophysical properties of the complexed lanthanide ion has been investigated using Eu^{3+} and Tb^{3+} as models. Furthermore, the luminescence of the Dy^{3+} or Sm^{3+} complexes has been studied. For optical signal amplification, the 1550 nm transition of Er^{3+} , the 1330 nm transition of Nd^{3+} , and the 980 nm transition of Yb^{3+} are of interest and the corresponding complexes of these near-infrared emitting lanthanide ions were synthesized and their photophysical properties evaluated. Figure 1 summarizes the 4f energy levels of the seven Ln^{3+} ions studied in this paper.

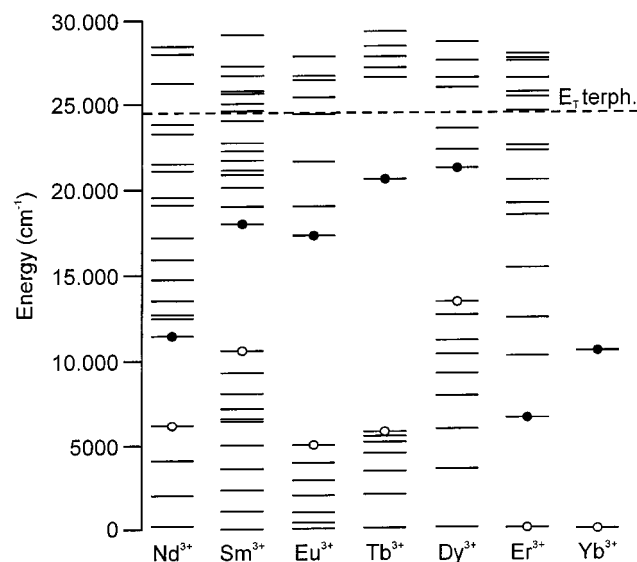
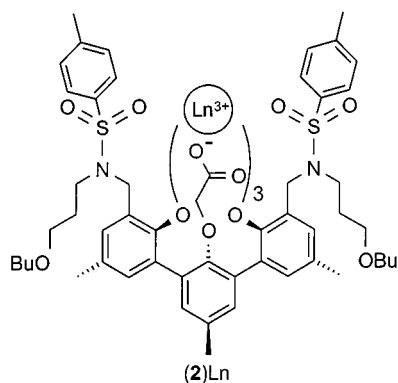
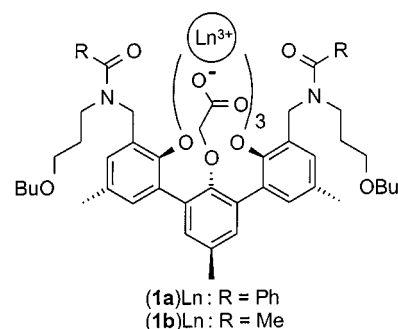


Figure 1. Energy diagram of the 4f energy levels responsible for the lanthanide luminescence; a filled circle represents the lowest luminescent excited state, an open circle represents the highest non-luminescent state. Adapted from G. Stein, E. Würzberg, *J. Chem. Phys.* **1975**, *62*, 208

The ligands $(1\mathbf{a}-\mathbf{b})\text{H}_3$ and $(2)\text{H}_3$ have been designed to provide eight hard oxygen donor atoms for encapsulation of

the lanthanide ion: three ether oxygens and three negatively charged carboxylate oxygens, and two additional amide or sulfonamide oxygens (see Scheme 1). The amide carbonyl oxygen is known to strongly coordinate to lanthanide ions.^[18] A route for the synthesis of these ligands has been developed, which allows for the incorporation of different sensitizers at the amide and sulfonamide positions, without changing either the synthetic route or the coordinating nature of the ligand. To demonstrate this, the acetamido and the benzamido group have been incorporated as coordinating moieties, and the luminescence properties of the complexes evaluated.

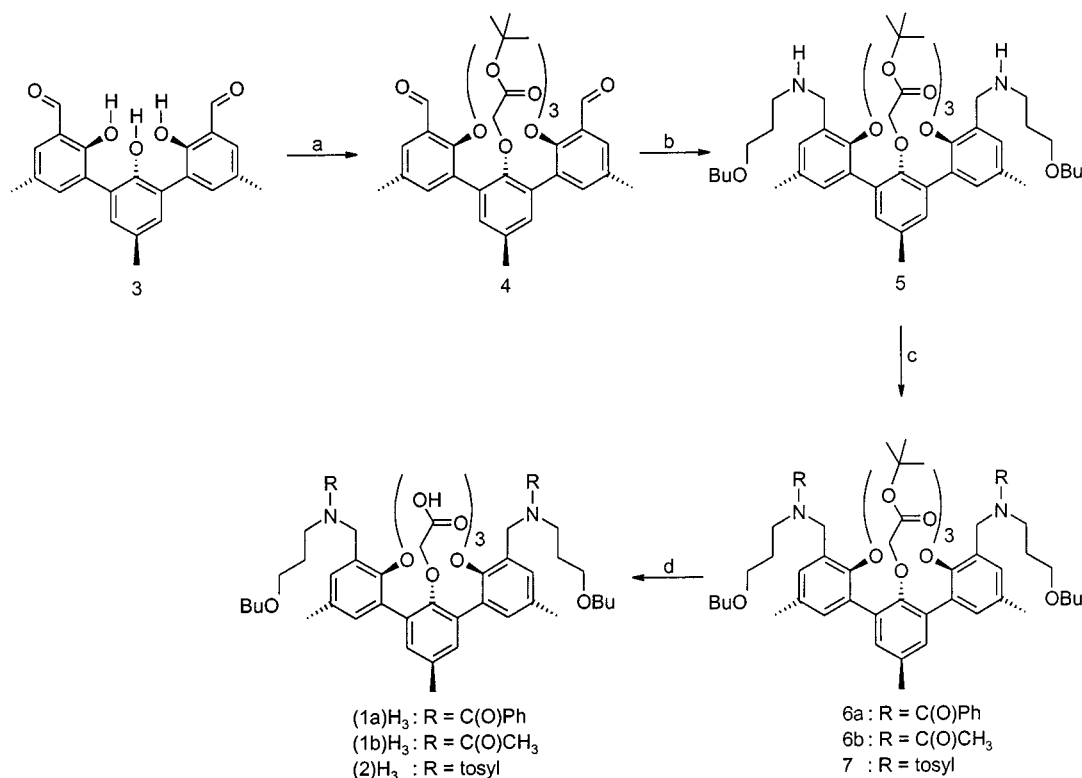


Scheme 1

Results and Discussion

Synthesis

The ligands $(1\mathbf{a}-\mathbf{b})\text{H}_3$ were synthesized starting from the diformyl terphenyl $\mathbf{3}$ ^[12] (see Scheme 2). Diformyl terphenyl $\mathbf{3}$ was treated with *tert*-butyl bromoacetate in acetonitrile in the presence of K_2CO_3 giving triester $\mathbf{4}$ in 90% yield. The $^1\text{H-NMR}$ spectrum of $\mathbf{4}$ shows the signals at $\delta = 1.38$ and 1.21 for the outer *tert*-butyl groups and the inner *tert*-butyl group, respectively, with a relative intensity of 2:1. Reductive amination of $\mathbf{4}$ with *n*-butoxy propylamine and hydrogen gas in the presence of 10% Pd/C as a catalyst yielded the bisamine $\mathbf{5}$ in quantitative yield. Reaction of $\mathbf{5}$ with the appropriate acid chloride in CH_2Cl_2 with Et_3N as a base gave the bis(amides) $\mathbf{6a-b}$ in 60 to 80% yield. Mild hydrolysis of the *tert*-butyl esters with trifluoroacetic acid gave the triacid derivatives $(1\mathbf{a}-\mathbf{b})\text{H}_3$ in quantitative yield. Complete hydrolysis was confirmed by the $^1\text{H NMR}$ spectra in



Scheme 2. Reaction conditions: (a) *tert*-butyl bromoacetate, K₂CO₃, CH₃CN; (b) *n*-butoxy propylamine, H₂, 10% Pd/C, EtOH; (c) appropriate acid chloride or *p*-toluenesulfonyl chloride, CH₂Cl₂, Et₃N; (d) TFA

which the signals for the *tert*-butyl groups are absent, and by the IR spectrum in which a peak at ca. 1750 cm⁻¹ is observed for the carboxylic acids ($\nu_{C=O}$).

The triacid sulfonamide ligand (2) H_3 was synthesized analogously to (1a–b) H_3 (see Scheme 2). Reaction of 5 with *p*-toluenesulfonyl chloride in CH₂Cl₂ with Et₃N as a base gave the bis(sulfonamide) 7 in 80% yield. Mild hydrolysis of the *tert*-butyl esters with trifluoroacetic acid gave (2) H_3 in quantitative yield. The corresponding lanthanide complexes were readily formed upon addition of lanthanide nitrate salts to solutions of the ligands in methanol in the presence of Et₃N as a base. FAB Mass spectrometry (see Supporting Information) indicated that all complexes have a 1:1 stoichiometry.^[20]

Structure of the (1a)Y and (2)Y Complexes

The diamagnetic complexes (1a)Y and (2)Y were characterized by ¹H NMR spectroscopy. At room temperature, the spectrum of (1a)Y in [D₆]DMSO is broadened due to hindered rotation around the tertiary amide and the phenyl groups. The spectrum taken at 100 °C is sharp (see Figure 2), and a time-averaged plane of C_s symmetry is apparent. The benzyl protons and the protons at the α -position of the outer carboxylates in the (1a)Y complex appear as an AB system, whereas in the free ligand (1a) H_3 , these protons appear as singlets. These AB patterns confirm the rigidity of the complex and the coordination of the amide carbonyls to the lanthanide ion. The assignment of the peaks was confirmed by COSY^[21] and TOCSY^[22] experiments. The IR

spectra of the (1a–b)Ln complexes show that all carboxylic acids are deprotonated. The peak corresponding to the amide carbonyl is located at 1630 cm⁻¹ ($\nu_{N-C=O}$), and is not shifted relative to the amide carbonyl in the free ligand.

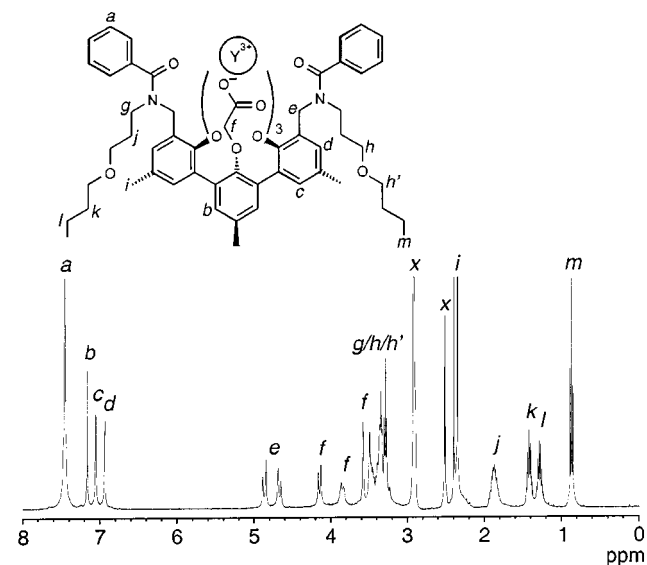


Figure 2. ¹H NMR (400 MHz) spectrum of (1a)Y in [D₆]DMSO at 100 °C

The proton NMR spectrum of (2)Y is sharp at room temperature (see Figure 3) and is similar to the spectrum of (1a)Y at 100 °C. The observed AB pattern for the benzyl protons confirms the coordination of the sulfonamide oxy-

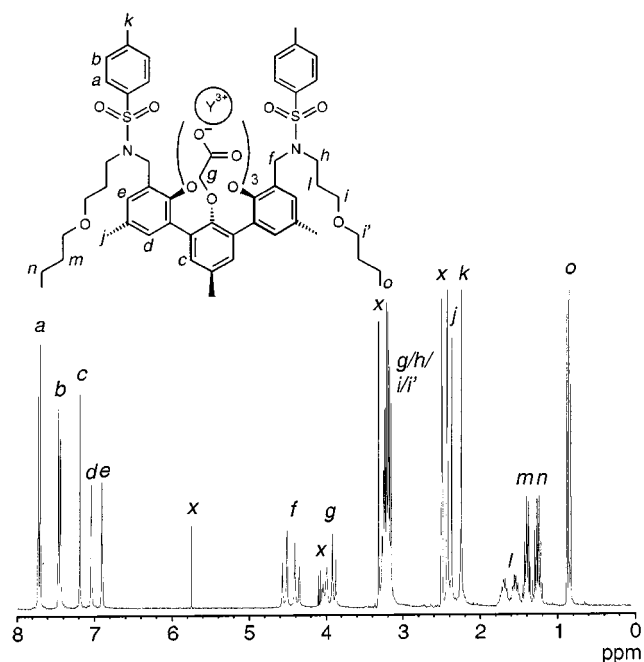


Figure 3. ^1H NMR (300 MHz) spectrum of (2)Y in $[\text{D}_6]\text{DMSO}$ at room temperature

gens to the lanthanide ion. Rotation around the sulfonamide bond appeared to be rapid, even at room temperature, and no loss of the apparent C_s symmetry is observed despite the chirality generated^[23] at the sulfur atoms by the monodentate coordination of the sulfonamide oxygen. This can be attributed to the weaker sulfonamide coordination bonds as compared to the amide bonds, which provide a more rapid de- and recoordination equilibrium leading to the apparent C_s symmetry. The spectrum shows two sharp doublets for the tosyl protons indicating that the tosyl groups can rotate freely at room temperature, contrary to the benzoyl groups in (1a)Y. In the IR spectra of the (2)Ln complexes, the peaks of the coordinating sulfonamide carbonyls are not shifted relative to the free ligand (2)H₃.

Luminescence Properties of the Eu^{3+} and Tb^{3+} Complexes

The luminescence properties of the Eu^{3+} and Tb^{3+} complexes were evaluated to obtain structural information on the complexes. Previous work has shown that the terphenyl moiety, which is in close proximity to the lanthanide ion, can act as an antenna-chromophore.^[12] The transfer of energy from the antenna to the lanthanide ion is generally considered to take place through the triplet level of the chromophore by means of a Dexter mechanism, which is strongly distance-dependent.^[24] The terphenyl triplet energy state of 24,600 cm^{-1} was estimated from the phosphorescence spectrum of (1a)Gd and (2)Gd^[25] at 77 K, which was in agreement with previously reported values.^[3] The excitation spectra of (1a)Eu and (2)Eu show a band at 280 nm that correspond to the absorption band of the terphenyl moiety, and clearly indicate that the Eu^{3+} ion can be excited through the terphenyl moiety. The emission spectra of these complexes in methanol, excited at 300 nm, show the lumin-

escence bands that correspond to the typical Eu^{3+} $^5\text{D}_0 \rightarrow ^7\text{F}_n$ transitions, with the strongest emissions in the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (around 593 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (around 615 nm) transition regions (solid lines in Figure 4 and Figure 5). The (1b)Eu complex has a similar emission spectrum (not shown). Deaeration of the samples only resulted in a slight increase in the luminescence intensity (less than 10%), indicating that the terphenyl triplet state is hardly quenched by oxygen and thus that the energy transfer to the Eu^{3+} ion is fast ($> 10^8 \text{ s}^{-1}$).^[26]

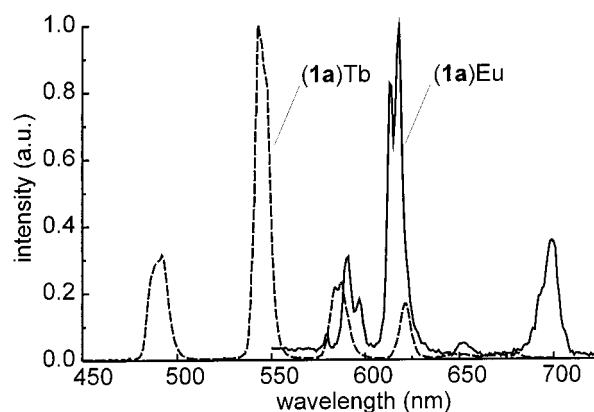


Figure 4. Emission spectra of the (1a)Eu (solid line) and (1a)Tb (dashed line) complexes in methanol (0.1 mM) upon excitation of the terphenyl ligand at 300 nm

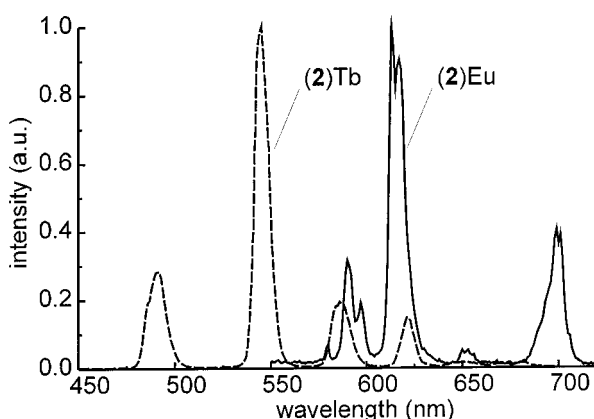


Figure 5. Emission spectra of the (2)Eu (solid line) and (2)Tb (dashed line) complexes in methanol (0.1 mM) upon excitation of the terphenyl ligand at 300 nm

For (1a–b)Eu and (2)Eu, a peak is observed for the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission at 579 nm, indicating that the symmetry of the first coordination sphere is not centrosymmetric. Since the $^7\text{F}_0$ state is nondegenerate, the single peak indicated that there is only one time-averaged luminescent Eu^{3+} species in solution. The Eu^{3+} spectra further show a splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission (around 593 nm) and a splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission (around 615 nm) caused by the ligand field. Strictly, three sublevels are expected for the $^7\text{F}_1$ level and five sublevels for the $^7\text{F}_2$ level, when the Eu^{3+} ion is in a C_s symmetry environment. Under the given conditions, i.e. at room temperature and with an emission bandwidth of 1 nm, only two sublevels are observed for each of these J-levels. From these data, the $\text{Eu}(^7\text{F}_1)$ and

Eu(7F_2) energy levels can be determined (see Table 1). The values of the ligand field splitting are approximately 200 cm^{-1} for the 7F_1 state and 130 cm^{-1} for the 7F_2 state, and are in agreement with previously reported values for organic Eu^{3+} complexes.^[4,27]

Table 1. Eu(7F_1) and Eu(7F_2) energy levels (in cm^{-1}) relative to the Eu(7F_0) level in the *m*-terphenyl-based complexes, calculated from the luminescence spectra in methanol

Energy level	(1a)Eu [cm^{-1}]	(1b)Eu [cm^{-1}]	(2)Eu [cm^{-1}]
7F_1	321	292	292
	491	491	491
7F_2	928	928	928
	1060	1060	1060

Kirby and Richardson have established that the intensity ratio of the $^5D_0 \rightarrow ^7F_2$ transition to the $^5D_0 \rightarrow ^7F_1$ transition is a good measure of the symmetry of the first coordination sphere of the Eu^{3+} ion.^[28] In a centrosymmetric environment, the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition of Eu^{3+} dominates, whereas distortion of the symmetry around the ion causes an intensity enhancement of electric dipole transitions such as the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition. They found that this ratio is 8.0 for a single crystal $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ (DBM = 1,3-diphenyl-1,3-propanedionate) in which the Eu^{3+} ion has an asymmetric coordination sphere, whereas an intensity ratio of 0.67 for the centrosymmetric $[\text{Eu}(\text{ODA})_3]$ complex (ODA = oxydiacetate) was found. In the present case, the $(^5D_0 \rightarrow ^7F_2)/(^5D_0 \rightarrow ^7F_1)$ ratio is approximately 4 for all complexes, which is significantly higher than the value of 0.67. This can be expected since the first coordination sphere is not centrosymmetric, but has a time-averaged C_s symmetry, as has been concluded from the $^1\text{H-NMR}$ data of the (1a)Y and (2)Y complexes. The emission spectrum of (1a)Eu in $[\text{H}_6]\text{DMSO}$ (not shown) closely resembles the corresponding spectrum in methanol, demonstrating that the structure of the first coordination sphere is essentially the same in both solvents.

The (1a)Tb and (2)Tb complexes exhibit bright green luminescence in methanol upon excitation of the terphenyl unit at 300 nm (dashed lines in Figure 4 and 5). The peaks in the emission spectrum correspond to the $^5D_4 \rightarrow ^7F_n$ transitions, with the strongest emission corresponding to the $^5D_4 \rightarrow ^7F_5$ transition around 545 nm. The spectra show some structuring within the emission bands, but they do not provide the basis for a reliable diagnostic probe of the symmetry of the complex, as is the case for the Eu^{3+} spectra.^[29]

The time-resolved luminescence spectra of the (1a–b)Eu, (2)Eu, (1a)Tb, and (2)Tb complexes in $[\text{H}_1]\text{methanol}$ show mono-exponential decays, with luminescence lifetimes of approximately 0.80 ms for the Eu^{3+} complexes and 1.80 ms for the Tb^{3+} complexes. The known sensitivity of Eu^{3+} and Tb^{3+} luminescence towards quenching by hydroxyl groups of the solvent^[30] provides an experimental tool to estimate the degree of shielding by the ligands. An empirical relationship has been established that estimates the number of coordinated methanol molecules (*n*):^[31,32]

$$n = q(1/\tau_h - 1/\tau_d - k_{\text{corr}}) \quad (1)$$

where *q* is 2.1 for Eu^{3+} and 8.4 for Tb^{3+} , τ_h is the luminescence lifetime of the complex in $[\text{H}_4]\text{methanol}$ - and τ_d is the luminescence lifetime of the complex in $[\text{D}_1]\text{methanol}$, k_{corr} is a factor to correct for methanol molecules which coordinate in the second sphere and is 0.125 ms^{-1} for Eu^{3+} and 0.03 ms^{-1} for Tb^{3+} . The luminescence lifetimes of the (1a–b)Eu, (2)Eu, (1a)Tb, and (2)Tb complexes are significantly longer than those of the free Eu^{3+} (0.27 ms) and Tb^{3+} ions (0.65 ms) in $[\text{H}_4]\text{methanol}$, showing that effective solvent shielding has been achieved by complexation of the ions in the terphenyl ligands (see Table 2). Using Equation (1), our experiments showed that only one methanol molecule is coordinated to the complexed lanthanide ion in (1a–b)Ln and one to two methanol molecules are coordinated to the complexed lanthanide ion in (2)Ln (see Table 2).

Table 2. Luminescence lifetimes of the Eu^{3+} and Tb^{3+} complexes measured in CH_3OH (τ_h) and CH_3OD (τ_d), as well as the number of coordinated solvent molecules (*n*) determined from Equation (1)

Complex	τ_h [ms]	τ_d [ms]	<i>n</i>
(1a)Eu	0.80	1.74	1.2 ± 0.5
(1b)Eu	0.80	1.62	1.1 ± 0.5
(2)Eu	0.68	1.79	1.7 ± 0.5
(1a)Tb	1.83	2.68	1.2 ± 1.5
(2)Tb	1.80	2.42	0.94 ± 1.5

A model for the structure which is in agreement with the photophysical data of the Eu^{3+} and Tb^{3+} complexes involves coordination of the lanthanide ion to three ether oxygens, three carboxylate oxygens, two amide oxygens, and one methanol molecule, in the case of the (1a–b)Ln complexes, resulting in a coordination number of nine for the first coordination sphere. This is in agreement with the experimentally determined coordination number of 9 of Eu^{3+} and Tb^{3+} ions in methanol.^[33] The model also applies to the (2)Ln complexes. The photophysical data, however, suggest that a coordinated sulfonamide oxygen can be temporarily replaced by a methanol molecule. Despite the fact that the $^1\text{H NMR}$ data of (1a)Y at room temperature indicate that amide pendant arms in the (1a–b)Eu complexes can be in slightly different conformations owing to the hindered rotation around the tertiary amide, the photophysical data clearly indicate that this does not affect the first coordination sphere of the Eu^{3+} ion. A change in amide C-substituent (acetyl or benzoyl) also does not cause a change in the first coordination sphere.

Luminescence Properties of the Dy^{3+} and Sm^{3+} Complexes

Two other lanthanide ions that have emission bands in the visible region are Dy^{3+} and Sm^{3+} , but the luminescence of these ions is more sensitive to quenching by solvent hydroxyl groups than the Eu^{3+} and Tb^{3+} luminescence.^[3] Therefore, the emission spectra were recorded in $[\text{H}_6]\text{DMSO}$, a strongly coordinating solvent without efficient quenching hydroxyl groups. Upon excitation of the

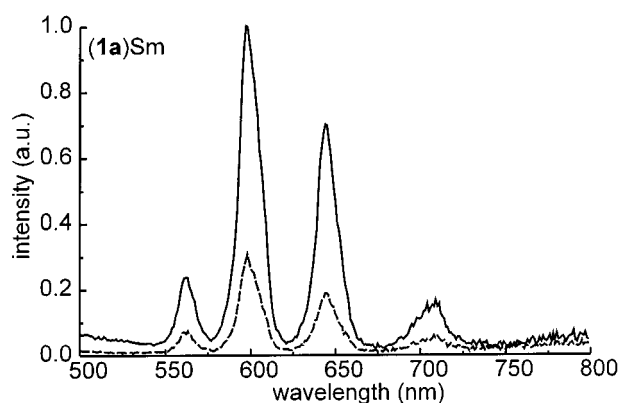


Figure 6. Emission spectra of 1 mM solutions of **(1a)Sm** in $[H_6]DMSO$ (dashed line) and $[D_6]DMSO$ (solid line) upon excitation of the terphenyl ligand at 300 nm

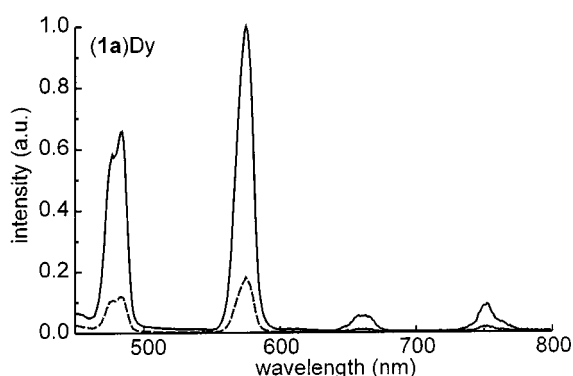


Figure 7. Emission spectra of 1 mM solutions of **(1a)Dy** in $[H_6]DMSO$ (dashed line) and $[D_6]DMSO$ (solid line) upon excitation of the terphenyl ligand at 300 nm

(1a)Sm (see Figure 6) and **(1a)Dy** (see Figure 7) complexes at 300 nm, the typical luminescence bands are observed, corresponding to the $^4F_{9/2} \rightarrow ^6H_j$ transitions, and $^4G_{5/2} \rightarrow ^6H_j$ transitions, respectively. The **(1a)Sm** complex shows two intense emission bands at 600 and 640 nm, and two weaker bands at 560 and 700 nm. The **(1a)Dy** complex shows four emission bands in the visible region, two strong bands at 475 and 575 nm and two weaker bands at 655 nm and at 745 nm. The luminescence intensity increases dramatically upon changing the solvent from $[H_6]DMSO$ (dashed lines in Figure 6 and 7) to $[D_6]DMSO$ (solid lines in Figure 6 and 7) demonstrating the sensitivity of Dy^{3+} and Sm^{3+} towards quenching by C–H vibrations, even though these vibrations are less energetic than O–H vibrations.^[3]

Luminescence Properties of the Er^{3+} , Nd^{3+} , and Yb^{3+} Complexes

Although sensitized emission has been studied in detail for Eu^{3+} and Tb^{3+} complexes,^[6,7,34] and efficient antenna-chromophores with appropriate triplet energy levels have been reported, the field of sensitized near-infrared lanthanide luminescence is still relatively unexplored. The main difference between the sensitization of Eu^{3+} and Tb^{3+} and the sensitization of Nd^{3+} , Yb^{3+} , and Er^{3+} is that the former require chromophores with triplet states above about $22,000\text{ cm}^{-1}$, whereas the latter lanthanide ions can be excited

through chromophores with much lower triplet states (see Figure 1). However, it has been reported that Nd^{3+} , Yb^{3+} , and Er^{3+} can also accept the excitation energy from chromophores with high lying triplet states. Indeed, after laser excitation at 350 nm, sensitized emission at 1540 nm is observed for **(1a)Er**, at 880, 1060, and 1330 nm for **(1a)Nd**, and at 980 nm for **(1a)Yb** (see Figure 8).

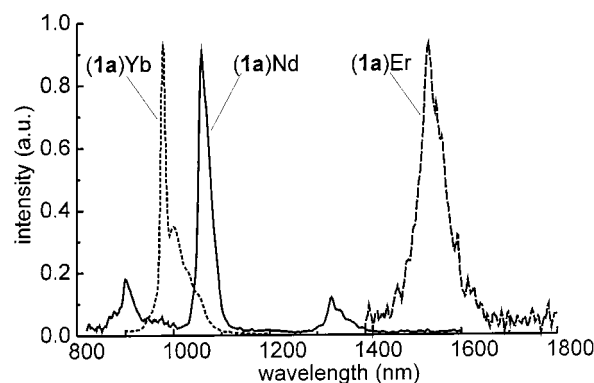


Figure 8. Near-infrared emission spectra of **(1a)Nd**, **(1a)Yb** and **(1a)Er** in $[H_6]DMSO$ (1 mM) upon laser excitation of the terphenyl ligand at 350 nm

Table 3. Luminescence lifetimes measured in $[H_6]DMSO$ (τ_h) and $[D_6]DMSO$ (τ_d) as well as the quenching rate constants by the methyl groups of $[H_6]DMSO$ (k_q)

Complex	τ_h [μs]	τ_d [μs]	k_q [10^4 s^{-1}] ^[a]
(1a)Yb	9.1	19.9	6.0
(2)Yb	10.3	23.6	5.5
(1a)Er	2.1	3.3	16.3
(2)Er	2.4	3.5	13.3
(1a)Nd	1.2	2.5	47.1
(2)Nd	1.2	2.5	40.8
(1a)Eu	1.86 ms	2.30 ms	0.010
(2)Eu	1.87 ms	2.25 ms	0.009

^[a] $k_q [H_6]DMSO = 1/\tau_h - 1/\tau_d$

Time-resolved luminescence experiments showed luminescence lifetimes of the complexes in $[H_6]DMSO$ (τ_h) and $[D_6]DMSO$ (τ_d) in the range of microseconds (see Table 3), with the Yb^{3+} complexes having the longest lifetimes and the Nd^{3+} complexes the shortest. The lifetimes compare favorably with the recently published data on Yb^{3+} and Nd^{3+} in these solvents.^[35,36] Upon changing the solvent from $[H_6]DMSO$ to $[D_6]DMSO$, the lifetimes increase significantly indicating that for this class of lanthanide ions, the C–H oscillators are efficient quenchers of the excited luminescent state. The relative quenching rate constants of the C–H oscillators of the solvent molecules (k_q , see Table 3) were calculated using Equation (2).

$$k_q = 1/\tau_h - 1/\tau_d \quad (2)$$

The calculations show that the quenching rates are the highest for Nd^{3+} complexes, and lowest for the Yb^{3+} complexes. This is in accordance with the well-established energy gap law^[37] that states that the smaller the harmonic number of vibrational quanta that is required to match the energy gap between the lowest luminescent state and the highest nonluminescent state of the lanthanide ion, the

more effective the vibronic quenching is (see also Figure 1). For the C–H vibration with vibrational quanta of 2950 cm^{-1} , the number of harmonics (n_h) necessary to match the energy gap is largest for Yb^{3+} ($n_h = 3\text{--}4$), followed by Er^{3+} ($n_h = 2\text{--}3$) and smallest for Nd^{3+} ($n_h = 1\text{--}2$). For comparison, the lifetimes of the Eu^{3+} complexes have been added to Table 3. The energy gap between the lowest luminescent state and highest nonluminescent state of Eu^{3+} (with $n_h = 6\text{--}7$) is much larger than the energy gap of the NIR-emitting lanthanide ions. The calculated quenching rate constants in Table 3 are not absolute values that allow direct comparison, because the C–D vibration also quenches the lanthanide excited state (but less efficiently than the C–H vibration), and therefore the quenching rate constants are lower limits. The observed trend, however, demonstrates that quenching becomes rapidly more efficient when n_h decreases.

For future applications in polymer waveguide optical amplifiers, the near-infrared emitting complexes must have high luminescence quantum yields. The intrinsic luminescence quantum yield (ϕ_{lum}) of the complexed ions is given by Equation (3):

$$\phi_{\text{lum}} = \tau/\tau_0 \quad (3)$$

where τ_0 is the natural lifetime (i.e. the luminescence lifetime in the absence of quenching processes) and τ is the observed luminescence lifetime. The natural lifetimes of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} and the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of Yb^{3+} have been calculated from their respective absorption spectra, and are 14 ms for (1a)Er and 2 ms for (1a)Yb. The natural lifetime of Nd^{3+} cannot be determined in this way, since the emissions do not involve a transition back to the ground state. Instead a literature value of 0.25 ms was taken for Nd^{3+} .^[38] This leads to intrinsic luminescence quantum yields of 0.02% for (1a)Er, of 0.78% for (1a)Yb, and of 0.84% for (1a)Nd in $[\text{D}_6]\text{DMSO}$. These low luminescence quantum yields are caused by the fact that the C–H vibrations in the ligand are efficient quenchers. Deuteration of the ligands will improve the luminescence quantum yields, as has been demonstrated for Eu^{3+} complexes.^[3,12,39]

Conclusion

In summary, the *m*-terphenyl-based ligands reported here bearing amide or sulfonamide functionalities form neutral complexes with trivalent lanthanide cations. The known luminescence behavior of Eu^{3+} was used to establish the structure of the complexes showing that the ligand occupies eight of the coordination sites of the ion, and a solvent molecule occupies the remaining coordination site. It has been demonstrated that by incorporating different lanthanide ions, various emission wavelengths become accessible, ranging from 500 to 1550 nm. The near-infrared emitting complexes exhibit sensitized-emission with a luminescence lifetime in the microsecond time-scale. The complexes are very soluble in organic solvents, which is essential for the

production of polymer-based optical amplifiers. Further improvements of these complexes for future applications in optical amplifiers are deuteration of the ligands, and the incorporation of dyes to facilitate sensitized excitation in the visible region around 630 nm.

Experimental Section

General: Melting points were determined with a Reichert melting point apparatus and are uncorrected. – Mass spectra were recorded on a Finnigan MAT 90 spectrometer using *m*-NBA (nitrobenzyl alcohol) as a matrix, unless stated otherwise. – IR spectra were recorded with a Biorad 3200 or a Nicolet 55XC FT-IR spectrophotometer using KBr pellets. – Elemental analyses were performed on a Carlo Erba EA 1106 apparatus. – $^1\text{H-NMR}$ (250 MHz) and $^{13}\text{C-NMR}$ (62.7 MHz) spectra were recorded with a Bruker AC 250 spectrometer in CDCl_3 unless stated otherwise, using residual CHCl_3 ($\delta = 7.26$) and CDCl_3 ($\delta = 77.0$) as the internal standard, respectively. – Preparative column chromatography separations were performed on Merck silica gel (particle size 0.040–0.063 mm, 230–400 mesh). CH_2Cl_2 , CHCl_3 , and hexane (mixture of isomers) were distilled from CaCl_2 and stored over molecular sieves (4 Å). Ethyl acetate was distilled from K_2CO_3 and stored over molecular sieves (4 Å). Triethylamine (Et_3N) was distilled in vacuo and stored over KOH. Acetonitrile and ethanol were of analytical grade and were dried over molecular sieves (4 Å) prior to use. *n*-Butoxypropylamine, *tert*-butyl bromoacetate, and the $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ salts were purchased from Aldrich and used without further purification. All reactions were carried out under an argon atmosphere. Standard workup involved washing the organic layers with water, drying over magnesium sulfate, filtration of the salts, and concentrating to dryness in vacuo.

1-[(*tert*-Butoxycarbonyl)methoxy]-2,6-bis{2'-[(*tert*-butoxycarbonyl)methoxy]-3'-formyl-5'-methylphenyl}-4-methylbenzene (4): To a mixture of **3** (1.9 g, 5.1 mmol) and K_2CO_3 (2.7 g, 20.2 mmol) in acetonitrile (250 mL) was added *tert*-butyl bromoacetate (3.2 g, 16.1 mmol) and the mixture was heated at reflux for 8 h. Subsequently, the reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was redissolved in CH_2Cl_2 (200 mL) and washed twice with 0.5 N HCl, followed by standard workup. The crude product was purified by flash column chromatography [ethyl acetate/hexane 1:3 (v/v)] to give triester **4** as an off-white solid: yield 80%, m.p. 130–132 °C. – $^1\text{H NMR}$ (CDCl_3): $\delta = 10.6$ (s, 2 H), 7.67 (d, $J = 2.3$ Hz, 2 H), 7.43 (d, $J = 2.3$ Hz, 2 H), 7.21 (s, 2 H), 4.20 (s, 4 H), 3.90 (s, 2 H), 2.38 (s, 3 H), 2.36 (s, 6 H), 1.38 (s, 18 H), 1.21 (s, 9 H). – $^{13}\text{C NMR}$ (CDCl_3): $\delta = 191.2$, 167.7, 167.0, 157.0, 151.6, 138.6–127.9, 82.3, 81.4, 70.9, 69.7, 28.0, 27.8, 20.7, 20.6. – MS (FAB): m/z 741.2 [(M + Na) $^+$]. – $\text{C}_{41}\text{H}_{50}\text{O}_{11}$: calcd. C 68.51, H 7.01; found: C 68.75, H 7.08.

1-[(*tert*-Butoxycarbonyl)methoxy]-2,6-bis{2'-[(*tert*-butoxycarbonyl)methoxy]-3'-(*n*-butoxypropylaminomethyl)-5'-methylphenyl}-4-methylbenzene (5): To a solution of **4** (1.54 g, 2.14 mmol) in ethanol (150 mL) was added *n*-butoxypropylamine (0.56 g, 4.28 mmol) and the solution was stirred at room temperature for 30 min. Subsequently, Pd/C (10%, 100 mg) was added and the suspension was stirred overnight at room temperature under a hydrogen atmosphere. The reaction mixture was filtered over Hyflo filter aid and the filtrate was concentrated in vacuo. The bisamine **5** was obtained as a colorless oil in quantitative yield. – $^1\text{H NMR}$ (CDCl_3): $\delta = 7.11$ (s, 2 H), 7.08 (d, $J = 2.0$ Hz, 2 H), 7.05 (d, $J = 2.0$ Hz, 2 H), 4.12 (s, 4 H), 3.94 (s, 2 H), 3.86 (s, 4 H), 3.49 (t, $J = 6.5$ Hz, 4 H),

3.40 (t, $J = 6.5$ Hz, 4 H), 2.73 (t, $J = 7.0$ Hz, 4 H), 2.32 (s, 3 H), 2.29 (s, 6 H), 1.80 (m, 4 H), 1.57 (m, 4 H), 1.40 (s, 18 H), 1.36 (m, 4 H), 1.23 (s, 9 H), 0.90 (t, $J = 7.2$ Hz, 6 H). – ^{13}C NMR (CDCl_3): $\delta = 168.3, 167.5, 152.6, 151.4, 133.1\text{--}130.2, 81.4, 80.8, 70.6, 70.4, 69.7, 69.3, 68.9, 53.4, 49.4, 46.8, 39.6, 33.4, 31.8, 30.1, 28.0, 27.8, 20.7, 19.3, 13.9$. – MS (FAB): m/z 949.4 [(M + H) $^+$], calcd. for $\text{C}_{55}\text{H}_{85}\text{N}_2\text{O}_{11}$: 949.6].

Typical Procedure for the Synthesis of 6a–b and 7: To a solution of **5** (0.5 g, 0.53 mmol) and Et_3N (0.20 g, 2.0 mmol) in CH_2Cl_2 (75 mL) was added 3 mmol of the appropriate acid chloride or *p*-toluenesulfonyl chloride, and the resulting solution was stirred overnight at room temperature. After the addition of CH_2Cl_2 (100 mL), the reaction mixture was washed twice with 0.5 N HCl, followed by standard workup. The crude product was purified by flash column chromatography.

1-[(tert-Butoxycarbonyl)methoxy]-2,6-bis[2'-[(tert-butoxycarbonyl)methoxy]-3'-[N-(*n*-butoxypropyl)benzoylamidomethyl]-5'-methylphenyl]-4-methylbenzene (6a): The crude product was purified by flash column chromatography [ethyl acetate/hexane 2:3 (v/v)] to give the bis(benzoylamide) **6a** as a colorless oil: yield 80%. – ^1H NMR (CDCl_3): $\delta = 7.54\text{--}7.31$ (m, 10 H), 7.20–7.00 (m, 6 H), 5.03 (s, 2 H), 4.77 (s, 2 H), 4.22–4.08 (m, 2 H), 4.02–3.82 (m, 4 H), 3.72–3.50 (m, 4 H), 3.48–3.16 (m, 8 H), 2.33 (s, 9 H), 2.10–1.96 (m, 2 H), 1.92–1.78 (m, 2 H), 1.64–1.52 (m, 2 H), 1.50–1.15 (m, 33 H), 0.97–0.82 (m, 6 H). – ^{13}C NMR (CDCl_3): $\delta = 172.3, 167.9, 167.1, 151.9, 151.3, 136.5\text{--}126.6, 81.5, 80.9, 70.6, 70.4, 69.6, 68.4, 67.6, 60.4, 48.4, 46.3, 43.1, 42.3, 31.9, 28.7, 27.9, 21.0, 20.7, 19.3, 13.9$. – MS (FAB): m/z 1157.6 [(M + H) $^+$], calcd. for $\text{C}_{69}\text{H}_{93}\text{N}_2\text{O}_{13}$: 1157.7].

1-[(tert-Butoxycarbonyl)methoxy]-2,6-bis[3'-[N-(*n*-butoxypropyl)acetamidomethyl]-2'-[(tert-butoxycarbonyl)methoxy]-5'-methylphenyl]-4-methylbenzene (6b): The crude product was purified by flash column chromatography [ethyl acetate/hexane 2:1 (v/v)] to give the bis(acetamide) **6b** as a colorless oil: yield 53%. – ^1H NMR (CDCl_3): $\delta = 7.11\text{--}7.07$ (m, 2 H), 7.00 (s, 2 H), 6.90 (s, 1 H), 6.78 (d, $J = 2.8$ Hz, 1 H), 4.76 (s, 4 H), 4.03 (s, 4 H), 3.89–3.85 (m, 2 H), 3.48–3.30 (m, 12 H), 2.34–2.19 (m, 12 H), 2.06 (s, 4 H), 1.85–1.80 (m, 4 H), 1.53–1.42 (m, 4 H), 1.30–1.24 (m, 4 H), 1.20–1.18 (m, 4 H), 1.38 (s, 27 H), 0.89–0.81 (m, 6 H). – ^{13}C NMR (CDCl_3): $\delta = 171.8, 171.2, 168.3, 168.2, 168.0, 167.2, 167.1, 167.4, 152.3, 151.9, 151.4, 133.8\text{--}126.1, 81.8, 81.0, 70.9, 70.8, 70.6, 70.2, 69.8, 68.5, 67.3, 48.0, 45.2, 44.0, 42.4, 38.5, 31.8, 28.5, 27.9, 21.7, 21.3, 20.9, 19.4, 13.9$. – MS (FAB) m/z 1033.5 [(M + H) $^+$], calcd. for $\text{C}_{59}\text{H}_{89}\text{N}_2\text{O}_{13}$: 1033.6].

1-[(tert-Butoxycarbonyl)methoxy]-2,6-bis[2'-[(tert-butoxycarbonyl)methoxy]-3'-[N-(*n*-butoxypropyl)-*p*-toluenesulfonylamidomethyl]-5'-methylphenyl]-4-methylbenzene (7): The crude product was purified by flash column chromatography [ethyl acetate/hexane 1:3 (v/v)] to give the bis(sulfonamide) **7** as a colorless oil: yield 69%. – ^1H NMR (CDCl_3): $\delta = 7.73$ (d, $J = 8.2$ Hz, 4 H), 7.27 (d, $J = 8.3$ Hz, 4 H), 7.19 (d, $J = 1.8$ Hz, 2 H), 7.07 (s, 2 H), 7.03 (d, $J = 1.8$ Hz, 2 H), 4.58 (s, 4 H), 4.01 (s, 4 H), 3.88 (s, 2 H), 3.33–3.24 (m, 12 H), 2.40 (s, 6 H), 2.29 (s, 3 H), 2.25 (s, 6 H), 1.74–1.63 (m, 4 H), 1.52–1.38 (m, 4 H), 1.32 (s, 18 H), 1.27 (m, 4 H), 1.23 (s, 9 H), 0.86 (t, 6 H, $J = 7.0$ Hz). – ^{13}C NMR (CDCl_3): $\delta = 168.1, 167.2, 152.0, 151.3, 143.0, 137.1\text{--}127.1, 81.5, 81.0, 70.5, 70.2, 69.6, 68.0, 46.9, 46.6, 31.7, 28.6, 27.9, 21.5, 20.8, 19.2, 13.9$. – MS (FAB): m/z 1280.1 [(M + Na) $^+$], calcd. for $\text{C}_{69}\text{H}_{96}\text{N}_2\text{S}_2\text{O}_{15}\text{Na}$: 1279.6].

Typical Preparation of the Triacid Ligands (1a–b) H_3 and (2) H_3 : A solution of 0.30 mmol of the ligands **6a–b** or **7** in TFA (50 mL) was stirred overnight at room temperature. Subsequently, toluene

(25 mL) was added and the TFA/toluene mixture was azeotropically evaporated. The residue was taken up in CH_2Cl_2 (100 mL) and washed twice with 1 N HCl, followed by standard workup. The triacids were obtained as white solids in near quantitative yield.

2,6-Bis[3'-[N-(*n*-butoxypropyl)benzoylamidomethyl]-2'-[(hydroxycarbonyl)methoxy]-5'-methylphenyl]-1-[(hydroxycarbonyl)methoxy]-4-methylbenzene [(1a) H_3]: M.p.: 40–42 °C. – ^1H NMR (CD_3OD): $\delta = 7.50\text{--}7.30$ (m, 10 H), 7.15–7.10 (m, 4 H), 6.98 (s, 2 H), 4.60 (s, 2 H), 4.10–3.75 (m, 6 H), 3.65–3.15 (m, 12 H), 2.30 (s, 9 H), 1.86 (m, 2 H), 1.75 (m, 2 H), 1.60–1.10 (m, 8 H), 0.84–0.71 (m, 6 H). – ^{13}C NMR (CD_3OD): $\delta = 174.6, 172.2, 172.0, 153.5, 153.0, 137.6\text{--}127.7, 71.8, 71.5, 69.9, 68.7, 44.6, 44.0, 32.9, 32.8, 29.5, 28.5, 21.0, 20.4, 14.3$. – MS (FAB): m/z 1012.0 [(M + Na) $^+$], calcd.: 1011.5]. – IR (KBr): 1738 ($\text{C}=\text{O}_{\text{acid}}$), 1631 ($\text{C}=\text{O}_{\text{amide}}$) cm^{-1} . – $\text{C}_{57}\text{H}_{68}\text{N}_2\text{O}_{13}\cdot 1\text{H}_2\text{O}$: calcd. C 67.97, H 7.01, N 2.78; found: C 68.32, H 7.03, N 2.80.

2,6-Bis[3'-[N-(*n*-butoxypropyl)acetamidomethyl]-2'-[(hydroxycarbonyl)methoxy]-5'-methylphenyl]-1-[(hydroxycarbonyl)methoxy]-4-methylbenzene [(1b) H_3]: M.p.: 51–53 °C. – ^1H NMR (CD_3OD): $\delta = 7.14\text{--}7.11$ (m, 2 H), 7.09–6.83 (m, 4 H), 4.71 (s, 2 H), 4.67 (s, 2 H), 4.15–3.95 (m, 6 H), 3.40–3.29 (m, 12 H), 3.23–3.21 (m, 4 H), 2.29 (s, 3 H), 2.25 (s, 3 H), 2.22 (s, 3 H), 2.12 (s, 3 H), 2.01 (s, 3 H), 1.83–1.60 (m, 4 H), 1.50–1.39 (m, 4 H), 1.32–1.20 (m, 4 H), 0.87–0.79 (m, 6 H). – ^{13}C NMR (CD_3OD): $\delta = 174.1, 173.7, 172.2, 153.4, 153.0, 152.4, 135.6\text{--}128.4, 71.8, 71.7, 70.6, 70.1, 69.5, 68.5, 46.5, 45.0, 44.0, 37.9, 32.9, 30.5, 29.4, 28.8, 21.8, 21.3, 21.0, 20.8, 20.4, 14.3$. – MS (FAB) m/z 864.1 [(M – H) $^-$], calcd. for $\text{C}_{47}\text{H}_{63}\text{N}_2\text{O}_{13}$: 863.4]. – IR (KBr): 1740 ($\text{C}=\text{O}_{\text{acid}}$), 1630 ($\text{C}=\text{O}_{\text{amide}}$) cm^{-1} . – $\text{C}_{47}\text{H}_{64}\text{N}_2\text{O}_{13}\cdot 1\text{H}_2\text{O}$: calcd. C 63.93, H 7.53, N 3.17; found: C 64.09, H 7.74, N 3.36.

2,6-Bis[3'-[N-(*n*-butoxypropyl)4-methylbenzenesulfonylamidomethyl]-2'-[(hydroxycarbonyl)methoxy]-5'-methylphenyl]-1-[(hydroxycarbonyl)methoxy]-4-methylbenzene [(2) H_3]: M.p.: 60–62 °C. – ^1H NMR (CD_3OD): $\delta = 7.73$ (d, $J = 7.7$ Hz, 4 H), 7.38 (d, $J = 7.7$ Hz, 4 H), 7.16 (s, 2 H), 7.13 (s, 2 H), 7.12 (s, 2 H), 4.54 (s, 4 H), 4.14 (s, 4 H), 4.04 (s, 2 H), 3.35–3.20 (m, 12 H), 2.43 (s, 6 H), 2.36 (s, 3 H), 2.28 (s, 6 H), 1.72–1.58 (m, 4 H), 1.54–1.40 (m, 4 H), 1.40–1.20 (m, 4 H), 0.90 (t, $J = 7.2$ Hz, 6 H). – ^{13}C NMR (CD_3OD): $\delta = 172.3, 170.5, 153.2, 152.1, 144.9\text{--}128.1, 71.7, 70.9, 69.1, 41.4, 32.8, 30.7, 29.8, 21.6, 20.9, 20.4, 14.5$. – MS (FAB): $m/z = 1111.5$ [(M + Na) $^+$], calcd 1111.4]. – IR (KBr): $\nu = 1740$ ($\text{C}=\text{O}_{\text{acid}}$), 1337, 1159 ($\text{S}=\text{O}$) cm^{-1} . – $\text{C}_{57}\text{H}_{72}\text{N}_2\text{O}_{15}\text{S}_2$: calcd. C 62.85, H 6.66, N 2.57, S 5.89; found C 62.50, H 6.73, N 3.06, S 6.09.

Typical Procedure for the Preparation of the Lanthanide Complexes: To a solution of 0.05 mmol of triacids (1a–b) H_3 or (2) H_3 and Et_3N (0.25 mmol) in methanol (20 mL) was added the lanthanide nitrate salt (0.07 mmol). The resulting solution was stirred for 2 h, after which the solvent was evaporated. The complex was redissolved in CHCl_3 and washed twice with water, followed by standard workup. The complexes were obtained as solids in quantitative yields. The complexes were characterized by FAB-MS spectroscopy (see Supp. Mat.) and IR spectroscopy. The bis(amide) complexes (1a–b) Ln all gave similar IR spectra: A peak at 1640–1630 cm^{-1} ($\nu_{\text{N}=\text{O}}$) with a shoulder around 1600 cm^{-1} ($\nu_{\text{C}=\text{O}}$). In the IR spectra of the bis(sulfonamide) complexes (2) Ln a peak at 1595–1600 cm^{-1} ($\nu_{\text{C}=\text{O}}$), and two peaks around 1330 and 1160 cm^{-1} ($\nu_{\text{S}=\text{O}}$) were observed.

Photophysical Studies. – Visible Region: Steady-state luminescence measurements were performed with a Photon Technology International (PTI) Alphascan spectrofluorimeter. The samples were excited by a 75 W quartz-tungsten-halogen lamp followed by a SPEX 1680 double monochromator. The emitted light was detected at an

angle of 90° by a Hamamatsu R928 photomultiplier, and subsequently fed to a photon-counting interface. Time-resolved luminescence measurements were performed with an Edinburgh Analytical Instruments FL900 system. The excitation source consisted of a pulsed Xe-lamp (μ s-pulsed output). The luminescence signal was detected by a Hamamatsu R928 photomultiplier and fed to a time-to-amplitude converter and a multichannel analyser (Time Correlated Single Photon Detection). – **NIR Region:** Steady state photoluminescence measurements were performed using the 351.1/363.8 nm lines of an Ar ion pump laser at a power of 60 mW for excitation. The laser beam was modulated with an acousto-optic modulator at a frequency of 40 Hz. The luminescence signal was focused into a monochromator and detected with a liquid nitrogen cooled Ge detector, using standard lock-in techniques. Luminescence lifetime measurements (Edinburgh Analytical Instruments LP900 system) were performed by monitoring the luminescence decay after excitation with a 0.5 ns pulse of a LTB MSG 400 nitrogen laser ($\lambda_{\text{exc}} = 337$ nm, pulse energy 20 μ J, 10 Hz repetition rate). Decay signals were recorded using a liquid nitrogen cooled Ge detector with a time resolution of 0.3 μ s. The signals were averaged using a digitizing Tektronix oscilloscope. All decay curves were analyzed by deconvolution of the measured detector response and fitted with mono-exponential curves.

Supporting Information Available: The absorption spectra of the complexed lanthanide ions in (1a)Er, (1a)Nd, and (1a)Yb, and the FAB-MS data of the complexes. See footnote on the first page of this article.

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- [1] V.-M. Mikkala, M. Helenius, I. K. Hemmilä, J. Kankare, H. Takalo, *Helv. Chim. Acta* **1993**, *76*, 1361–1378.
- [2] M. Iwamuro, Y. Hasegawa, Y. Wada, K. Murakoshi, T. Kitamura, N. Nakashima, T. Yamanaka, S. Yanagida, *Chem. Lett.* **1997**, 1067–1068.
- [3] M. P. Oude Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruël, J. W. Hofstra, F. A. J. Geurts, D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2* **1998**, 2141–2150.
- [4] K. A. Gschneider, Jr., L. Eyring, *Handbook on the physics and chemistry of rare earths, Vol. 1, Metals*, North Holland Publishing Company, Amsterdam, **1978**.
- [5] I. K. Hemmilä, *Applications of fluorescence in immunoassays*, Wiley and Sons, New York, **1991**.
- [6] F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. van der Tol, J. W. Verhoeven, *J. Am. Chem. Soc.* **1995**, *117*, 9408–9414.
- [7] N. Sabbatini, M. Guardigli, J.-M. Lehn, *Coord. Chem. Rev.* **1993**, *123*, 201–228, and references cited herein.
- [8] E. Desurvire, *Phys. Today* **1994**, *97*, 20–27.
- [9] D. An, Z. Yue, R. T. Chen, *Appl. Phys. Lett.*, **1998**, *72*, 2806–2807.
- [10] S. Lin, R. J. Feuerstein, A. R. Mickelson, *J. Appl. Phys.* **1996**, *79*, 2868–2874.
- [11] W. J. Miniscalco, *J. Lightwave Technol.* **1991**, *9*, 234–250.
- [12] M. P. Oude Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruël, J. W. Hofstra, F. A. J. Geurts, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1997**, *119*, 138–144.
- [13] M. P. Oude Wolbers, F. C. J. M. van Veggel, J. W. Hofstra, F. A. J. Geurts, D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2* **1997**, 2275–2282.
- [14] L. H. Slooff, A. Polman, M. P. Oude Wolbers, F. C. J. M. van Veggel, D. N. Reinhoudt, J. W. Hofstra, *J. Appl. Phys.* **1998**, *83*, 497–503.
- [15] M. P. Oude Wolbers, F. C. J. M. van Veggel, F. G. A. Peters, E. S. E. van Beelen, J. W. Hofstra, F. A. J. Geurts, D. N. Reinhoudt, *Chem. Eur. J.* **1998**, *4*, 772–780.
- [16] M. H. V. Werts, J. W. Hofstra, F. A. J. Geurts, J. W. Verhoeven, *Chem. Phys. Lett.*, **1997**, *276*, 196–201.
- [17] N. Sabbatini, M. Guardigli, I. Manet, R. Ungaro, A. Casnati, R. Ziessel, G. Ulrich, Z. Asfari, J.-M. Lehn, *Pure Appl. Chem.* **1995**, *67*, 135–140.
- [18] D. Parker, J. A. G. Williams, *J. Chem. Soc., Dalton Trans.* **1996**, 3613–628, and references cited therein.
- [19] D. M. Rudkevich, W. Verboom, E. B. van der Tol, C. van Staveren, F. Kaspersen, J. W. Verhoeven, D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2* **1995**, 131–134.
- [20] Satisfactory elemental analyses could not be obtained for the complexes, probably due to the incomplete combustion of lanthanide carbides and/or carbonates that may form during the combustion (see also ref. [12]).
- [21] A. Bax, R. Freeman, *J. Magn. Reson.* **1981**, *44*, 542–561.
- [22] A. Bax, D. G. Davis, *J. Magn. Reson.* **1985**, *65*, 355–360.
- [23] W. D. Kim, G. E. Kiefer, J. Huskens, A. D. Sherry, *Inorg. Chem.* **1997**, *36*, 4128–4134.
- [24] [24a] S. Sato, M. Wada, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1955–1962. – [24b] M. Kleinerman, *J. Chem. Phys.* **1969**, *51*, 2370–2381. – [24c] D. L. Dexter, *J. Chem. Phys.* **1953**, *21*, 836–850.
- [25] Since the complexed Gd³⁺ ion has no energy levels below 32,000 cm⁻¹, it cannot depopulate the *m*-terphenyl triplet state via energy transfer.
- [26] The energy transfer rate can be estimated from this oxygen-dependence by using the Stern–Volmer Equation for the diffusion-controlled oxygen quenching of the terphenyl triplet state: $I_0/I = 1 + k_{\text{diff}}\tau_T[\text{O}_2]$, where I_0 and I are the luminescence intensities in the absence and presence of oxygen, respectively, k_{diff} is taken as 10^{10} M⁻¹s⁻¹, τ_T is the lifetime of the terphenyl triplet state, and $[\text{O}_2]$ is 2.1 mM, S. L. Murov, I. Carmichael, G. L. Hug, *Handbook of photochemistry, 2nd Ed.*, Marcel Dekker, New York, **1993**.
- [27] N. Martin, J.-C. G. Bünzli, V. McKee, C. Piguet, G. Hopfgartner, *Inorg. Chem.* **1998**, *37*, 577–589.
- [28] [28a] A. F. Kirby, D. Foster, F. S. Richardson, *Chem. Phys. Lett.* **1983**, *95*, 507–512. – [28b] A. F. Kirby, F. S. Richardson, *J. Phys. Chem.* **1983**, *87*, 2544–2556.
- [29] F. S. Richardson, *Chem. Rev.* **1982**, *82*, 541–552.
- [30] J. L. Kropp, M. W. Windsor, *J. Chem. Phys.* **1965**, *42*, 1599–1608.
- [31] [31a] W. DeW. Horrocks, Jr., D. R. Sudnick, *Acc. Chem. Res.* **1981**, *14*, 384–392. – [31b] R. C. Holz, C. A. Chang, W. DeW. Horrocks, Jr., *Inorg. Chem.* **1991**, *30*, 3270–3275.
- [32] A. Beeby, J. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams, M. Woods, *J. Chem. Soc., Perkin Trans. 2* **1999**, 493–503.
- [33] S. T. Frey, W. DeW. Horrocks, Jr., *Inorg. Chim. Acta* **1995**, *229*, 383–390, and references cited therein.
- [34] H. Takalo, I. K. Hemmilä, T. Sutela, M. Latva, *Helv. Chim. Acta* **1996**, *79*, 789–802.
- [35] A. Beeby, S. Faulkner, *Chem. Phys. Lett.* **1997**, *266*, 116–122.
- [36] [36a] Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J.-H. Kim, N. Nakashima, T. Yamanaka, S. Yanagida, *J. Phys. Chem.* **1996**, *100*, 10201–10205. – [36b] Y. Hasegawa, K. Murakoshi, Y. Wada, S. Yanagida, J.-H. Kim, N. Nakashima, T. Yamanaka, *Chem. Phys. Lett.* **1996**, *248*, 8–12.
- [37] G. Stein, E. Würzberg, *J. Chem. Phys.* **1975**, *62*, 208–210.
- [38] M. J. Weber, *Physical Rev.* **1968**, *171*, 283–291.
- [39] [39a] R. S. Dickins, D. Parker, A. S. de Sousa, J. A. G. Williams, *Chem. Commun.* **1996**, 697–698. – [39b] I. K. Hemmilä, V.-M. Mikkala, H. Takalo, *J. Fluorescence* **1995**, *5*, 159–163.

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