

New Sensitizer-Modified Calix[4]arenes Enabling Near-UV Excitation of Complexed Luminescent Lanthanide Ions

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Received April 10, 1995[⊗]

Abstract: The synthesis is described of a series of calix[4]arenes with three different sensitizer chromophores ("antenna") attached to the lower rim via a short spacer. In the Eu^{3+} and Tb^{3+} complexes of these calixarenes, photoexcitation of the antenna can induce lanthanide emission via intramolecular energy transfer. Although the higher energy of the Tb^{3+} luminescent state makes it more difficult to sensitize than in the case of Eu^{3+} , especially a triphenylene antenna is found to have strong sensitizing ability toward not only Eu^{3+} but also Tb^{3+} , allowing excitation of the lanthanide with wavelengths extending to 350 nm.

Introduction

Time-resolved immunoassay systems based on delayed luminescence become valuable analytical tools for in vitro diagnostics, replacing the use of radioisotope-labeled species.¹ Complexation of Eu^{3+} and Tb^{3+} ions in suitable ligands yields highly luminescent species which can be used as probes for a variety of such applications.² Cryptand-type ligands containing 2,2'-bipyridine (bpy) and/or 3,3'-biisoquinoline-2,2'-dioxide (biqO₂) combine the shielding effect (complexation effect) and the sensitizer ("antenna") moiety of the pendant groups.^{3,4}

In addition to many other applications calixarenes are suitable building blocks for ionophores for trivalent cations.^{5–9} Although Eu^{3+} ions are commonly used as probes in time-resolved luminescence systems, Tb^{3+} ions appear more attractive because of a higher intrinsic quantum yield. Sabbatini et al.¹⁰ have shown that the Tb^{3+} complex of a *p*-tert-butylcalix[4]arene tetraacetamide shows a high luminescence quantum yield (0.2) and a long luminescence lifetime (1.5 ms). The luminescence quantum yield could even be improved when one of the amide groups was replaced by a sensitizer group (phenacyl or diphenylacetylcarbonyl)¹¹ or when the calixarene skeleton was

functionalized at the upper rim with phenyl groups, the resulting biphenyls serving as sensitizers.¹² However, such Tb^{3+} complexes are not attractive for immunoassay systems because of their overall charge.¹³ Besides the small effect on the quantum yield by introducing one or more sensitizers in the ligand, the excitation wavelength is normally around 270–300 nm. For the application in time-resolved immunoassay systems, the most preferable excitation wavelength is however >330 nm, which allows the use of standard optics.

Recently we reported the synthesis of calixarene derivatives, containing three carboxylic acid groups, which form overall neutral complexes with lanthanide cations.¹⁴ We demonstrated that the lanthanide ion was effectively shielded from the solvent and that functionalization of the carboxamido side chain did not disturb the shielding efficiency. We found that excitation of a pyridine chromophore, attached to this side chain, gives rise to energy transfer to the complexed lanthanide ion but that the excitation wavelength ($\lambda = 280$ nm) and efficiency of energy transfer are rather low.

In the present paper, we report the synthesis and luminescence characteristics of both charged and neutral Eu^{3+} and Tb^{3+} complexes of calixarene derivatives substituted with three carboxylic ester (**9d,e**) and acid groups (**10a–d**), respectively, and one aromatic sensitizer group: naphthalene, phenanthrene, or triphenylene. Especially with triphenylene, long-wavelength (up to 350 nm) excitation of both Eu^{3+} and Tb^{3+} can be achieved.

Results and Discussion

Synthesis. The key step in the synthesis of the ionophores **10a–d** (see Chart 2) comprises reaction of calix[4]arene triester monoacid chloride **8**¹⁵ with the amino-substituted sensitizers *viz.* 1-(aminomethyl)naphthalene (**11**), 9-(aminomethyl)phenanthrene (**12**), *N*-(2-methyltriphenylene)propylamine (**7**), and 2-(aminomethyl)triphenylene (**6**) (Chart 1). 9-(Aminomethyl)phenanthrene (**12**) was prepared in a yield of 73% by reduction of

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[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1995.

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Chart 1

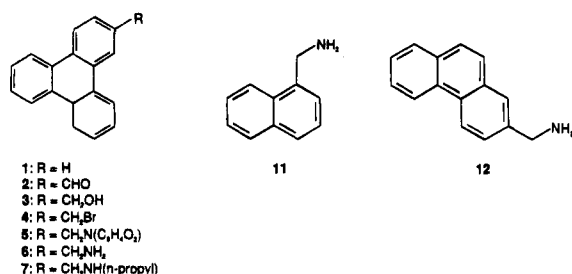
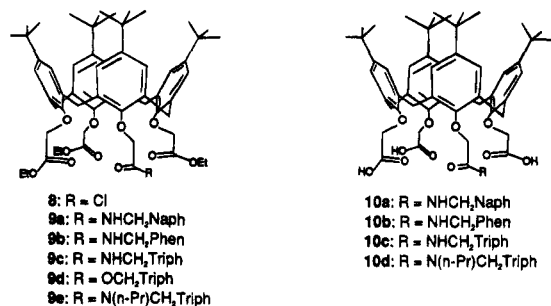


Chart 2



9-cyanophenanthrene with B₂H₆ in THF. Despite the low selectivity between the 1- and 2-positions in aromatic substitution reactions of triphenylene,¹⁶ triphenylene-2-carboxaldehyde (2) can be prepared from triphenylene (1) and bis(chloromethyl) ether/TiCl₄ in 78% yield. The ¹H NMR spectrum shows a singlet at 9.10 ppm for the H-1 hydrogen atom which proves the functionalization of the 2-position. Reductive amination of 2 with *n*-propylamine/NaCNBH₃ in THF afforded *N*-(2-methyltriphenylene)propylamine (7) in 96% yield. Reduction of triphenylene-2-carboxaldehyde (2) with B₂H₆ in THF afforded 2-(hydroxymethyl)triphenylene (3) in 91% yield. Reaction of 3 with PBr₃ gave 2-(bromomethyl)triphenylene (4) in 94% yield. A subsequent Gabriel reaction of 4 afforded phthalimide 5, which after deprotection with hydrazine monohydrate, yielded in 94% the desired 2-(aminomethyl)triphenylene (6). Reaction of monoacid chloride 8 with the aminomethyl-substituted compounds 6, 7, 11, 12 and the hydroxymethyl-substituted compound 3 afforded the triester monoamide calix[4]arenes 9a–c,e and the tetraester 9d, respectively, in 78–83% yield upon recrystallization of the crude reaction mixture. Mild hydrolysis of the ester bonds in preference to the amide bond in compounds 9a–c,e using K₂CO₃ in refluxing MeOH–H₂O (5:1) gave the triacid monoamide derivatives 10a–d in 76–81% yield. The ¹H NMR spectra of these derivatives show two characteristic AB systems for the methylene hydrogens, indicating the cone conformation and a 2:1:1 ratio of the *tert*-butyl groups of the calix[4]arene. The corresponding Eu(III) and Tb(III) complexes Eu(10a–d) and Tb(10a–d) were prepared by refluxing a solution of the calix[4]arene triacid monoamides 10a–d in acetonitrile in the presence of EuCl₃ or TbCl₃, triethyl ortho-

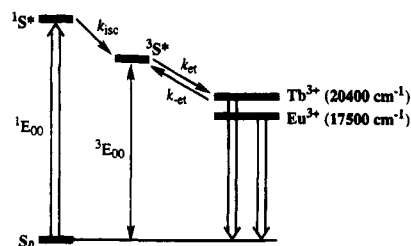


Figure 1. Energy scheme for the absorption–energy transfer–luminescence process. Depicted are the main luminescent energy levels (⁵D₀ for Eu³⁺ and ⁵D₄ for Tb³⁺).

Table 1. FAB Mass Spectral Data of Complexes Eu(10a–d) and Tb(10a–d)

compd	measd	calcd
Eu(10a)	1168.3	1168.2
Tb(10a)	1176.5	1176.2
Eu(10b)	1219.2	1219.3
Tb(10b)	1226.5	1226.2
Eu(10c)	1184.2 ^a	1184.3
Tb(10c)	1274.9	1274.3
Eu(10d)	1311.5	1311.4
Tb(10d)	1318.1	1318.4

^a M⁺ – 2CO₂.

formate, and triethylamine as a base. FAB-MS spectra of the complexes show an intense signal corresponding to [ligand + lanthanide cation] (Table 1).

Luminescent Properties. Recently we reported¹⁴ the effective solvent shielding of lanthanide ions in overall neutral complexes with calix[4]arene triacids. Excitation of a pyridine side chain chromophore gives energy transfer to complexed lanthanide ions, a phenomenon also observed by others^{10,12} for other types of aromatic chromophores attached to calixarenes. Such an attached chromophore can in principle function as an “antenna” that allows the excitation of the lanthanide luminescence at wavelengths where neither the lanthanide ion nor the complexing calixarene display significant absorption. This is of particular importance if such complexes are employed as luminescent markers. Applications require excitation at relatively long wavelengths as transmitted by regular optics and produced by standard (UV) light sources. These requirements set a lower limit of ~330 nm to the wavelength of the excitation light, which is close to, for example, one of the Hg or N₂ emission lines (335 and 337 nm, respectively), but longer wavelengths (e.g. 365 nm (Hg) or 354 nm (Nd/YAG third harmonic)) would be preferred. The antenna chromophores currently available for calixarene–lanthanide complexes absorb very weakly or not at all above ca. 320 nm (i.e. <31 250 cm^{–1}). From Figure 1 the limitations inherent in designing efficient antenna systems absorbing at longer wavelength can be derived. If we assume that the antenna sensitizer displays a singlet–triplet energy gap (¹E₀₀–³E₀₀) of at least 5000 cm^{–1}, which appears a lower limit for π -systems,¹⁷ and that its triplet energy must be at least 3500 cm^{–1} above the main luminescent state of the lanthanide ion to make energy transfer fast and irreversible, the long wavelength absorption edge (¹E₀₀) of the antenna cannot be much above 346 nm for Tb³⁺ or above 385 nm for Eu³⁺ complexes. It thus appears that, although especially for Tb³⁺ the margins are narrow, there is room for extending the absorption of antenna chromophores that operate along the triplet mechanism depicted in Figure 1 into a more useful region than presently available.

In order to test this hypothesis we have compared the luminescent properties of the complexes of which the synthesis

(15) We prepared the starting triester monoacid calix[4]arene via a slight modification to what has been reported earlier: Acetic acid (4.0 mL, 100%) and nitric acid (6.7 mL, 65%) were added to a vigorously stirred solution of *p*-*tert*-butylcalix[4]arene tetraethyl ester²³ (2.0 g) in CH₂Cl₂ (100 mL). The solution was stirred for 45 min followed by standard workup. After recrystallization from methanol, triester monoacid calix[4]arene was obtained in a yield of 91%, mp 166–167 °C (lit.^{15a} 88%, mp 166–169 °C). (a) Böhmer, V.; Vogt, W.; Harris, S. J.; Raymond, G. L.; Collins, E. M.; Deasy, M.; McKervey, M. A.; Owens, M. J. *Chem. Soc., Perkin Trans. 1* 1990, 431. (b) Barrett, G.; Böhmer, V.; Ferguson, G.; Gallagher, J. F.; Harris, S. J.; Leonard, R. G.; McKervey, M. A.; Owens, M.; Tabatabai, M.; Vierengel, A.; Vogt, W. J. *Chem. Soc., Perkin Trans. 2* 1992, 1595.

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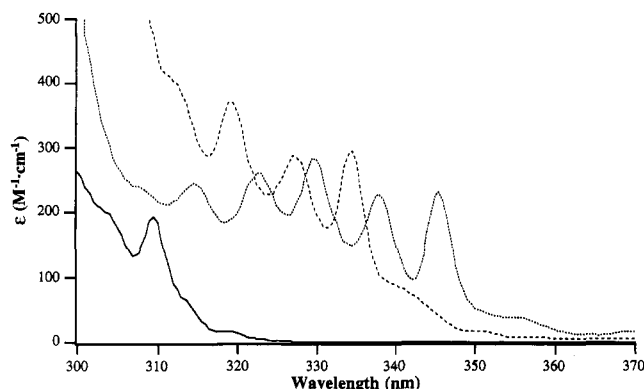


Figure 2. Absorption spectra of naphthalene (—), phenanthrene (···), and triphenylene (---) in CH_3OH .

Table 2. Singlet and Triplet Energies and the Triplet Quantum Yield in Polar Solvents of the Antenna Chromophores Investigated¹⁷

compd	$^1E_{00}$ (cm^{-1})	$^3E_{00}$ (cm^{-1})	$^1E_{00}-^3E_{00}$ (cm^{-1})	ϕ_{isc}
naphthalene	32 099 (312 nm)	21 316	10 783	0.80
phenanthrene	28 839 (347 nm)	21 483	7 356	0.85
triphenylene	29 424 (340 nm)	23 406	6 018	0.89

is described above and that contain three different antenna systems, i.e. naphthalene, phenanthrene, and triphenylene. Table 2 compiles the singlet and triplet energies of these chromophores, while in Figure 2 their absorption spectra are shown (above 300 nm). From the data in Table 2 and the mechanism discussed above (cf. Figure 1), it may be expected that all three antenna chromophores should be capable of sensitizing the luminescence of both Eu^{3+} and Tb^{3+} , although for Tb^{3+} the driving force for energy transfer from $^3\text{S}^*$ to the lanthanide is rather small for naphthalene and phenanthrene.

In order to probe whether sensitization actually occurs, the emission intensities of the various calixarene-antenna/ $\text{Ln}(\text{III})$ complexes were compared for excitation wavelengths in the 300–400-nm region. In these experiments, dilute 10^{-4} M aerated methanol solutions were used and corrections were made for the differences in excitation intensity as a function of the wavelength employing Rhodamine-B as a quantum counter. Under these conditions the emission intensities are proportional to the product of the molar extinction and the luminescence quantum yield. This gives a fair measure for the relative efficiencies of the systems as luminescent probes at each of the excitation wavelengths investigated.

In Figure 3 the results for the various Eu^{3+} complexes (monitored at 616 nm) are compared. Somewhat unexpectedly the naphthalene antenna turned out to be rather unsuccessful even in the region between 300 and 320 nm, where it shows significant absorption (see Figure 2). Thus even at $\lambda_{\text{exc}} = 300$ nm the luminescence of $\text{Eu}(\mathbf{10a})$ is enhanced by no more than 2.5 times relative to $\lambda_{\text{exc}} = 390$ nm, the latter corresponding to direct excitation in a weak ($\epsilon = 3 \text{ M}^{-1}\text{cm}^{-1}$ in water) lanthanide transition.¹⁸ By contrast, a phenanthrene antenna as in $\text{Eu}(\mathbf{10b})$ leads to an amplification of 32.9 times for $\lambda_{\text{exc}} = 300$ nm as compared to $\lambda_{\text{exc}} = 390$ nm. Furthermore, this antenna also allows significant amplification upon excitation in its weaker long-wavelength absorption band that extends (cf. Figures 2 and 3) to ~ 355 nm. Even more efficient amplification (up to 105 times at 300 nm and up to 13.3 times at 350 nm relative to direct 390-nm excitation for $[\text{Eu}(\mathbf{9d})]^{3+}$) could be realized using triphenylene as an antenna. For this antenna we have also

studied the effect of variation in the bridging group between antenna and calixarene as well as of other calixarene side chains. Interestingly very strong effects of such structural changes were observed. Calixarene $\text{Eu}(\mathbf{10c})$ is a homologue of the naphthalene and phenanthrene systems discussed above, and its behavior may be taken as evidence for the high efficiency of triphenylene as an antenna chromophore as compared to other aromatic species. However, small structural variations have a dramatic effect on the efficiency. In $[\text{Eu}(\mathbf{9e})]^{3+}$, with an *n*-propyl group at the bridging amide-nitrogen and with three ethyl ester groups instead of the three carboxylates, the sensitizing action of the antenna group is lost virtually completely. Saponification of the ester groups ($\text{Eu}(\mathbf{10d})$) partly restores the antenna effect as does “substitution” of the *n*-propylcarboxamide by an ester moiety ($[\text{Eu}(\mathbf{9d})]^{3+}$), the latter modification being more productive than the former and in fact producing the most effective system in the series.

The results obtained for various Tb^{3+} complexes (monitored at the appropriate wavelength (545 nm)) are compiled in Figure 4. In this case not only naphthalene but also phenanthrene turns out to be quite inefficient in sensitizing the Tb^{3+} luminescence as compared to triphenylene.

It appears likely that this is mainly due (see Table 2) to the relatively low triplet energy of the former two chromophores as compared to that of the luminescent state of Tb^{3+} (see Figure 1) which makes energy transfer slower and/or reversible.

With triphenylene as an antenna significant Tb^{3+} luminescence can be induced up to $\lambda_{\text{exc}} = 350$ nm, i.e. at wavelengths extending to the absorption edge of the antenna (see Figure 2). As with Eu^{3+} , strong structural influences on the efficiency of the antenna effect are observed. Again, the ligand with an *n*-propyl group at the amide-nitrogen atom ($\text{Tb}(\mathbf{10d})$) performs rather poorly, while both $[\text{Tb}(\mathbf{9d})]^{3+}$ and $\text{Tb}(\mathbf{10c})$ display high activity, with again $[\text{Tb}(\mathbf{9d})]^{3+}$ being the most effective.

The data presented above appear to validate the mechanism depicted in Figure 1, from which it was predicted that triphenylene should be able to sensitize the luminescence of both Eu^{3+} and Tb^{3+} , while with phenanthrene, the latter should be marginal in view of energetic considerations. This means that especially triphenylene must be considered as a highly efficient antenna chromophore that allows population via near-UV excitation of the luminescent state of not only Eu^{3+} but also Tb^{3+} . This is of considerable interest because the inherent luminescence quantum yield of complexed Tb^{3+} ions is in general much higher (~ 0.03 – 0.4) than that of Eu^{3+} ions (~ 0.001 – 0.3).¹⁹

On the other hand, the data presented above clearly show that optimization of the antenna function in calixarene-antenna/ $\text{Ln}(\text{III})$ systems requires rather strict structural control. The quantum yield of lanthanide luminescence resulting from antenna excitation can be expressed by eq 1:

$$\phi_{\text{lum}} = \phi_{\text{isc}} \phi_{\text{et}} k_r \tau \quad (1)$$

ϕ_{isc} stands for the intersystem-crossing efficiency of the antenna, ϕ_{et} stands for that of the energy transfer step (including the possible effects of reversibility), while k_r and τ are the radiative rate constant and the luminescence lifetime of the lanthanide ion.

In Table 3 luminescence lifetimes of the present lanthanide complexes with a triphenylene antenna chromophore are compiled as measured in methanolic solution. While especially for the Eu^{3+} complexes a significant structure dependence of τ is observed, the differences are much smaller than and

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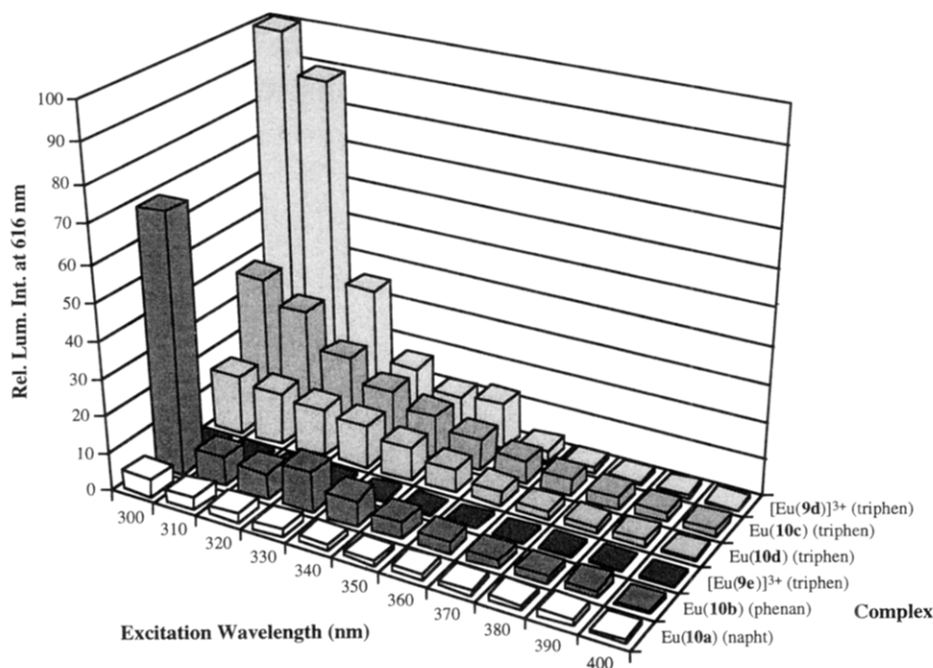


Figure 3. Relative luminescence intensity of the Eu^{3+} complexes ($\lambda_{\text{em}} = 616 \text{ nm}$) as a function of the excitation wavelength at equal excitation intensity and complex concentration ($1 \times 10^{-4} \text{ M}$, solvent CH_3OH).

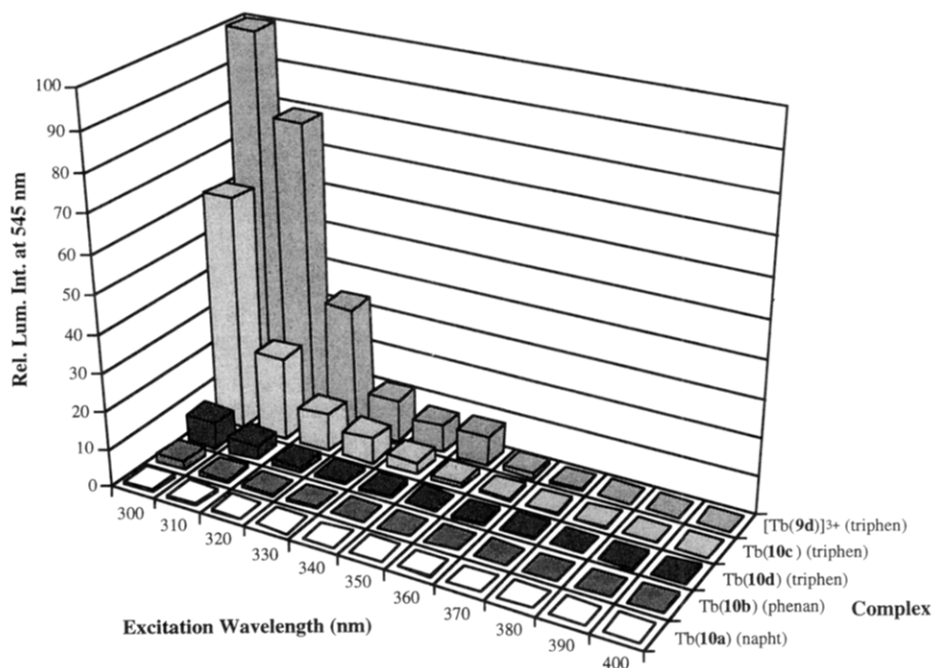


Figure 4. Relative luminescence intensity of the Tb^{3+} complexes ($\lambda_{\text{em}} = 545 \text{ nm}$) as a function of the excitation wavelength at equal excitation intensity and complex concentration ($1 \times 10^{-4} \text{ M}$, solvent CH_3OH).

Table 3. Luminescence Lifetime^a of Various Eu^{3+} and Tb^{3+} Complexes with a Triphenylene Antenna Chromophore Measured in CH_3OH at Room Temperature

complex	τ (ms)	complex	τ (ms)
$[\text{Eu}(\mathbf{9d})]^{3+}$	0.29	$[\text{Tb}(\mathbf{9d})]^{3+}$	0.65
$[\text{Eu}(\mathbf{9e})]^{3+}$	0.50	$[\text{Tb}(\mathbf{9e})]^{3+}$	0.81
$\text{Eu}(\mathbf{10c})$	0.23	$\text{Tb}(\mathbf{10c})$	0.54
$\text{Eu}(\mathbf{10d})$	0.73	$\text{Tb}(\mathbf{10d})$	0.54

^a Lifetime did not change upon deoxygenation.

sometimes even opposite to those observed (see Figures 3 and 4) between the luminescence efficiencies resulting from antenna excitations. In view of these findings we assume that structural effects on ϕ_{et} must be a dominant factor in determining the observed difference in ϕ_{lum} .

A strong indication for the correctness of this assumption was obtained by studying the effect of oxygen on the antenna-sensitized luminescence. While the luminescence decay time of the lanthanide is essentially oxygen insensitive (see Table 3), the intensity of this luminescence as elicited by 300-nm excitation of the antenna chromophore is dramatically enhanced by deoxygenation for many of the complexes studied (see Table 4 and Figure 5). This clearly indicates that in those cases energy transfer is slow and/or reversible²⁰ so that a significant fraction of the $^3\text{S}^*$ species are trapped by oxygen quenching instead of contributing to the population of the luminescent state of the lanthanide.

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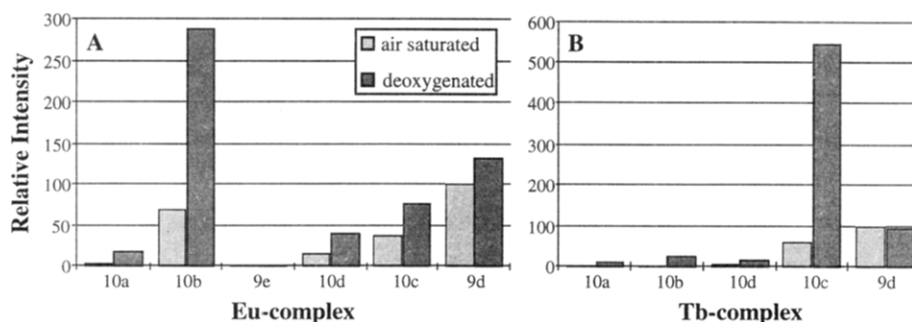


Figure 5. Relative luminescence intensities of Eu^{3+} (A) and Tb^{3+} complexes (B) ($\lambda_{\text{em}} = 616$ and 545 nm, respectively) before and after deoxygenation ($\lambda_{\text{ex}} = 300$ nm). The emission intensities of $[\text{Eu}(\mathbf{9d})]^{3+}$ and $[\text{Tb}(\mathbf{9d})]^{3+}$ in air-saturated solution were arbitrarily set to 100.

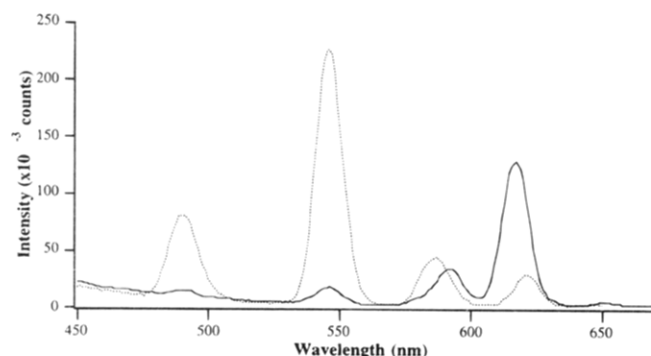


Figure 6. Corrected emission spectra of $[\text{Eu}(\mathbf{9d})]^{3+}$ (—) and $[\text{Tb}(\mathbf{9d})]^{3+}$ (···) in CH_3OH at room temperature, $\lambda_{\text{ex}} = 300$ nm.

Table 4. Ratios of Lanthanide Luminescence Intensity in CH_3OH after (I_{deox}) and before (I_{ox}) Deoxygenation ($\lambda_{\text{ex}} = 300$ nm)

complex	$I_{\text{deox}}/I_{\text{ox}}$	complex	$I_{\text{deox}}/I_{\text{ox}}$
$[\text{Eu}(\mathbf{9d})]^{3+}$	1.33	$[\text{Tb}(\mathbf{9d})]^{3+}$	0.96
$[\text{Eu}(\mathbf{9e})]^{3+}$	2.43	$[\text{Tb}(\mathbf{9e})]^{3+}$	
$\text{Eu}(\mathbf{10a})$	3.97	$\text{Tb}(\mathbf{10a})$	12.3
$\text{Eu}(\mathbf{10b})$	4.14	$\text{Tb}(\mathbf{10b})$	13.4
$\text{Eu}(\mathbf{10c})$	2.03	$\text{Tb}(\mathbf{10c})$	8.82
$\text{Eu}(\mathbf{10d})$	2.49	$\text{Tb}(\mathbf{10d})$	2.30

Concluding Remarks

The data presented above demonstrate that calix[4]arene/Ln-(III) complexes can be extended with antenna chromophores, enabling excitation of both Eu^{3+} and Tb^{3+} luminescence at wavelengths extending to at least 350 nm. Especially a triphenylene antenna chromophore was found to display very effective sensitizing properties.²¹

Clearly more work is required to optimize the properties (e.g. water solubility) of the present complexes, as well as to enhance the long-wavelength absorptivity of the triphenylene chromophore in order to produce calix[4]arene/Ln(III) complexes with properties suitable for practical applications in bioassays.

Experimental Section

Synthesis. General Procedure. Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AC 250 spectrometer in CDCl_3 with Me_4Si as the internal standard unless stated otherwise. FAB-MS (fast atom bombardment mass spectrometry) and electron impact (EI) spectra were obtained using a Finnigan Mat 90 spectrometer. In the first case *m*-nitrobenzyl alcohol was used as a matrix. CH_2Cl_2 was distilled from CaCl_2 and stored over molecular sieves. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone

ketyl, whereas *N,N*-dimethylformamide (DMF), toluene, and hexanes (mixed isomers) were dried on 4-Å molecular sieves. All reactions were carried out under an argon atmosphere. Chromatographic separations mentioned were performed on silica gel 60 (SiO_2) (E. Merck, particle size 0.040–0.063 mm, 230–400 mesh). Triphenylene (**1**), 1-(aminomethyl)naphthalene (**11**), and 9-cyanophenanthrene (**13**) were purchased from Aldrich. The presence of solvent in the analytical samples was confirmed by ^1H NMR spectroscopy. All reactions were carried out in an argon atmosphere. Standard workup means that the organic layers were finally washed with water, dried over magnesium sulphate (MgSO_4), filtered, and concentrated *in vacuo*.

Triphenylene-2-carboxaldehyde (2). To a solution of triphenylene (**1**) (1.0 g, 4.38 mmol) and freshly distilled TiCl_4 (1.65 g, 8.70 mmol) in dry CH_2Cl_2 (75 mL) was added dropwise bis(chloromethyl) ether (2.5 g, 21.7 mmol) at 0 °C. The reaction was stirred at room temperature for 3 h, whereupon again TiCl_4 (1.65 g, 8.70 mmol) and bis(chloromethyl) ether (2.5 g, 21.7 mmol) were added. After the mixture was stirred for another 3 h, the reaction was quenched by the addition of 2 M HCl (100 mL). The organic layer was washed with 2 M HCl (2 × 100 mL), followed by standard workup. The crude reaction product was crystallized from CH_2Cl_2 /hexanes to obtain an orange/brown colored solid: yield 78%; mp 147–148 °C; ^1H NMR δ 12.63 (s, 1 H), 9.10 (s, 1 H), 8.9–8.5 (m, 5 H), 8.11 (d, 1 H, $J = 8.4$ Hz), 7.9–7.5 (m, 4 H); ^{13}C NMR δ 192.2 (d); mass spectrum (EI) m/e 156.1 (M^+ , calcd 156.3). Anal. Calcd for $\text{C}_{19}\text{H}_{12}\text{O} \cdot 0.1\text{H}_2\text{O}$: C, 88.42; H, 4.69. Found: C, 88.14; H, 4.69.

2-(Hydroxymethyl)triphenylene (3). To a solution of **2** (0.50 g, 1.95 mmol) in dry THF (75 mL) was added $\text{BH}_3 \cdot \text{THF}$ (3 mL, 1.0 M solution) at 0 °C. The cooling bath was removed, and the solution was stirred for 2 h at room temperature. 1.0 M NaOH (75 mL) was added, followed by standard workup. The product was triturated with CH_2Cl_2 to give pure **3**: yield 93%; mp 151–152 °C; ^1H NMR δ 8.9–8.5 (m, 7 H), 7.9–7.5 (m, 6 H), 4.95 (s, 2 H), 1.90 (br s, 1 H); ^{13}C NMR δ 61.0 (t); mass spectrum (EI) m/e 258.0 (M^+ , calcd 258.3), 229.0 ($\text{M}^+ - \text{CH}_2\text{OH}$). Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{O} \cdot 0.3\text{H}_2\text{O}$: C, 86.59; H, 5.58. Found: C, 86.21; H, 5.15.

2-(Bromomethyl)triphenylene (4). To a solution of **3** (0.50 g, 1.94 mmol) in toluene (75 mL) was added PBr_3 (0.79 g, 2.90 mmol) at room temperature. The solution was stirred for 2 h at 50 °C. NaOH (0.1 M, 75 mL) was added, and the organic layer was washed with saturated NaHCO_3 (2 × 50 mL), followed by standard workup. The product was obtained as a white solid: yield 94%; mp 137 °C; ^1H NMR δ 8.8–8.5 (m, 6 H), 7.8–7.6 (m, 5 H), 4.76 (s, 2 H); ^{13}C NMR δ 33.9 (t); mass spectrum (EI) m/e 320.0 (M^+ , calcd 320.0), 241.0 ($\text{M}^+ - \text{Br} + \text{H}$). Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{Br}$: C, 71.05; H, 4.08. Found: C, 71.02; H, 3.93.

2-(Phthalimidomethyl)triphenylene (5). To a solution of **4** (0.50 g, 1.56 mmol) in DMF (25 mL) was added potassium phthalimide (0.32 g, 1.72 mmol). The solution was stirred overnight at 40 °C. The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (50 mL) and washed with 0.1 M NaOH (3 × 50 mL). The product was obtained as a white solid in a quantitative yield: mp 212–213 °C; ^1H NMR δ 8.8–8.5 (m, 6 H), 7.9–7.5 (m, 9 H), 5.09 (s, 2 H); ^{13}C NMR δ 168.1 (s), 41.9 (t); mass spectrum (EI) m/e 387.1 (M^+ , calcd 387.1). Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{NO}_2 \cdot 0.2\text{H}_2\text{O}$: C, 82.93; H, 4.45; N, 3.58. Found: C, 82.86; H, 4.28; N, 3.57.

(21) In fact we have noted that sensitized lanthanide luminescence by intermolecular energy transfer between triphenylene and Eu^{3+} (not Tb^{3+}) ions occurs in deoxygenated acetonitrile solution. Such intermolecular sensitization of lanthanide luminescence appears to be unprecedented.²⁴

2-(Aminomethyl)triphenylene (6). A solution of **5** (0.50 g, 1.29 mmol) and hydrazine monohydrate (0.32 g, 6.46 mmol) in EtOH (50 mL) was refluxed for 2 h. Concentrated HCl (0.5 mL) was added, and the mixture was refluxed for an additional 2 h. The solvent was removed *in vacuo*, and H₂O (50 mL) and CH₂Cl₂ (50 mL) were added to the residue. The organic layer was washed with H₂O (2 × 50 mL) and subsequent acidification of the organic layer with concentrated HCl (1 mL) gave a yellow precipitate. The precipitate was washed with 1 M NaOH (3 × 50 mL) and extracted with CH₂Cl₂ (3 × 50 mL). Evaporation of the organic solvent afforded a yellow oil: yield 94%; ¹H NMR δ 8.8–8.5 (m, 6 H), 7.8–7.5 (m, 5 H), 4.01 (s, 2 H), 1.67 (br s, 2 H); ¹³C NMR δ 46.7 (t); mass spectrum (EI) *m/e* 257.119 (M⁺, calcd for C₁₉H₁₅N 257.120).

N-(Triphenylenemethyl)propylamine (7). A solution of **2** (1.66 g, 6.48 mmol), *n*-propylamine (3.8 g, 64.8 mmol), and 2 drops of acetic acid (100%) in THF (50 mL) was refluxed for 1 h. After the reaction mixture was allowed to cool to room temperature, NaCNBH₃ (0.8 g, 12.7 mmol) was added. The mixture was stirred overnight. The reaction was quenched by the addition of water (30 mL) and acidified with concentrated HCl (2 mL). The product was filtered off and washed with CH₂Cl₂ (50 mL), water (50 mL), and diethyl ether (50 mL). The solid was dissolved in a mixture of 1 M NaOH (50 mL)/CH₂Cl₂ (50 mL) whereupon the water layer was extracted with CH₂Cl₂ (50 mL). The combined organic layers were washed with water (50 mL), followed by standard workup. Compound **7** was obtained as a white solid: yield 86%, mp 166–167 °C; ¹H NMR δ 8.7–8.3 (m, 6 H), 7.7–7.3 (m, 5 H), 3.92 (s, 2 H), 2.60 (t, 2 H, *J* = 8.4 Hz), 1.6–1.4 (m, 2 H), 1.40 (s, 1 H), 0.86 (t, 3 H, *J* = 8.4 Hz); ¹³C NMR δ 54.3 (t), 51.5 (t), 23.3 (t), 11.9 (q); mass spectrum (EI) *m/e* 299.2 (M⁺, calcd for C₂₂H₂₁N 299.4).

9-(Aminomethyl)phenanthrene (12). To a solution of 9-cyanophenanthrene (**13**) (0.5 g, 2.5 mmol) in THF (75 mL) was added B₂H₆ (16 mL, 16.0 mmol) at –78 °C. The temperature was allowed to rise to room temperature within 2 h. The reaction mixture was stirred overnight. Subsequently 2 M HCl (50 mL) was added and the THF removed *in vacuo*. The residue was redissolved in CH₂Cl₂ (50 mL) and acidified with concentrated HCl (2 mL). The precipitate was filtered off and redissolved in CH₂Cl₂ (50 mL) and 2 M NaOH (50 mL), followed by standard workup: yield 73%, mp 108–110 °C (lit.²² mp 108–109 °C).

General Procedure for the Preparation of Compounds 9a–e. To a solution of triester monoacid chloride **8**¹⁵ (2.2 g, 2.1 mmol) in CH₂Cl₂ (50 mL) were added an appropriate amine or alcohol (2.2 mmol) and triethylamine (0.84 g, 8.2 mmol). The mixture was stirred overnight at room temperature. Water (50 mL) was added, followed by standard workup. Recrystallization from acetonitrile (**9a–c,e**) or CH₂Cl₂/MeOH (**9d**) gave compounds **9a–e** as white solids.

Triethyl [[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[[(1-naphthalene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetate (9a): yield 76%, mp 105–107 °C; ¹H NMR δ 8.85 (t, 1 H, *J* = 6.0 Hz), 8.06 (d, 1 H, *J* = 7.8 Hz), 7.86 (d, 2 H, *J* = 7.8 Hz), 7.74 (d, 1 H, *J* = 7.8 Hz), 7.6–7.4 (m, 3 H), 6.85 (d, 4 H, *J* = 7.1 Hz), 6.73 (s, 1 H), 6.71 (dd, 3 H, *J* = 2.5 and 7.1 Hz), 5.18 (d, 2 H, *J* = 6.0 Hz), 4.94 (d, 1 H, *J* = 6.0 Hz), 4.9–4.6 (m, 9 H), 4.49 (s, 1 H), 4.42 (s, 1 H), 4.3–4.0 (m, 2 H), 3.86 (q, 4 H, *J* = 7.2 Hz), 3.26, 3.21 (d, 4 H, *J* = 13.3 Hz), 1.4–1.2 (m, 9 H), 1.2–1.0 (m, 18 H), 0.99 (s, 18 H); mass spectrum (FAB) *m/e* 1104.3 (M⁺, calcd 1104.4). Anal. Calcd for C₆₉H₈₅NO₁₁·H₂O: C, 74.78; H, 7.65; N, 1.19. Found: C, 74.58; H, 7.57; N, 1.22.

Triethyl [[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[[(9-phenanthrene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetate (9b): yield 78%, mp 153–155 °C; ¹H NMR δ 8.97 (t, 1 H, *J* = 6.1 Hz), 8.76 (d, 1 H, *J* = 7.1 Hz), 8.67 (d, 1 H, *J* = 7.1 Hz), 8.13 (d, 1 H, *J* = 7.1 Hz), 7.90 (d, 1 H, 7.1 Hz), 7.8–7.5 (m, 4 H), 6.90 (d, 4 H, *J* = 2.5 Hz), 6.77 (s, 2 H), 6.72 (dd, 2 H, *J* = 2.5 Hz and 5.0 Hz), 5.21 (d, 2 H, *J* = 6.1 Hz), 4.9–4.4 (m, 12 H), 4.22, 4.11, 3.75 (q, 6 H, *J* = 7.5 Hz), 3.32, 3.18 (d, 4 H, *J* = 13.2 Hz), 1.30, 0.94 (t, 9 H, *J* = 7.5 Hz), 1.19 (s, 18 H), 1.09 (s, 9 H), 0.99 (s, 9 H); mass spectrum (FAB) *m/e* 1155.2 [(M + H)⁺, calcd 1155.5]. Anal. Calcd for C₇₃H₈₇NO₁₁·H₂O: C, 73.83; H, 7.81; N, 1.25. Found: C, 73.58; H, 7.61; N, 1.22.

Triethyl [[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[[(2-triphenylene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetate (9c): yield 79%, mp 103–105 °C; ¹H NMR δ 9.05 (t, 1 H, *J* = 6.1 Hz), 8.7–8.5 (m, 6 H), 6.5–6.7 (m, 5 H), 6.87 (s, 2 H), 6.79 (s, 2 H), 6.73 (d, 4 H, *J* = 2.5 Hz), 4.48 (d, 2 H, *J* = 6.1 Hz), 4.9–4.7 (m, 7 H), 4.46 (d, 2 H, *J* = 13.4 Hz), 4.3–4.0 (m, 4 H), 4.0–3.8 (m, 2 H), 3.78 (s, 1 H), 3.70 (s, 1 H), 3.30 (d, 2 H, *J* = 13.4 Hz), 3.21 (d, 2 H, *J* = 13.4), 1.3–1.2 (m, 9 H), 1.16 (s, 9 H), 1.09 (s, 9 H), 1.04 (s, 18 H); mass spectrum (FAB) *m/e* 1205.2 [(M + H)⁺, calcd 1204.6]. Anal. Calcd for C₇₇H₈₉NO₁₁·1.2H₂O: C, 75.43; H, 7.51; N, 1.14. Found: C, 75.12; H, 7.52; N, 1.26.

Triethyl [[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[[(2-triphenylene)methyl]carbonyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetate (9d): yield 81%, mp 87–89 °C; ¹H NMR δ 8.7–8.5 (m, 6 H), 7.7–7.5 (m, 5 H), 6.79 (s, 4 H), 6.70–6.6 (m, 4 H), 5.36 (s, 2 H), 4.97 (s, 2 H), 4.9–4.6 (m, 10 H), 4.08 (q, 6 H, *J* = 8.4 Hz), 3.12 (d, 2 H, *J* = 12.5 Hz), 3.01 (d, 2 H, *J* = 12.5 Hz), 1.2–1.0 (m, 9 H), 1.05 (s, 18 H), 0.95 (s, 18 H); mass spectrum (FAB) *m/e* 1205.2 [(M + H)⁺, calcd 1204.6], 1228.2 [(M + Na)⁺, calcd 1227.6]. Anal. Calcd for C₇₇H₈₉O₁₂·H₂O: C, 75.59; H, 7.41. Found: C, 75.59; H, 7.39.

Triethyl [[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[propyl[(2-triphenylene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetate (9e): yield 76%, mp 154–155 °C; ¹H NMR δ 8.7–8.6 (m, 6 H), 7.6–7.7 (m, 5 H), 6.89 (s, 8 H), 4.85 (d, 4 H, *J* = 13.4 Hz), 4.80 (s, 8 H), 4.21 (q, 6 H, *J* = 8.3 Hz), 4.06 (s, 2 H), 3.19 (d, 4 H, *J* = 13.4 Hz), 2.70 (t, 2 H), 1.62 (m, 2 H), 1.26 (t, 9 H, *J* = 8.3 Hz), 1.09 (s, 36 H), 0.96 (t, 3 H, *J* = 8.3 Hz); mass spectrum (FAB) *m/e* 1246.7 [(M + H)⁺, calcd 1246.6], 1268.7 [(M + Na)⁺, calcd 1268.6]. Anal. Calcd for C₈₀H₉₅NO₁₁·1.5H₂O: C, 75.44; H, 7.76; N, 1.10. Found: C, 75.54; H, 7.86; N, 1.05.

General Procedure for the Preparation of Compounds 10a–d.

A mixture of calixarenes **9a–c,e** (0.5 mmol) and potassium carbonate (0.69 g, 5 mmol) in a 5:1 MeOH–water solution (15 mL) and CH₂Cl₂ (1 mL) was refluxed for 20 min and then poured into water (100 mL). Subsequently, the pH was adjusted to 4 and the product was extracted with CH₂Cl₂ (2 × 50 mL) to give, after evaporation of the solvent, **10a–d** as white solids.

[[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[[(1-naphthalene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetic Acid (10a): yield 81%, mp 177–179 °C; ¹H NMR δ 8.09 (d, 1 H, *J* = 9.2 Hz), 7.70 (d, 2 H, *J* = 9.2 Hz), 7.53 (d, 1 H, *J* = 7.7 Hz), 7.5–7.3 (m, 3 H), 7.17 (s, 2 H), 7.11 (s, 2 H), 6.69 (s, 2 H), 6.42 (s, 2 H), 5.07 (d, 2 H, *J* = 6.7 Hz), 4.71 (d, 2 H, *J* = 13.3 Hz), 4.7–4.5 (m, 4 H), 4.34 (s, 2 H), 4.19 (d, 2 H, *J* = 13.3 Hz), 4.12 (s, 2 H), 3.27, 3.18, 3.15 (d, 4 H, *J* = 13.3 Hz), 1.32 (s, 18 H), 0.95 (s, 9 H), 0.76 (s, 9 H); mass spectrum (FAB) *m/e* 1020.8 [(M + H)⁺, calcd 1021.3], 1058.6 [(M + K)⁺, calcd 1059.4]. Anal. Calcd for C₆₃H₇₃NO₁₁·H₂O: C, 72.88; H, 7.28; N, 1.35. Found: C, 73.25; H, 7.14; N, 1.65.

[[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[[(9-phenanthrene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetic Acid (10b): yield 78%, mp 153–155 °C; ¹H NMR δ 8.6–8.4 (m, 2 H), 8.02 (d, 1 H, *J* = 8.3 Hz), 7.82 (d, 1 H, *J* = 8.3 Hz), 7.74 (s, 1 H), 7.6–7.3 (m, 5 H), 7.15 (s, 2 H), 7.12 (s, 2 H), 6.68 (s, 2 H), 6.43 (s, 2 H), 5.04 (d, 2 H, *J* = 6.7 Hz), 4.61 (d, 2 H, *J* = 13.4 Hz), 4.6–4.5 (m, 4 H), 4.38 (s, 2 H), 4.25 (d, 2 H, *J* = 13.4 Hz), 4.04 (br s, 2 H), 3.23, 3.13 (d, 4 H, *J* = 13.4 Hz), 1.35 (s, 18 H), 0.96 (s, 9 H), 0.77 (s, 9 H); mass spectrum (FAB) *m/e* 1069.1 [(M – H)[–], calcd 1069.3]. Anal. Calcd for C₆₇H₇₅NO₁₁·3H₂O: C, 71.56; H, 7.27; N, 1.25. Found: C, 71.94; H, 6.87; N, 1.21.

[[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[[(2-triphenylene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetic Acid (10c): yield 83%, mp 166–168 °C; ¹H NMR δ 8.7–8.5 (m, 6 H), 7.8–7.4 (m, 6 H), 7.09 (s, 4 H), 6.60 (s, 2 H), 6.40 (s, 2 H), 4.9–4.6 (m, 8 H), 4.42 (s, 2 H), 4.29 (s, 2 H), 4.23 (d, 2 H, *J* = 13.5 Hz), 3.21 (d, 2 H, *J* = 13.5 Hz), 3.04 (d, 2 H, *J* = 13.5 Hz), 1.31 (s, 18 H), 0.92 (s, 9 H), 0.74 (s, 9 H); mass spectrum (FAB) *m/e* 1142.8 [(M + Na)⁺, calcd 1142.8]. Anal. Calcd for C₇₁H₇₅NO₁₁·3H₂O: C, 72.74; H, 6.96; N, 1.19. Found: C, 72.73; H, 7.10; N, 0.89.

[[1⁵,3⁵,5⁵,7⁵-Tetra-*tert*-butyl-7²-[[propyl[(2-triphenylene)methyl]carbamoyl]methoxy]-1,3,5,7-tetrabenzocyclooctophane-1²,3²,5²-trilyl]trioxy]triacetic Acid (10d): yield 88%, mp 135–137 °C; ¹H NMR

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(DMSO-*d*₆) δ 9.08 (s, 1 H), 8.9–8.7 (m, 5 H), 7.84 (d, 1 H, J = 8.8 Hz), 7.8–7.6 (m, 4 H), 6.90 (s, 8 H), 4.77 (d, 4 H, J = 13.9 Hz), 4.58 (s, 8 H), 4.40 (s, 2 H), 3.20 (d, 4 H, J = 13.9 Hz), 2.94 (t, 2 H, J = 7.5 Hz), 1.8–1.6 (m, 2 H), 1.08 (s, 36 H), 0.93 (t, 3 H, J = 7.5 Hz); mass spectrum (FAB) m/e 1160.8 [(M – H)[–], calcd 1160.6], 879.6 [(M – N(CH₃CH₂CH₂)CH₂Triph)[–], confirmed by parent–daughter scan]. Anal. Calcd for C₇₄H₈₃NO₁₁: C, 76.46; H, 7.20; N, 1.20. Found: C, 76.40; H, 6.99; N, 1.19.

General Procedure for the Preparation of Complexes Eu(10a–d) and Tb(10a–d). The lanthanide salts Eu(III)Cl₃·6H₂O and Tb(III)Cl₃·6H₂O (1.1 equiv) and the drying agent triethyl orthoformate (5 drops) were first dissolved in acetonitrile and heated under reflux for 2 h. Triethylamine (3 equiv) and the calixarene triacid derivatives 10a–d (1 equiv) were added, and reflux was continued for another 2 h. The solution was concentrated to dryness. Chloroform (100 mL) and H₂O (100 mL) were added, and the organic layer was concentrated *in vacuo*. The Eu(III) and Tb(III) complexes were obtained in quantitative yields and have mp's > 300 °C. All complexes gave satisfactory elemental analyses. The mass spectral data are summarized in Table 1.

Procedure for the Preparation of Complexes [Eu(9d,e)]³⁺ and [Tb(9d,e)]³⁺. The lanthanide complexes [Eu(9d,e)]³⁺ and [Tb(9d,e)]³⁺ were prepared by reaction of the ligand (9d,e, 1 equiv) with the lanthanide salt (Eu(NO₃)₃·5H₂O or Tb(NO₃)₃·5H₂O, 1 equiv) in spectrograde methanol. The resulting solutions of the complexes were immediately used for the luminescence measurements.

Luminescence Measurements. Absorption spectra were recorded on a Varian Cary 3 UV–visible spectrophotometer.

Continuous emission spectra were recorded on a Spex Fluorolog 2 spectrofluorimeter. Figure 6 gives representative results of such spectra.

Where indicated, deoxygenation was achieved by purging with argon. Time resolved emission spectra were obtained using a Lumonics EX700

XeCl excimer laser (308 nm) as excitation source. The resulting luminescence was observed by a gated diode array detector coupled to an EG&G OMA III data handling system. Spectra were averaged over 100 shots to improve the signal to noise ratio. From these spectra luminescent lifetimes were calculated by fitting the integrated signal in time. Monoexponential decay was observed in all cases.

Spectrograde methanol (Merck Uvasol) was used to prepare solutions of the compounds.

Acknowledgment. The research described in this paper was supported by the Technology Foundation (S.T.W.), Technical Science Branch of the Netherlands Organization for Scientific Research (NWO).

Supporting Information Available: Table listing elemental analyses of Eu(III) and Tb(III) complexes of 10a–d (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951154V

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