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Calix[4]azacrowns as Novel Molecular Scaffolds for the Generation of Visible and Near-Infrared Lanthanide Luminescence

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Two calix[4]azacrowns, capped with two aminopolyamide bridges, were used as ligands for the complexation of lanthanide ions [Eu(III), Tb(III), Nd(III), Er(III), La(III)]. The formation of 1:2 and 1:1 complexes was observed, and stability constants, determined by UV absorption and fluorescence spectroscopy, were found to be generally on the order of log $\beta_{11} \approx 5$–6 and log $\beta_{12} \approx 10$. The structural changes of the ligands upon La(III) complexation were probed by ^{1}H NMR spectroscopy. The two ligands were observed to have opposite fluorescence behaviors, namely, fluorescence enhancement (via blocking of photoinduced electron transfer from amine groups) or quenching (via lanthanide–chromophore interactions) upon metal ion complexation. Long-lived lanthanide luminescence was sensitized by excitation in the π,π^* band of the aromatic moieties of the ligands. The direct involvement of the antenna triplet state was demonstrated via quenching of the ligand phosphorescence by Tb(III). Generally, Eu(III) luminescence was weak ($\Phi_{\mathrm{lum}} \leq 0.01\%$) and much shorter lived ($\tau_{\mathrm{lum}} = 0.36$ ms) than the Tb(III) emission. The latter, on the other hand, reached lifetimes of up to 2.60 ms and quantum yields as high as 12% for one of the ligands. Water/deuterium oxide exchange experiments showed the presence of only one solvent molecule in the coordination sphere of the lanthanides. However, Eu(III) luminescence was efficiently quenched by NH oscillators and the presence of a ligand-to-metal charge transfer state. Near-infrared luminescence of Nd(III) was also generated by energy-transfer sensitization.

Introduction

Lanthanide ions are known to show long-lived spectrally distinct luminescence.[1] Lifetimes are generally on the order of several hundreds of microseconds to milliseconds for visible-light-emitting Eu(III) and Tb(III) and tens of microseconds for near-infrared-emitting Nd(III) and Er(III). These long lifetimes, caused by parity-forbidden transitions resulting from 4f orbitals, and characteristic linelike emission spectra have triggered the application of lanthanides for the development of luminescent materials,[2−6] chemosensors,[7−10] and luminescent labels.[11,12] On the other hand, the forbidden nature of the involved transitions implies that lanthanides

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are very poor light absorbers; thus, the population of their luminescent states by direct excitation is inefficient. This drawback can be overcome by using organic chromophores (antennae), which absorb light and are able to sensitize lanthanide emitting states by efficient energy transfer.[13,14] In most cases the antenna chromophore is itself a ligand or is linked to a ligand, enabling complex formation with lanthanide ions. Because of the generally large Stokes shifts between antenna absorption (ca. 250−400 nm) and lanthanide emission [ca. 500−700 nm for Eu(III) and Tb(III) and >900 nm for Nd(III) and Er(III)] these complexes have often been referred to as molecular devices for wavelength conversion.[15]

Calixarenes are particularly interesting compounds for their use as molecular scaffolds for the design of luminescent lanthanide complexes, since they can be conveniently functionalized with metal-ion coordination motifs.[16−38] The selection of the ligand is a crucial point with respect to an efficient energy transfer from the antenna to the lanthanide, which depends on their distance and relative orientation. Another important factor is the shielding of the lanthanide from the luminescence quenching by the chemical environment (e.g., nonradiative deactivation via vibrational OH modes of water). The introduction of the antenna chromophore can be accomplished by one of the following strategies: (a) use of the aromatic moieties of the calixarene itself[16−21,24,27,30,32−35,38] or (b) attachment of a chromophore to the upper or lower rim of the calixarene.[19,22,23,25,26,28,29,31,33,36,37]

In the present work we were interested in calix[4]azacrowns with aminopolyamide bridges.[39−57] These compounds contain amide and amine functionalities, both known for their capability to bind lanthanide ions via interaction with $C{=}O$ oxygen atoms and amine nitrogen atoms.[58−61] However, so far little work has been dedicated to the metal cation complexation properties of azacrown calixarene derivatives. In early qualitative studies by Ostaszewski et al. using FAB mass spectrometry, the binding of divalent (alkali-earth ions) and trivalent metal cations [Sc(III), Y(III), In(III), Gd(III), Bi(III)] by calix[4]azacrowns with one polyamide bridge was reported to be weak.[39] However, more

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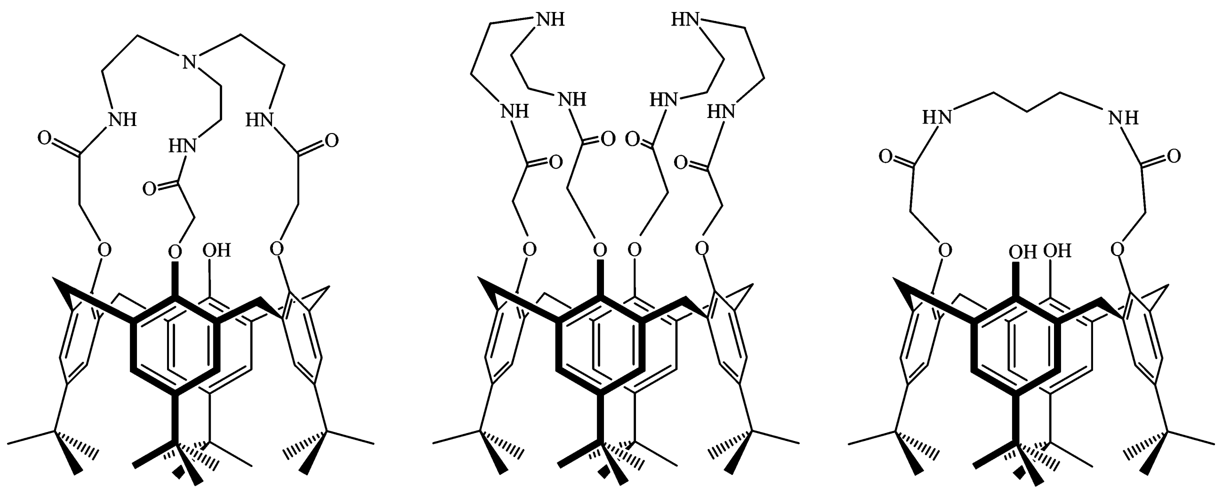
Chart 1



1 **2** **3**

recently it has been shown that the incorporation of two aminopolyamide bridges leads to quite high stability constants with divalent alkali-earth [Mg(II), Sr(II), Ba(II)] and transition metal cations [Co(II), Ni(II), Cu(II), Zn(II)].[50,51,56]

We used **1** and **2** (cf. Chart 1) for the complexation of lanthanide ions [Eu(III), Tb(III), Nd(III), Er(III), La(III)], which was investigated by UV absorption spectroscopy, fluorescence spectroscopy, and ^{1}H NMR spectroscopy. Calix[4]azacrown **3** (cf. Chart 1), containing only amide groups but no amine functions, was included for the sake of comparison. Different fluorescence properties of the calix[4]azacrowns and their lanthanide complexes were noted. The lanthanide complexes were further investigated with respect to their ability to generate visible and near-infrared lanthanide luminescence. To this end the aromatic moieties of the calixarenes were exploited as organic antennae.

Experimental Section

Materials. Triflates of Eu(III), Tb(III), Nd(III), Er(III), and La(III) (98%), deuterated solvents (acetonitrile-d_3, dimethyl sulfoxide-d_6, and deuterium oxide; all $\geq$99.8 atom % D), and 2,4,6-trimethylphenol (>99%) were purchased from Aldrich and used as received. Acetonitrile was of spectroscopic grade from Romil Ltd. Ligands **1**, **2**, and **3** were prepared following previously described procedures.[39,51]

Spectroscopic Measurements. For all experiments, Ln-**1** refers to a metal-to-ligand (lanthanide-to-calix[4]azacrown) ratio $R = 0.6$, while Ln-**2** stands for a ratio of $R = 1.6$. All UV spectroscopic measurements were performed with a Techcomp 8500 UV−vis spectrometer at room temperature (298 K) and with cells of 1 cm optical path length. Measurements of calixarene fluorescence and lanthanide luminescence in the UV−vis wavelength range were carried out at 293 K with a Cary Eclipse spectrometer from Varian Instruments equipped with a pulsed Xenon flash lamp and a red-sensitive R928 photomultiplier. Stability constants of the lanthanide complexes were determined by titration of a known volume (3.5 mL) of an acetonitrile solution of the calix[4]azacrown (ca. 70 μM) with aliquots from stock solutions of lanthanide triflate. The stoichiometry of the complexes and their log β_{ij} values were determined by analysis of the absorption and fluorescence spectra with the HYPERQUAD2003 program.[62,63] The reported values are based on at least two independent measurements. Special care was taken with regard to a linear relationship between absorbances or fluorescence intensities and concentration. For this reason diluted ligand solutions (ca. 70 μM) with absorbances between 0.1 and 0.2 at the excitation wavelength were used. Job plots were performed by measuring the absorbance or fluorescence intensity dependence on the metal cation content of the system, keeping the sum of ligand and metal cation concentration constant.

^{1}H NMR spectra were recorded at 298 K using a Bruker Advance-300 pulsed Fourier transform NMR spectrometer. The complexation behavior of **1** and **2** with La(III) ions was studied by dissolving La(III) triflate and the respective ligand (ca. 1 mM) in acetonitrile-d_3. The ratio R was varied between 0 and 2 until the chemical shift changes, $\Delta\delta$, remained constant.

Fluorescence lifetimes of **1**, **2**, and **3** were measured by single-photon timing. A modular laser system composed of a diode pumped Nd:YVO4 laser (Millenia Xs, Spectra-Physics) as the pumping source of a Ti:S femtosecond laser (Tsunami, Spectra-Physics) was used. The decay was multiexponential for **1** and **2**; thus, the amplitude-averaged fluorescence lifetime, $\langle\tau_f\rangle$, which was calculated according to eq 1 (α − weighted preexponential factor), is stated in these cases.

$$\langle\tau_{\mathrm{f}}\rangle = \sum_{i=1}^{n}\alpha_i\tau_i \text{ with } \sum_{i=1}^{n}\alpha_i = 1 \qquad (1)$$

The emission spectrum in the near-infrared (NIR) range and the respective excitation spectrum in the UV range were recorded at room temperature (298 K) with a modular double-grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Jobin Yvon-Spex) coupled to a H9170-75 Hamamatsu photomultiplier and a R928 Hamamatsu photomultiplier. The spectra were acquired using the front face mode and were corrected for detection and optical spectral response.

Phosphorescence spectra of the Gd(III) complexes were measured at the temperature of liquid nitrogen (77 K) with a Fluorolog Spex phosphorimeter.

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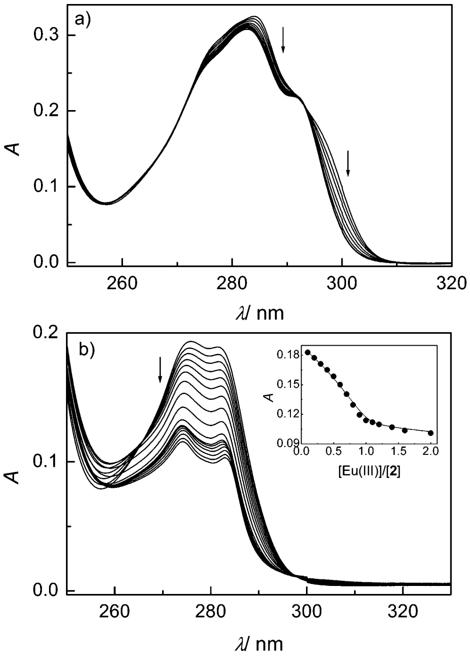

Figure 1. Changes in the absorption spectra of (a) **1** and (b) **2** upon titration with Eu(III) triflate ([**1**] = 7.65 × 10^{-5} M, [**2**] = 6.89 × 10^{-5} M). The inset shows the titration curve at $\lambda_{obs} = 279$ nm and the corresponding fit.

Quantum yields of calixarene fluorescence, Eu(III) and Tb(III) luminescence were determined using optically matched solutions (OD ca. 0.1) of phenol (Φ_f = 7.5% in *n*-hexane),[64] tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate (Φ_{lum} = 2.8% in water), and quinine sulfate dihydrate (Φ_f = 54.6% in 0.5 M sulfuric acid), respectively, as standards.[3]

Results

UV Absorption Studies. The UV absorption spectra of **1** and **2** in acetonitrile were dominated by a structured band between 270 and 290 nm, akin to the observations made for similar calix[4]arenes or monomeric methoxybenzenes.[32,65] These absorption bands correspond to π,π^* transitions of the aromatic moieties. Upon addition of lanthanide triflates, the spectra showed significant changes (cf. Figure 1), albeit dependent on the ligand structure. Ligand **1** showed a small hypsochromic shift (2 nm) of the band originally located at 284 nm and a slight decrease of absorption intensity (by 6% at $R = 0.7$), leading to an isosbestic point at 293 nm. The observation of the latter feature allowed the conclusion that *at least* one lanthanide complex was formed. For **2**, lanthanide-induced changes of the absorption spectrum were also observed. The absorption at 276 nm showed a small hypsochromic shift (1 nm), while the band at 281 nm was bathochromic shifted by 2 nm. The intensity of the π,π^* absorption band decreased markedly (by 44% at $R = 1.6$), leading to an apparent isosbestic point at 266 nm until a metal-to-ligand ratio of $R = 0.5$, which was lost upon further addition of lanthanide salt. The observed changes indicated the formation of at least two different complexes.

Table 1. Stability Constants (log β_{ij}) of Lanthanide Complexes with **2** in Acetonitrile

	R^a	log $\beta_{ij}{}^b$
Eu(III)	1:1	4.69 ± 0.32
	1:2	9.52 ± 0.01
Tb(III)	1:1	5.67 ± 0.30
	1:2	10.66 ± 0.70
Nd(III)	1:1	5.71 ± 0.02
	1:2	10.66 ± 0.70
Er(III)	1:1	4.94 ± 0.30
	1:2	10.54 ± 0.02
La(III)	1:1	6.01 ± 0.20
	1:2	9.80 ± 0.20

[a] Metal-to-ligand ratio. [b] Determined by absorption spectroscopy: T = 298 K, [**2**] = 6.89 × 10^{-5} M.

The complex stability constants in the form of log β_{ij} values were calculated by analysis of the absorption spectra. It could be demonstrated that, in the case of ligand **1**, 1:2 complexes of the type [Ln-$\mathbf{1}_2$]$^{3+}$ (Ln = Eu, Tb, Nd, Er, La) were formed. The stability constants are on the order of log $\beta_{12} \approx 10-11$, albeit somewhat smaller (log $\beta_{12} \approx 8$) for La(III). However, these data have to be interpreted with caution, since the small changes in the UV spectra did not allow a sufficiently accurate determination of complex stability constants (cf. Supporting Information). On the other hand, as anticipated from the changes in the absorption spectra (vide supra), ligand **2** forms two complexes, namely, [Ln-$\mathbf{2}_2$]$^{3+}$ and [Ln-**2**]$^{3+}$. The stability constants for the two complexes (cf. Table 1), as determined from the log β_{ij} values, are on the order of log $K_{12} = 4.8-6.0$ and log $K_{11} = 3.8-5.0$. The values for 1:1 lanthanide complexation are comparable with those for calix[4]arenes with pendant ether-amide arms (log $K_{11} \approx 4-5$) in acetonitrile.[60]

Fluorescence Measurements. Excitation of **1** and **2** resulted in a broad emission band centered at 309 nm, as has been observed earlier for similar calixarenes.[27,32,65] This emission was assigned to the fluorescence resulting from the π,π^* singlet excited state of the aryl moieties. The origin of the fluorescence was established by recording excitation spectra, which resembled the absorption spectra of the ligands (cf. Supporting Information). Interestingly, the fluorescence quantum yield (Φ_f) of **1** and **2** was considerably diminished compared to that of **3**, being smallest for **1** (i.e., Φ_f (**1**) = 1.4%, Φ_f (**2**) = 2.3%, and Φ_f (**3**) = 15.2%). The same trend was reflected by the fluorescence lifetime, which is shorter for **1** and **2** than for **3**: $\langle\tau_f\rangle$ (**1**) = 0.47 ns, $\langle\tau_f\rangle$ (**2**) = 1.29 ns, and τ_f (**3**) = 4.40 ns. The lifetime of the model compound 2,4,6-trimethylphenol was the same (4.40 ns) as that for **3**.

Upon addition of lanthanide triflates to solutions of **1** or **2**, dramatic changes in the fluorescence spectra were observed (cf. Figure 2). Strikingly, the two calix[4]azacrowns showed totally opposite behavior. The fluorescence of **1** was enhanced by a factor of ca. 6.5 [6.8 for Eu(III), 6.4 for Tb(III), 6.5 for Nd(III), 6.6 for Er(III), and 6.2 for La(III)] upon reaching a plateau at a metal-to-ligand ratio of R = 0.5, corresponding to the 1:2 complex stoichiometry discussed above. However, no shift of the fluorescence maximum was observed for **1**. On the other hand, upon addition

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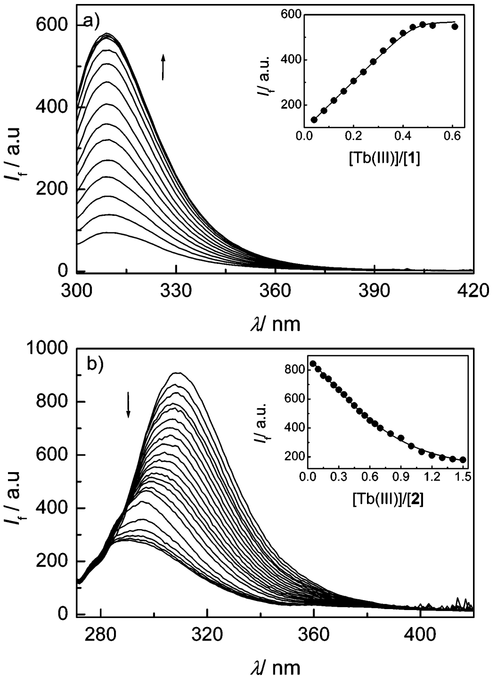

Figure 2. Changes in the fluorescence spectra of (a) **1** and (b) **2** upon titration with Tb(III) triflate ([**1**] = 3.83×10^{-5} M, [**2**] = 6.89×10^{-5} M). The insets show the titration curve at (a) $\lambda_{obs} = 313$ nm and (b) $\lambda_{obs} = 312$ nm and the corresponding fits.

of a lanthanide salt the fluorescence of **2** was quenched and its maximum experienced a hypsochromic shift (e.g., 17 nm for $R = 1.6$ in case of Tb-**2**). Further, the titration curves for ligand **2** with all investigated lanthanides had two points at which the quenching levelled off, namely, at $R = 0.6$ and 1.2, which supports the formation of two complexes (vide supra). The fluorescence titrations yielded virtually the same log β_{ij} values as the UV absorption titrations (cf. Supporting Information).

To gain more information about the stoichiometries of the involved complexes, we performed Job plots based on the pronounced changes of the fluorescence intensities upon addition of Tb(III). For **1**, the Job plot revealed two maxima at [Tb(III)]/([Tb(III)] + [**1**]) ≈ 0.3 and 0.5, which corroborates the involvement of two stoichiometries, [Tb-**1**$_2$]$^{3+}$ and [Tb-**1**]$^{3+}$. However, the analysis of the fluorescence titration yielded only one complex, [Tb-**1**$_2$]$^{3+}$. Most likely, the 1:1 complex has a much smaller stability constant than the 1:2 complex and was therefore not observed in the titration analysis. For ligand **2**, we performed a similar Job plot analysis based on the rather large changes of the UV spectra with increasing amounts of Tb(III). The corresponding plot had two maxima at [Tb(III)]/([Tb(III)] + [**2**]) ≈ 0.3 and 0.6, which confirmed the involvement of two complex stoichiometries, [Tb-**2**$_2$]$^{3+}$ and [Tb-**2**]$^{3+}$, as was also found in the UV and fluorescence titration experiments.

^{1}H NMR Studies. The ^{1}H NMR spectra of the free ligands **1** and **2** in chloroform-d_1 have been discussed recently,[51] leading to the conclusion that both calixarenes adopt a *cone* conformation. As pointed out by Gutsche et al. and others the difference between the chemical shifts of the axial (H_{ax}) and equatorial (H_{eq}) methylene protons of the calixarene platform can be used to evaluate the symmetry of the cone conformation of calixarenes.[32,60,66−70] However, a recent report demonstrated that this relation does not hold for bridged calixarenes, among them structures very similar to the ones investigated in this work.[42,71] The use of the chemical shift differences of the *tert*-butyl and aromatic protons (Ar*H*) of neighboring (proximal) phenyl rings was suggested instead.[42] For ligand **1** and **2**, only minor differences (<0.07 ppm) between the *tert*-butyl or phenyl protons of proximal aromatic rings were observed in acetonitrile-d_3, which points to a *symmetrical cone* conformation. The same was valid for ligand **2** in chloroform-d_1, while ligand **1** showed pronounced differences (0.45 ppm for *tert*-butyl and 0.39 for Ar*H*). This suggests that ligand **1** adopts a *distorted cone* conformation in chloroform-d_1.

To gain information about the conformation of the calix[4]azacrown complexes and the mode of coordination of the lanthanide ions, ^{1}H NMR studies of the La(III) complexes with **1** and **2** were performed. UV absorption and fluorescence measurements with **2** revealed that La(III) exhibits complexation behavior (cf. Table 1 and Supporting Information) similar to that observed for the other investigated lanthanides. However, with **1**, a considerably lower stability constant (log $\beta_{12} \approx 8$) was measured. Therefore, the following results should be considered as case studies for La(III).

For **1** in acetonitrile-d_3, chemical shift changes were observed at $R = 0.5$ (cf. Supporting Information), which remained constant for $R = 1.0$. On the basis of the criteria applied for the free ligands (vide supra),[42] it was concluded that the symmetrical cone conformation of the free ligand **1** is conserved in the La(III) complexes. This was supported by the observation of one AB system (7.36 and 7.23 ppm, $J = 2.4$ Hz) and two singlets (7.32 and 7.19 ppm) for the aromatic protons, two AB spin systems (4.11 and 3.41 ppm, $J = 13.2$ Hz; 4.31 and 3.45 ppm, $J = 12.1$ Hz) for the methylene protons of the calixarene platform, and two singlets (1.22 and 1.19 ppm; ratio 1:3) for the *tert*-butyl protons.[67,72] In comparison to the free ligand **1**, pronounced downfield shifts were noted for all methylene protons adjacent to the amine nitrogen ($\Delta\delta = +0.55$ and $+0.91$), the methylene protons of two CH_2−NHCO ($\Delta\delta = +0.52$), and the *NH* amide protons ($\Delta\delta = +0.49$) of the two arms attached to opposite (distal) phenyl rings. On the other hand, upfield shifts of the phenolic *OH* protons ($\Delta\delta$ between −0.05 and −0.27 ppm), the axial methylene protons (H_{ax}) of the calixarene platform ($\Delta\delta$ between −0.07 and −0.27 ppm), and the protons of the methylene group linked to the amide

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Table 2. Photophysical Properties of Eu(III) and Tb(III) Complexes with **1** and **2** at 293 K

	τ (ms)[a]	τ_{H_2O} (ms)[b]	τ_{D_2O} (ms)[b]	q[c]	Φ_{lum}[d]
Eu-**1**	0.36	0.12	0.34	–[e]	<0.0001
Tb-**1**	0.82	0.38	0.41	0.7	0.0002
Eu-**2**	0.35	0.22	1.21	0.9 (1.3)	0.0001
Tb-**2**	2.60	1.26	2.61	0.9	0.12

[a] $\lambda_{obs} = 543$ nm (Tb) or 614 nm (Eu); error 10%, except for τ_{H_2O} of Eu-**1** (30%). [b] Measured in acetonitrile with either 10% (v/v) water or deuterium oxide. [c] $q = A'(1/\tau_{H_2O} - 1/\tau_{D_2O} - \Delta k)$ with $A' = 1.2$ ms; $\Delta k = 0.25\ \mathrm{ms}^{-1} - 0.075\ \mathrm{ms}^{-1} \times n_{NH-amide} - 1.20\ \mathrm{ms}^{-1} \times n_{NH-amine}$ for Eu(III) and $A' = 5.0$ ms; $\Delta k = 0.06\ \mathrm{ms}^{-1} - 0.09\ \mathrm{ms}^{-1} \times n_{NH-amine}$ for Tb(III); cf. ref 77. The value in parentheses corresponds to a refined equation for Eu(III) by Horrocks and co-workers (cf. ref 80) with $A' = 1.11$ ms, $\Delta k = 0.31\ \mathrm{ms}^{-1} - 0.075\ \mathrm{ms}^{-1} \times n_{NH-amide} - 0.99\ \mathrm{ms}^{-1} \times n_{NH-amine}$. [d] Measured with $Ru(bpy)_3^{2+}$ [for Eu(III) luminescence] and quinine sulfate [for Tb(III) luminescence] as standards (cf. Experimental Section); error 30%. [e] The value for Eu-**1** was not calculated because of the large absolute error, which would be introduced by the low lifetime τ_{H_2O} coupled with its high uncertainty.

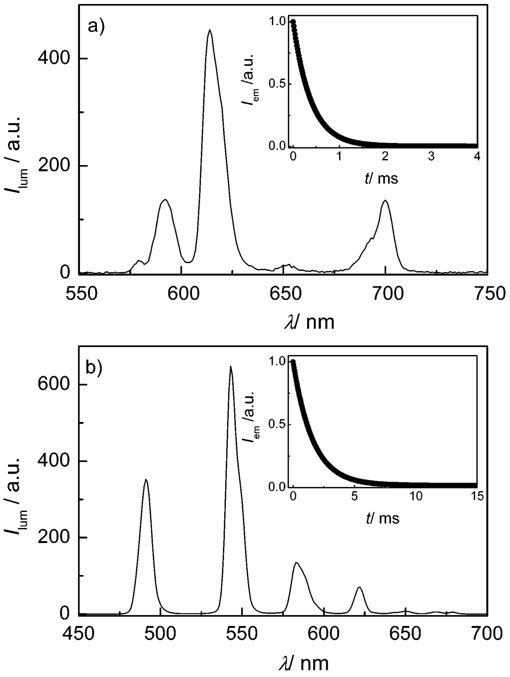

Figure 3. Lanthanide luminescence spectra ($\lambda_{exc} = 266$ nm) and decay traces of (a) Eu-**2** and (b) Tb-**2**.

nitrogen (CH_2−NHCO) of the third arm ($\Delta\delta = -0.05$ ppm) were observed.

Calix[4]azacrown **2** showed changes of the chemical shifts up to $R = 1$ in acetonitrile-d_3 (cf. Supporting Information). The symmetrical cone conformation of free **2** is preserved in the La(III) complexes as indicated by the presence of two singlets at 7.61 and 7.60 ppm for the aromatic protons, two AB spin systems for the methylene protons (4.47 and 3.47 ppm, $J = 13.3$ Hz; 4.18 and 3.47 ppm, $J = 13.3$ Hz) of the calixarene platform, and one singlet at 1.21 ppm for the *tert*-butyl protons.[42] Compared to free ligand **2**, solely the axial methylene protons (H_{ax}) were upfield shifted ($\Delta\delta$ between −0.11 and −0.26 ppm), while all other protons showed downfield shifts ($\Delta\delta$ between +0.08 and +0.76 ppm).

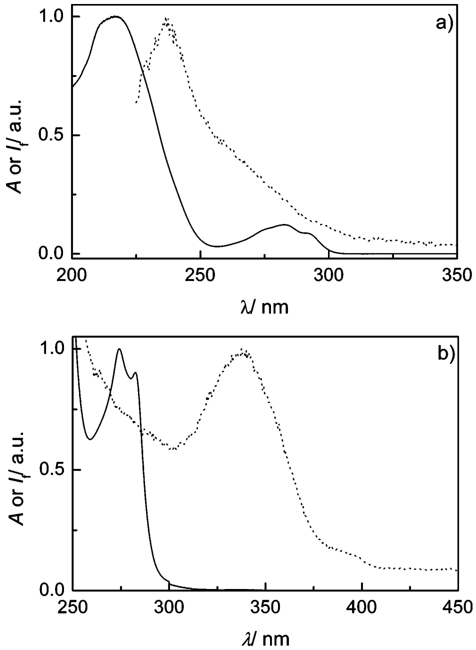

Figure 4. Absorption (full line) and excitation spectra ($\lambda_{em} = 614$ nm, dotted line) of Eu(III) complexes with (a) **1** and (b) **2**.

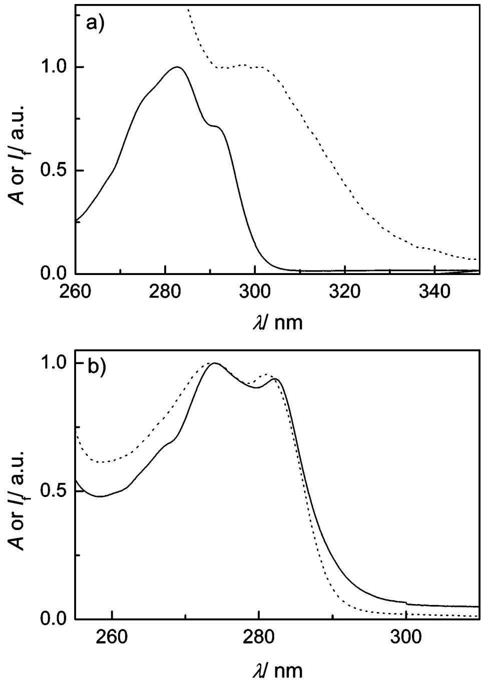

Figure 5. Absorption (full line) and excitation spectra ($\lambda_{em} = 543$ nm, dotted line) of Tb(III) complexes with (a) **1** and (b) **2**.

Lanthanide Luminescence Measurements. The aromatic moieties of the ligands were explored as sensitizers for the generation of lanthanide luminescence. The combined photophysical parameters are presented in Table 2. Upon excitation in the π,π^* absorption band ($\lambda_{exc} = 293$ nm for **1** and 266 nm for **2**) typical linelike luminescence spectra of Eu(III) and Tb(III) were observed (cf. Figure 3). For the Eu-**1** and Eu-**2** complexes, emission bands at 579, 592, 614, 652, and 700 nm were observed, which are assigned to $^5D_0 \rightarrow {}^7F_J$ transitions with $J = 0, 1, 2, 3$, and 4, respectively.[1] Tb-**1** and Tb-**2** emitted with maxima at 491, 543, 583, 622, 650, 669, and 679 nm, corresponding to $^5D_4 \rightarrow {}^7F_J$ transitions with $J = 6, 5, 4, 3, 2, 1$, and 0, respectively.[1] Excitation spectra, monitoring the strongest emission line of Eu(III) or

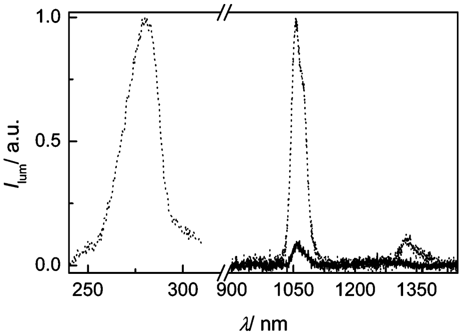

Figure 6. Nd(III) luminescence spectra (right, $\lambda_{exc} = 281$ nm) of Nd-**1** (full line) and Nd-**2** (dotted line) and excitation spectrum (left, $\lambda_{em} = 1058$ nm) of Nd-**2**.

Tb(III), are similar to the absorption spectra, which supports the energy transfer process from the aromatic moieties to the lanthanide (cf. Figures 4 and 5). In the case of Eu-**2**, an additional band at ca. 340 nm was detected. On the basis of earlier observations for Eu(III) complexes with Lehn's cryptand $[Eu \subset 2.2.1]^{3+}$ and various calixarenes, this band can be related to a charge transfer (CT) state.[16,18,27,38,73]

Large differences for the quantum yield of lanthanide-based luminescence were observed. Eu(III)-based luminescence was generally weak with quantum yields of $\Phi_{lum} \leq 0.01\%$. Tb(III) luminescence of Tb-**1** was also found to be weak ($\Phi_{lum} = 0.02\%$). Strikingly, the luminescence of Tb-**2** has a substantially higher quantum yield of 12%. The latter value compares nicely with the largest luminescence quantum yields observed for related Tb(III)−calix[4]arene complexes using the calixarene aromatic moieties as antennae.[17,19,24,30,32,34]

This situation is similarly reflected by the lifetimes of luminescence, which were found to be around 0.36 ms for Eu-**1** and Eu-**2** and 0.82 ms for Tb-**1**. On the other hand a significantly longer lifetime of 2.60 ms was measured for Tb-**2**, which is one of the longest solution lifetimes ever observed for Tb(III)−calixarene complexes.[17,20,24,30,32]

The sensitization of the near-infrared (NIR) luminescence of Nd(III) and Er(III) by excitation of the ligands at 281 nm was also attempted. For complex Nd-**2**, luminescence characterized by a strong emission band at 1058 and a weaker one at 1328 nm was detected (cf. Figure 6), corresponding to $^4F_{3/2} \rightarrow {}^4F_{11/2}$ and $^4F_{3/2} \rightarrow {}^4F_{13/2}$ transitions, respectively.[33,74] The excitation spectrum showed a maximum at 281 nm, which supports the occurrence of energy transfer from the calixarene to Nd(III). However, with ligand **1**, an approximately 12 times weaker Nd(III) luminescence spectrum was detected (cf. Figure 6). No luminescence of Er(III) was observed with **1** or **2**.

Discussion

Stability of the Lanthanide Complexes. Previous qualitative studies of calix[4]azacrowns capped with one lateral bridge reported weak binding of di- and trivalent cations.[39] However, the measured binding constants for lanthanides with ligands **1** and **2** are quite substantial and are not in agreement with a weak binding. Two reasons might account for the largely improved complexation properties: (a) the presence of two azacrown bridges instead of one, leading to an increased number of donor sites and a larger degree of pre-organization of the ligand, and (b) the presence of additional amine nitrogen donor atoms.

The stability constants of the different lanthanide complexes vary without obvious trends within 1 order of magnitude. Thus, no clear-cut cation size dependence was observed. This might be the result of the masking effect known to be exerted by amine nitrogen atoms.[58] Further, both ligands showed low complexation selectivity within the series of investigated lanthanides. In addition to the masking effect mentioned before, an often antagonistic interrelationship between cation size and charge density, solvation, and ligand flexibility might be responsible for such behavior.[58]

Coordination Environment of Lanthanides. Studies of the ^{1}H NMR spectra of free **1** and **2** and their respective complexes with La(III) showed that the lanthanide is coordinated in different chemical environments with respect to the ionophoric cavity. For **1**, the largest downfield shifts were noted for protons near the tertiary amine group, namely, those of the neighboring ethylene units, the amide functions, and the methylene units linked to the carbonyl groups. However, the protons of the two distal arms were more influenced than those of the third arm (cf. Supporting Information). This suggests the possible binding of the lanthanide outside the ionophoric cavity.

Calix[4]azacrown **2** showed pronounced changes for the protons close to the secondary amine groups, namely those of the neighboring ethylene units, the amide NH groups, and the methylene units linked to the carbonyl groups. The protons on both bridges were influenced to the same extent. These observations support a symmetrical complexation inside the ionophoric cavity by both macrocyclic bridges.

Fluorescence Enhancement of Calix[4]azacrown 1. The fluorescence of the aromatic moieties of **1** was enhanced upon lanthanide complexation. It might be anticipated that this effect is related to the blocking of the amine nitrogen lone pair by metal ion complexation (vide supra).[7] To prove this hypothesis, a solution of **1** was titrated with trifluoroacetic acid (cf. Figure 7). The titration curve showed the same shape like for the lanthanides; it levelled at 0.4 equiv of acid with a fluorescence enhancement factor of 7.1. Furthermore, for **3**, which has no amine function on the bridge, no significant changes of the fluorescence upon addition of Tb(III) ions or trifluoroacetic acid were observed (cf. Figure 7). These two experiments clearly demonstrate the involvement of the amine nitrogen in the fluorescence enhancement of **1**. Photoinduced electron transfer (PET) from the electron-donating tertiary amine to the aromatic moieties of the calixarene, which is switched off upon involvement of the nitrogen lone pair in metal complexation, can be assumed to be the transduction mechanism. This conclusion is supported by the strong fluorescence quenching (90%) of

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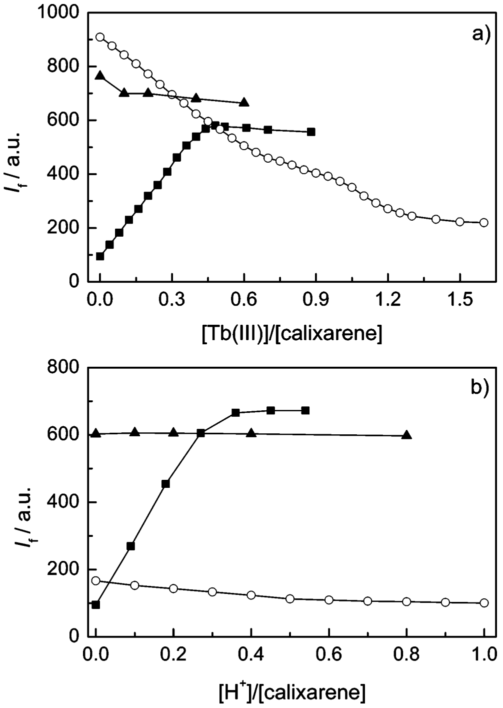

Figure 7. Fluorescence titration curves (λ_{obs} = 309 nm) of **1** (■), **2** (○), and **3** (▲) upon addition of (a) Tb(III) triflate and (b) trifluoroacetic acid.

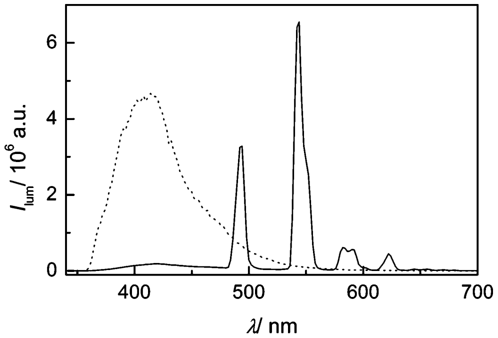

Figure 8. Phosphorescence spectra (λ_{exc} = 280 nm) of Tb-**2** (full line) and Gd-**2** (dotted line) in frozen acetonitrile at 77 K.

1 compared to that of **3** as verified by the quantum yield and lifetime measurements (cf. Results).

Fluorescence Quenching of Calix[4]azacrown 2. In contrast to **1**, compound **2** showed strong fluorescence quenching as result of lanthanide ion complexation. On the other hand no significant changes of the fluorescence were observed upon the addition of trifluoroacetic acid, similar to the situation for **3** (cf. Figure 7). This is surprising since **2** also contains electron-donating secondary amine groups on the bridges, albeit weaker than the tertiary amine group in **1**. The blocking of PET upon lanthanide complexation, which would result in an enhancement of the fluorescence, seems to be of minor importance compared to other effects which lead to fluorescence quenching, for instance the participation of accelerated intersystem crossing (ISC) due to lanthanides as heavy atoms.

Sensitization of Visible Luminescence of Eu(III) and Tb(III). As demonstrated for other calixarenes, the luminescence of Eu(III) and Tb(III) can be sensitized by energy transfer from triplet excited states of the aromatic moieties of the calixarene.[16−21,24,27,30,32,34,35,38] The excitation energy of the π,π^* triplet state was measured as ca. 28 000 cm^{-1} by taking the onset of the phosphorescence spectrum of the Gd(III) complex at 77 K (27 600 cm^{-1} for Gd-**1** and 28 200 cm^{-1} for Gd-**2**). The phosphorescence emission maxima were observed at 414 and 422 nm for **1** and **2**, respectively. Other calix[4]arenes including those bearing amide functions or crown ethers have similar triplet state energies.[17,24,32] The π,π^*-excited triplet states of **1** and **2** are energetically well above the luminescent $^5D_0$ level of Eu(III) [17 300 cm^{-1}] and the $^5D_4$ level of Tb(III) [20 500 cm^{-1}],[75,76] allowing a thermodynamically favored energy transfer from the antenna chromophore to the lanthanide. As a result, the Eu(III) and Tb(III) complexes exhibited characteristic line-shaped lanthanide luminescence (cf. Results).

That the π,π^* triplet state of the aromatic moieties is responsible for the energy transfer was confirmed by the measurement of the phosphorescence spectrum of Tb-**2**, which was dominated by the typical emission lines of the lanthanide and showed only a very small band for the ligand at 420 nm (cf. Figure 8). The phosphorescence of the ligand was strongly quenched (>95%) compared to that in Gd-**2**, where energy transfer is not possible because of the high-lying excited-state energy levels of Gd(III).[29]

Eu(III) luminescence, which was generated by excitation in the π,π^* absorption band of **1** and **2**, is characterized by comparably short lifetimes (0.36 ms) and low quantum yields ($\leq$0.01%), which points to the participation of a CT state, formed between C═O carbonyl groups and Eu(III). This was supported by the observation of a rather broad CT band with a maximum at ca. 340 nm (29 400 cm^{-1}) in the excitation spectrum of Eu-**2**. In fact, the involvement of a CT state as an efficient nonradiative deactivation channel, resulting in very low luminescence quantum yields, has been demonstrated for several other Eu(III) complexes with calixarenes.[16−19,24,27,30,32,35,38] Additionally, the weak Eu(III) luminescence might be caused by nonradiative quenching by OH or NH oscillators,[77] or inefficient energy transfer as a result of the distance dependence of this mechanism, or both.[78] A general illustration of the energy-transfer sensitization of Eu(III) and Tb(III) is shown in Scheme 1.

To gain more information about the quenching of Eu(III) luminescence by the chemical environment, the lifetimes in acetonitrile containing either 10% H_2O or D_2O were measured (cf. Table 2). The addition of H_2O led to a decrease in the luminescence lifetimes, while the addition of D_2O caused no increase in case of **1** but did cause an increase for **2**. The application of a corrected Horrocks equation (cf. footnote *c* in Table 2),[77,79,80] which takes into account the quenching

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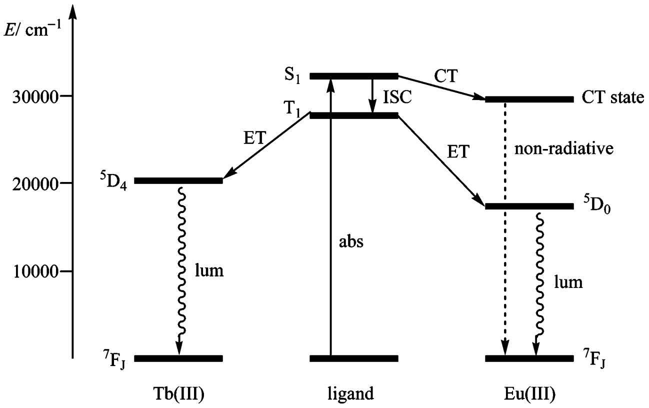
Scheme 1



by OH oscillators in the second coordination sphere and by amide and amine NH groups, leads to ca. 1 water molecule for Eu-**2**. For such a small number of coordinated water molecules, a lifetime (ca. 0.6−0.7 ms) longer than the measured one (0.22 ms) would be expected.[32] However, NH oscillators of amines, as present in ligand **2**, are known to exert rather large quenching effects on Eu(III) luminescence, which might serve as explanation for the observed lifetime quenching in Eu-**2**.[77]

Tb(III) luminescence was detected upon excitation in the antenna absorption bands of Tb-**1** and Tb-**2**. The two complexes showed quite different behavior with respect to luminescence lifetime and quantum yield. The luminescence of Tb-**1** was relatively short-lived (0.82 ms), and the quantum yield did not exceed 0.02%. Despite the low number of coordinated solvent or water molecules (ca. 1), the luminescence is weak, which points to a less efficient energy-transfer process. On the other hand much more encouraging values were observed in case of Tb-**2**. The luminescence quantum yield (12%) and the lifetime (2.60 ms) are among the highest ones ever measured for calixarene−lanthanide conjugates, which demonstrates very efficient antenna-to-lanthanide energy transfer and a high degree of shielding of the Tb(III) by the ligand. The highly protective nature of **2** relates to the low number of solvent or water molecules (ca. 1). Also, in contrast to Eu(III), amine and amide NH oscillators have practically no impact on the nonradiative deactivation of Tb(III).[77]

Sensitization of Near-Infrared Luminescence. The aromatic moieties of **1** and **2** can be also used as antennae for the sensitization of Nd(III) luminescence. The characteristic emission spectrum with a narrow main band at 1058 nm was observed in acetonitrile, albeit much stronger for **2**. Measurements in dimethyl sulfoxide-d_6 showed no improvement of the Nd(III) luminescence intensity, confirming effective shielding of the lanthanide by both ligands (vide supra).

The fact that NIR luminescence of Nd(III) was observed is striking for two reasons: (a) the small spectral overlap integral between antenna triplet-state emission and Nd(III) absorption and (b) the high number of CH bonds provided by **1** and **2**. With regard to the quenching by CH oscillators it should be noted that near-infrared emitting lanthanides have comparably small energy gaps, ΔE, between excited and ground-state levels [i.e., $\Delta E \approx 5200$ cm^{-1} for Nd(III) vs 12 300 cm^{-1} for Eu(III) and 14 800 cm^{-1} for Tb(III)]. Therefore excited-state quenching interactions by CH oscillators with vibrational quanta of 2950 cm^{-1} are expected to diminish NIR luminescence.

Conclusions

The complexation behavior of calix[4]azacrowns **1** and **2** with lanthanide ions [Eu(III), Tb(III), Nd(III), Er(III), La(III)] was investigated. Contrary to earlier reports for calix[4]azacrowns with one polyamide bridge, the binding constants were found to be reasonably high (log $\beta_{11} \approx 5-6$ and log $\beta_{12} \approx 10$; except for La-**1**, log $\beta_{12} \approx 8$). ^{1}H NMR studies yielded insights into the coordination mode of the lanthanide ions. While for ligand **1**, complexation outside the ionophoric cavity is assumed, the more flexible ligand **2** should be able to accommodate the lanthanide ion inside the cavity.

Fluorescence measurements of the π,π^*-excited singlet state of the aromatic moieties of the calixarene platform revealed opposite behavior of the two calix[4]azacrowns. In case of ligand **1**, the involvement of the amine nitrogen in the complexation resulted, via blocking of PET, in fluorescence enhancement upon addition of lanthanide. On the other hand complexes with ligand **2** showed fluorescence quenching with respect to the free ligand, most likely caused by lanthanide−chromophore interactions (e.g., heavy-atom-induced intersystem crossing).

Further, the potential of both ligands as organic antenna chromophores for the energy-transfer sensitization of luminescent excited states of lanthanides was demonstrated. Particularly efficient ($\Phi_{\mathrm{lum}} = 12\%$) and long-lived ($\tau_{\mathrm{lum}} = 2.60$ ms) luminescence was observed for Tb-**2**. This has been rationalized on the basis of an efficient energy transfer and shielding of the lanthanide from quenching by the chemical environment. The favorable emission characteristics of this complex suggest a promising application as a luminescent label. Generally, sensitization of Eu(III) luminescence was less favorable, which can be traced back to the involvement of a CT state and quenching by NH oscillators. For Nd(III), the successful sensitization of NIR luminescence was observed, which is quite astonishing, when its easy deactivation by CH oscillators and the expectedly small spectral overlap between calixarene and Nd(III) are taken into account.

Acknowledgment. We thank the Portuguese Foundation for Science and Technology (FCT), Lisbon, for financial support [Project POCI/QUI/58535/2004 and a postdoctoral grant for I.O. (SFRH/BPD/14593/2003)].

Supporting Information Available: UV absorption spectra, excitation spectra of ligand fluorescence, complex stability constants, Job plots, ^{1}H NMR data, and Tb(III) luminescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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