Synthesis of Functionalized Calix[4]arene Ligands Incorporating Bipyridine *N,N′*-Dioxide Chromophores and Luminescence of Their Lanthanide Complexes

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Members of a new family of lanthanide complexes of the cone-shaped podand **1** and the barrel-shaped cryptand **2**, based on calix[4]arenes incorporating bipyridine *N,N′*-dioxide chromophores, have been synthesized and characterized. The complexes were found to be stable in water and coordinating solvents. High molar absorption coefficients {ε = 28000 and 36000 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$ for $[\mathrm{Eu}(\mathbf{1})]^{3+}$ and $[\mathrm{Eu}(\mathbf{2})]^{3+}$, respectively} and high metal luminescence quantum yields {Φ = 0.19 and 0.11 for $[\mathrm{Eu}(\mathbf{1})]^{3+}$ and $[\mathrm{Eu}(\mathbf{2})]^{3+}$, respectively} were obtained. The effect of OH oscillators, attached at the lower rim of the calixarenes, on the non-radiative deactivation to the ground state has been demonstrated.

Luminescence spectroscopy is attracting immense interest in the scientific community owing to its potential application in growing fields of great economical and social impact, such as environmental sciences, medical diagnostics, and cell biology.[1][2][3][4] In particular, the synthesis, characterization, and application of many luminescent labels and sensors has opened up a lot of opportunities for solving complex analytical problems, among which the fluorescence immunoassay certainly has a central role.[1][5]

The major drawback in photoluminescence analysis, particularly when dealing with biological material, is the interference caused by autofluorescence and light scattering. Time resolved spectroscopy, which requires the use of labels with very long luminescence lifetimes, can efficiently exclude this kind of background light. For this reason, over the past decade great interest has been centered on the design of luminescent complexes containing the Eu^{3+} and Tb^{3+} ions, which possess luminescence lifetimes in the micro- to millisecond range.[1][6][7][8][9] To obtain an efficient luminescent label, the ligand needs to be able to form stable complexes with the lanthanide ions in coordinating solvents, to shield the ion from deactivating solvent molecules, and, particularly importantly, to absorb light and to transfer it to the metal ion with high efficiency, thereby overcoming the intrinsic low absorption coefficients of the metal ions.[6][7][8][9] With these goals in mind, and thanks to the great progress made in the field of supramolecular chemistry, many encapsulating ligands possessing the required characteristics have been synthesized,[6] and, among these, particular attention has been focused on functionalized calixarenes.[10][11][12][13][14][15][16][17][18][19] In this context, we report here on the synthesis of new functionalized calix[4]arene ligands incorporating bipyridine *N,N′*-dioxide chromophores and on the luminescence of their Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes.

Results

Ligands **1** and **2** and their lanthanide complexes were prepared as outlined in Schemes 1 and 2 using well-established synthetic procedures for 1,3-disubstituted calix[4]arene ethers in the cone conformation.[20][21] The initially designed ligand **1** was prepared by reaction of *p-tert*-butylcalix[4]arene with 5-bromomethyl-5′-methyl-2,2′-bipyridine *N,N′*-dioxide in anhydrous acetonitrile using $\mathrm{K_2CO_3}$ as base (Scheme 1). Ligand **2** (Scheme 2) was prepared under similar conditions starting from *p-tert*-butylcalix[4]arene and 5,5′-bromomethyl-2,2′-bipyridine *N,N′*-dioxide. Both ligands were isolated in a pure state after chromatography on neutral alumina. In solution at room temperature, they adopt a fixed cone conformation with the ligating groups on the same side of the plane formed by the macrocycle, as was deduced from their ^{1}H-NMR spectra. In both ligands, the methylene protons give rise to an AB quadruplet, at δ = 3.75 (J_{AB} = 13.1 Hz and $\Delta\nu$ = 168.5 Hz) in **1** and at δ = 3.81 (J_{AB} = 13.3 Hz and $\Delta\nu$ = 172.2 Hz) in **2**. The aromatic

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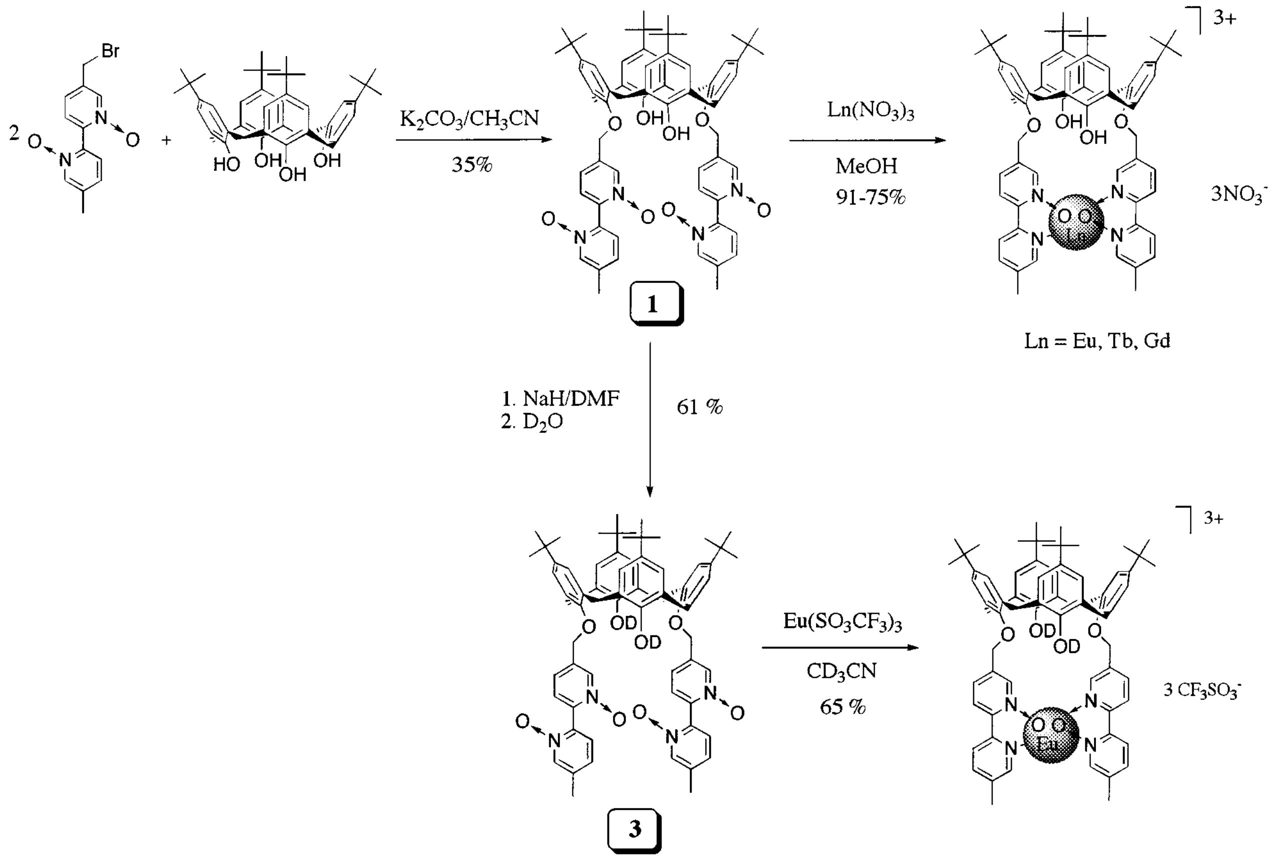
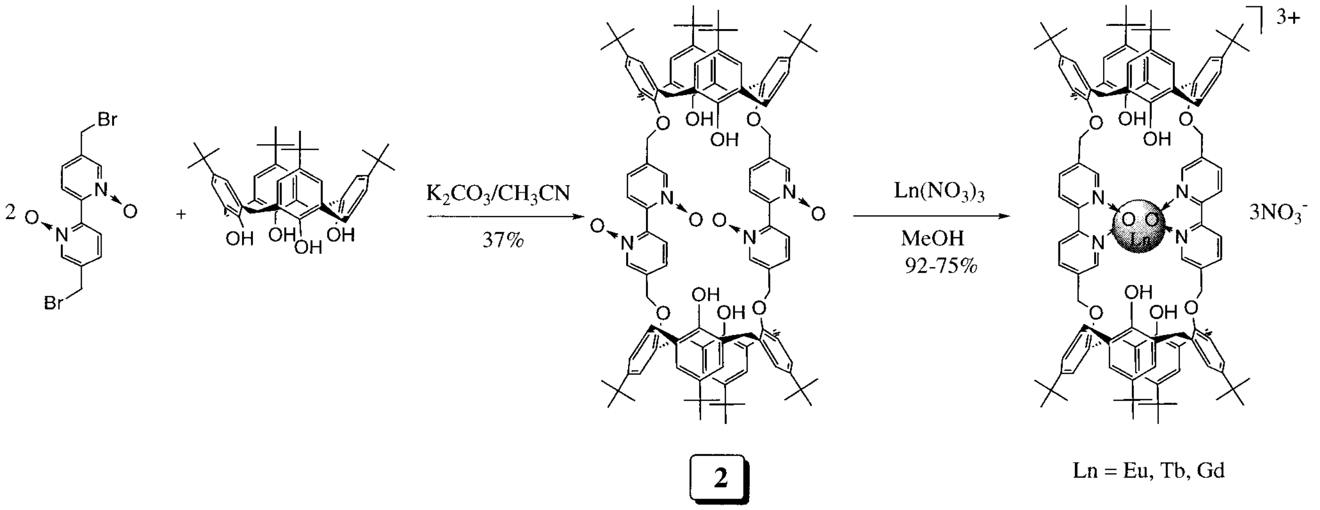
Scheme 1



Scheme 2



protons of the calix[4]arene skeleton give rise to two singlets at δ = 7.05 and 6.81 for **1** and at δ = 7.09 and 6.82 for **2**, while the phenol groups resonate at δ = 6.98 in **1** and δ = 7.03 in **2**. Ligand **3** was prepared by deprotonation of **1** by treatment with NaH in anhydrous dimethylformamide, followed by quenching with D_2O (Scheme 1). The proton-deuterium exchange was monitored by ^1H NMR, which showed the absence of phenolic proton signals, and was verified by FAB^+ MS.

The lanthanide complexes were prepared by treating equimolar quantities of the ligands with the appropriate nitrate salts in methanol. Double recrystallization from ethyl acetate/hexane gave the pure complexes, which were characterized by UV/Vis and IR spectroscopy, FAB^+ MS, and elemental analysis.

The Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes of the ligands **1** and **2** were found to be chemically and photochemically stable in methanolic solution, in line with expectation con-

Table 1. Absorption and luminescence properties of the Eu^{3+} and Tb^{3+} complexes in methanol solutions

	Absorption		Luminescence					
	λ_{max} [nm]	ε_{max} [M^{-1} cm^{-1}]	τ(300 K, OH) [ms]	Φ(300 K, OH)	τ(300 K, OH) [ms]	Φ(300 K, OH)	τ(77 K, OH) [ms]	τ(77 K, OH) [ms]
[Eu(**1**)]$^{3+}$	260	28000	0.69	0.19	0.69[a]	0.19	0.67	0.68[b]
[Eu(**2**)]$^{3+}$	260	36000	0.68	0.11	0.68	0.10	0.68	0.69
[Tb(**1**)]$^{3+}$	260	28500	–	–	–	–	0.85	0.86
[Tb(**2**)]$^{3+}$	262	36200	–	–	–	–	0.76	0.76

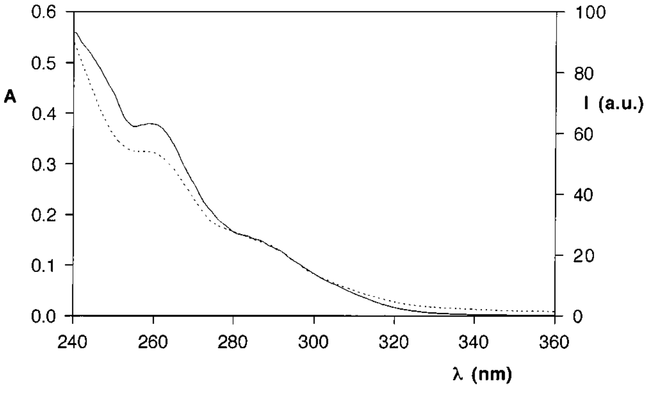
[a] 0.76 ms for the deuterated ligand; for more details, see text. – [b] 0.77 ms for the deuterated ligand; for more details, see text.

sidering the better complexation properties of the $bpyO_2$ groups compared with those of the bpy ligand.[22] Good stabilities were also observed in aqueous solution, although the solubilities in water were somewhat lower. For this reason, all the photophysical data collected in Table 1 were obtained using methanolic solutions. The absorption spectra of all the complexes are dominated by the bands of the $bpyO_2$ groups {see, for example, Figure 1 for [Eu(**1**)]$^{3+}$}, which are characterized by high molar absorption coefficients and cover the absorption bands due to the calixarene moieties, which lie in the same spectral region and have typically much lower absorption coefficients (of the order of 10^3 M^{-1} cm^{-1}).[10][11][12][13][14][15][16][17][18]

Room temperature excitation of the Gd complexes did not lead to any appreciable luminescence. At 77 K, a weak, structured phosphorescence band was observed {τ = 2.1 and 2.2 ms for [Gd(**1**)]$^{3+}$ and [Gd(**2**)]$^{3+}$, respectively}, the highest energy feature of which peaked at 475 nm.

Upon excitation in the absorption bands of the ligand, the Eu^{3+} complexes showed a very intense metal-centered luminescence {Φ = 0.19 and 0.11 for [Eu(**1**)]$^{3+}$ and [Eu(**2**)]$^{3+}$, respectively, see Table 1}, with a rather short lifetime. Neither the lifetimes nor the quantum yields showed any noticeable change upon deuteration of the solvent or lowering of the temperature (Table 1). The metal luminescence excitation spectra were very similar to the absorption spectra {see, for [Eu(**1**)]$^{3+}$, Figure 1}.

Figure 1. Absorption (full line) and metal luminescence excitation (λ_{em} = 615 nm, dotted line) spectra of a $1.4 \cdot 10^{-5}$ M methanolic solution of [Eu(**1**)]$^{3+}$



In contrast to the aforementioned observations for the Eu^{3+} complexes, the corresponding Tb^{3+} complexes did not exhibit any appreciable metal-centered luminescence at room temperature when excited in the absorption bands of the ligand. However, at 77 K, a quite intense luminescence from the Tb^{3+} ion was again observed (Table 1). Excitation spectra recorded under these conditions were very similar to the absorption spectra of the Tb^{3+} complexes.

Discussion

Gd^{3+} Complexes

The absence of low-energy, metal-centered (MC) excited states in the Gd complexes is often exploited for investigating the behaviour of the ligand-centered (LC) excited states in a structure identical to other lanthanide complexes.[23] For the complexes of ligands **1** and **2**, the absence of a fluorescence band, both at room temperature and at 77 K, prevents us from estimating the energy of the $^1\pi\pi^*$ LC level, while from the highest energy feature of the phosphorescence band observed at 77 K the zero-zero energy of the $^3\pi\pi^*$ LC level is found to be 21000 cm^{-1}.

Eu^{3+} Complexes

The similarity between the absorption and metal luminescence excitation spectra for all the complexes suggests that energy transfer from the $bpyO_2$ groups to the metal ion takes place. On the other hand, it is very difficult to evaluate the efficiency of the energy transfer process from the calixarene moiety because of its low absorption coefficient. The efficiency of the energy transfer from the $bpyO_2$ groups, together with the radiative and non-radiative rate constants of the luminescent $^5D_0$ Eu^{3+} level, can be estimated from the luminescence data collected in Table 1.[21][22][23][24]

The overall rate constant Σk for the decay of the luminescent $^5D_0$ Eu^{3+} level can be expressed by Eq. 1,

$$\Sigma k = 1/\tau = k_r + k_{nr} \qquad (1)$$

where k_r is the (temperature-independent) radiative rate constant and k_{nr} is the non-radiative rate constant. The non-radiative rate constant can be further divided into two terms; the first one, $k_{nr}(T)$, being temperature-dependent, which plays a role when short-lived, high-lying excited states are thermally accessible, and the second one, k'_{nr}, accounting for the phonon-assisted deactivation to the ground state. Usually, the most significant contribution to the temperature-independent term comes from the decay through coupling with high-energy vibrations of the solvent (O−H vibration in water and methanol solutions), $k_{nr}(OH)$, while the contribution from the coupling with other vibrations, k_{nr} (other vibr.), is usually small.

$$\Sigma k = 1/\tau = k_r + k_{nr}(T) + k_{nr}(OH) + k_{nr}(\text{other vibr.}) \qquad (2)$$

In rigid matrices of deuterated methanol or water at 77 K, $k_{nr}(T)$ and $k_{nr}(OH)$ can be neglected, and Eq. 2 becomes

$$\Sigma k\ (77\ K, OD) = 1/\tau(77\ K, OD) = k_r + k_{nr}(\text{other vibr.}) \qquad (3)$$

where τ(77 K, OD) is the lifetime measured at 77 K in deuterated solvents.

With the usual assumption that k_{nr}(other vibr.) can be neglected, k_r becomes equal to 1/τ(77 K, OD). In the present case, the values of k_r calculated in this way are 1470 and 1450 s^{-1} for $[Eu(\mathbf{1})]^{3+}$ and $[Eu(\mathbf{2})]^{3+}$, respectively. It is important to note at this point that these values are very high compared with those observed for other Eu^{3+} complexes,[6] for which the radiative rate constants lie in the range 350−900 s^{-1}. In fact, we thought it very unlikely that $[Eu(\mathbf{1})]^{3+}$ and $[Eu(\mathbf{2})]^{3+}$ could have such markedly different radiative rate constants compared to the previously observed values for complexes with many different ligands. As a first hypothesis, we thought that the OH groups present on the lower rim of the calixarene macrocycles, which point towards the metal ions, might, at least in part, be responsible for a non-negligible value of the term k_{nr} (other vibr.) in our systems. Considering the $k_{nr}(OH)$ values reported in the literature for Eu complexes, it is apparent that these contain a contribution of ca. 1000 s^{-1} per coordinated water molecule or ca. 500 s^{-1} per coordinated methanol molecule, i.e. ca. 500 s^{-1} per OH oscillator.[6][24][25] For the $[Eu(\mathbf{1})]^{3+}$ complex, where two OH oscillators are present in the ligand, a value of ca. 1000 s^{-1} for k_{nr}(other vibr.) could, in principle, be expected. In order to assess this hypothesis, we synthesized the Eu^{3+} complex with ligand **3**, possessing OD groups, since NMR measurements in deuterated methanol have shown that there is no exchange between the hydrogen of the OH groups of the complex and the deuterium atoms of the solvent. The observed lifetime of this complex in deuterated methanol was 0.76 ms at room temperature and 0.77 ms at 77 K. From Eq. 3, for the complex with the deuterated ligand, the term $k_r + k_{nr}$(other vibr.) becomes equal to 1300 s^{-1}. This value, although lower than that observed for the non-deuterated ligand, is still high, indicating that other oscillators present in the ligand might be responsible for the non-radiative deactivation to the ground state besides the OH groups. By comparison with the value obtained with the non-deuterated ligand, we can estimate that the contribution to the non-radiative rate constant attributable to the OH group is 170 s^{-1}. This contribution, although not negligible, shows that the OH groups are rather distant in relation to the metal ion. A similar contribution in the analogous complex possessing bpy groups instead of the $bpyO_2$ groups is consistent with the lifetime observed in acetonitrile solutions.[19]

The values of k_{nr}(300 K) and $k_{nr}(OH)$ can be estimated from the measured luminescence lifetimes (Table 1) according to Eqs. 4 and 5.

$$k_{nr}(300\ K) = 1/\tau(300\ K, OD) - 1/\tau(77\ K, OD) \qquad (4)$$

$$k_{nr}(OH) = 1/\tau(300\ K, OH) - 1/\tau(300\ K, OD) \qquad (5)$$

The calculated values are very low (< 50 s^{-1}) for both the complexes, showing that no solvent molecules are coordinated to the central metal ion and that thermally activated processes (typically, for Eu^{3+} complexes, ligand-to-metal charge-transfer processes) do not play a significant role in these systems, as previously reported for other complexes containing $bpyO_2$ groups.[26]

The efficiency of the ligand-to-metal energy-transfer process (η_{et}) is usually estimated from Eq. 6, with the assumption that k_{nr}(other vibr.) is negligible. In the present case, as discussed above, it is reasonable to consider this assumption as being less than fully adequate; the efficiency calculated from this equation is thus just a limiting value, and is found to be 0.19 and 0.11 for $[Eu(\mathbf{1})]^{3+}$ and $[Eu(\mathbf{2})]^{3+}$, respectively.

$$\eta_{et} = \Phi_l \cdot \tau(300\ K, OH)/\tau(77\ K, OD) \qquad (6)$$

A quite large difference is observed between the ligand-to-metal energy-transfer efficiencies estimated for $[Eu(\mathbf{1})]^{3+}$ and $[Eu(\mathbf{2})]^{3+}$. We believe that this difference is due to the greater conformational rigidity of ligand **2**, in which the additional calixarene moiety prevents the $bpyO_2$ groups from maximizing their interaction with the central metal ion.

A comment has to be made regarding the coordination number at the central metal ion. Ligands **1** and **2** provide a smaller number of donor atoms than that usually required by Eu^{3+} ions. While the photophysical data allow us to exclude coordination of the metal ion by solvent molecules, coordination by some counterions cannot be ruled out, although no changes were observed in the luminescence spectra and lifetime on replacing the nitrate by chloride anions. It is likely that anions are coordinated in the solid state, as often observed in lanthanide X-ray structures.[27]

Tb^{3+} Complexes

The lack of a metal-centered luminescence on exciting the ligand-centered band of $[Tb(\mathbf{1})]^{3+}$ and $[Tb(\mathbf{2})]^{3+}$ at room temperature is not surprising, since the low-lying (21000 cm^{-1}) triplet excited state of the $bpyO_2$ groups allows, as previously observed for other complexes,[6][22] an efficient non-radiative deactivation of the metal emitting state, via back energy transfer to the ligand. This process is no longer kinetically feasible at 77 K, where a strong metal luminescence is again observed (see Table 1). In this case, a detailed examination of the rate constants of all the processes occurring after excitation in the ligand-centered band is prevented by the aforementioned lack of room temperature metal-centered luminescence, although again a very large value of k_r can be estimated from Eq. 3, as observed for the Eu^{3+} complexes of this series. A contribution to the overall rate constant by the OH and other oscillators present in the ligands can also be invoked in this case.

Conclusion

Ligands **1** and **2**, containing $bpyO_2$ subunits, form Tb^{3+} and Eu^{3+} complexes that are stable in coordinating solvents such as methanol and water, and which show intense absorption bands in the UV region. The Tb^{3+} complexes, however, do not show any appreciable metal-centered luminescence at room temperature, presumably because of an efficient back energy transfer to the ligand. For the Eu^{3+} complexes, this process is not thermodynamically feasible, and a strong metal-centered luminescence appears on exciting the ligand-centered absorption bands. Interestingly, this luminescence is not affected by the temperature or by deuteration of the solvent, showing that the ligands efficiently shield the metal ion from solvent interaction, and that thermally activated processes do not play a significant role in these complexes. A small but non-negligible contribution to the non-radiative deactivation to the ground state due to the OH oscillators present in the ligand has been demonstrated.

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Experimental Section

General Methods: Nuclear magnetic resonance spectra were recorded at room temperature with Bruker SY-200 or AC-200 instruments operating at 200.1 MHz for ^1H. ^1H-NMR chemical shifts are reported in parts per million (ppm) relative to the proton residues in the solvents ($\delta = 7.26$ for $CDCl_3$). − Fast-atom bombardment (FAB, positive mode) spectra were recorded with a ZAB-HF-VB analytical apparatus with *m*-nitrobenzyl alcohol (*m*-NBA) as the matrix; Ar atoms were used for the bombardment (8 keV). All relevant patterns exhibited the expected isotopic profiles, as compared with simulated profiles. Electrospray mass spectra (ES-MS) were recorded with a Bio-Q analytical apparatus, in acetone solution, using grammicidim as internal standard. − Routine absorption spectra were measured in CH_3CN solutions at room temperature using a Kontron Uvikon 941 spectrophotometer. − FT-IR spectra were measured in KBr pellets or in solution with KBr cells with a Bruker IFS 25 spectrometer. − The molecular formulae given, as well as the purities of the samples, were assessed on the basis of ^1H-NMR, FAB^+-MS or ES-MS, and elemental analysis data.

Materials: p-tert-Butylcalix[4]arene[28], 5-bromomethyl-5′-methyl-2,2′-bipyridine *N*,*N*′-dioxide[28], and 5,5′-bromomethyl-2,2′-bipyridine *N*,*N*′-dioxide[29] were prepared according to literature procedures. Alumina (Merck), potassium carbonate (Prolabo), NaH (Fluka), europium(III) nitrate hexahydrate (Janssen), terbium(III) nitrate hexahydrate (Ventron), and gadolium(III) nitrate pentahydrate (Janssen) were obtained commercially as indicated.

Ligand **1**: A solution of *tert*-butylcalix[4]arene (0.500 g, 0.77 mmol) and potassium carbonate (0.817 g, 7.71 mmol) in dry acetonitrile (30 ml) was heated at 80°C for 30 min, after which solid 5-bromomethyl-5′-methyl-2,2′-bipyridine *N*,*N*′-dioxide (0.477 g, 1.62 mmol) was added. The mixture was heated at 80°C for 1 d and then quenched with water. Extraction with dichloromethane (5 × 50 ml), drying of the combined organic layers over magnesium sulfate, twofold chromatography (on alumina, using dichloromethane/methanol, 9:1, as eluent), and finally recrystallization from dichloromethane/hexane gave the analytically pure title compound (0.390 g, 47%) ($R_f = 0.55$, dichloromethane/methanol, 96:4, v/v). − ^1H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.62$ (s, 2 H), 8.10 (s, 2 H), 7.79 (s, 4 H), 7.55 (d, 2 H, $^3J = 8.1$ Hz), 7.14 (d, 2 H, $^3J = 8.1$ Hz), 7.05 (s, 4 H, Ar-*H* calix.), 6.98 (s, 2 H, O*H*), 6.81 (s, 4 H, Ar-*H* calix.), 5.04 (s, 4 H, bipy-CH_2-O), 3.75 (AB q, 8 H, $J_{AB} = 13.1$ Hz, $\Delta\nu = 168.5$ Hz, Ar-CH_2-Ar calix.), 2.30 (s, 6 H, bipy-CH_3), 1.28 (s, 18 H, *t*Bu), 0.95 (s, 18 H, *t*Bu). − IR (KBr): $\tilde{\nu} =$ 3408, 3049, 2958, 2868, 1688, 1602, 1484, 1393, 1364, 1278, 1201, 1171, 1123, 1025, 953, 872, 816 cm^{-1}. − UV/Vis (CH_3CN): λ (ε) = 264 (43100), 216 nm (103300 $M^{-1}cm^{-1}$). − FAB^+ MS (*m*-NBA): *m/z* = 1077.5 $[M + H]^+$, 1061.5 [M − O], 1045.5 [M − 2 O], 1029.5 [M − 3 O]. − $C_{68}H_{76}O_8N_4 \cdot H_2O$ ($M_r = 1077.38 + 18.01$): calcd. C 74.56, H 7.18, N 5.11; found C 74.52, H 7.13, N 5.08.

Ligand **2**: A mixture of *tert*-butylcalix[4]arene (0.473 g, 0.73 mmol) and potassium carbonate (0.387 g, 2.80 mmol) in dry acetonitrile (50 ml) was heated at 80°C for 30 min. After cooling to room temperature, 5,5′-bromomethyl-2,2′-bipyridine *N*,*N*′-dioxide (0.300 g, 0.80 mmol) was added and the suspension was heated overnight at 80°C. The solvent was then removed in vacuo and the organic products were extracted with dichloromethane (5 × 50 ml). Analytically pure compound **2** was obtained after twofold chromatography (alumina, dichloromethane/methanol, 9:1) and recrystallization from dichloromethane/hexane (0.469 g, 37%) ($R_f = 0.66$, dichloromethane/methanol, 96:4, v/v). − ^1H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.70$ (s, 4 H), 7.97 (d, 4 H, $^3J = 8.1$ Hz), 7.77 (d, 4 H, $^3J = 8.1$ Hz), 7.09 (s, 8 H, Ar-*H* calix.), 7.03 (s, 4 H, O*H*), 6.82 (s, 8 H, Ar-*H* calix.), 5.11 (s, 8 H, bipy-CH_2-O), 3.81 (AB q, 16 H, $J_{AB} = 13.3$ Hz, $\Delta\nu = 172.2$ Hz, Ar-CH_2-Ar calix.), 1.31 (s, 36 H, *t*Bu), 0.94 (s, 36 H, *t*Bu). − IR (KBr): $\tilde{\nu} =$ 3435, 3052, 2959, 2867, 1726, 1602, 1484, 1398, 1362, 1268, 1199, 1114, 1024, 953, 872, 811 cm^{-1}. − UV/Vis (CH_3CN): λ (ε) = 284 (45000), 220 nm (76900 $M^{-1}cm^{-1}$). − FAB^+ MS (*m*-NBA): *m/z* = 1723.0 $[M + H]^+$, 1706.0 [M − O], 1690.0 [M − 2 O], 1674.0 [M − 3 O]. − $C_{112}H_{128}O_{12}N_4 \cdot 2\ H_2O$ ($M_r = 1722.28 + 32.02$): calcd. C 76.51, H 7.57, N 3.19; found C 76.40, H 7.51, N 3.12.

Ligand **3**: To a solution of the calix[4]arene-25,27-diol **1** (0.065 g, 0.06 equiv.) in freshly distilled dimethylformamide (20 ml) was added sodium hydride in its commercial form (60%, 0.0036 g). The mixture was heated at 60°C overnight, after which D_2O was added. The solvent was removed and the analytically pure product was obtained after recrystallization from dichloromethane/hexane (0.040 g, 61%). − ^1H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.62$ (s, 2 H), 8.10 (s, 2 H), 7.79 (s, 4 H), 7.56 (d, 2 H, $^3J = 8.1$ Hz), 7.11 (d, 2 H, $^3J = 8.1$ Hz), 7.06 (s, 4 H, Ar-*H* calix.), 6.81 (s, 4 H, Ar-*H* calix.), 5.06 (s, 4 H, bipy-CH_2-O), 3.75 (AB q, 8 H, $J_{AB} = 13.1$ Hz, $\Delta\nu = 168.5$ Hz, Ar-CH_2-Ar calix.), 2.33 (s, 6 H, bipy-CH_3), 1.29 (s, 18 H, *t*Bu), 0.95 (s, 18 H, *t*Bu). − IR (KBr): $\tilde{\nu} =$ 3404, 3051, 2958, 2864, 1602, 1484, 1393, 1364, 1278, 1201, 1171, 1120, 1026, 955, 872, 814 cm^{-1}. − UV/Vis (CH_3CN): λ (ε) = 262 (42600), 215 nm (104600 $M^{-1}cm^{-1}$). − FAB^+ (*m*-NBA): *m/z* =

1079.2 [M + H]$^+$, 1063.2 [M − O], 1047.3 [M − 2 O], 1031.2 [M − 3 O]. − $C_{68}H_{74}D_2O_8N_4$ (M_r = 1079.39): calcd. C 75.67, H 6.91, N 5.19; found C 75.39, H 6.68, N 5.02.

General Procedure for the Synthesis of Lanthanide Complexes: To a solution of the appropriate ligand (0.020 g, 1 equiv.) in methanol (10 ml) was added the lanthanide salt (1.1 equiv.). The mixture was stirred at 60°C overnight and then allowed to cool to room temperature. In the case of the nitrate salts, the lanthanide complexes precipitated during the course of the reaction. The solvent was removed in vacuo and the solid was recrystallized twice from ethyl acetate/hexane. The analytically pure complexes were obtained in 75−92% yield.

*[Eu(**1**)]$(NO_3)_3$: Yield: 88%. − IR (KBr): ṽ = 3445, 3059, 2959, 2867, 1632, 1487, 1383, 1271, 1200, 1165, 1113, 1030, 955, 875, 828 cm^{-1}*. − FAB$^+$ (*m*-NBA): *m/z* = 1353.3 [M − NO_3]$^+$, 1337.3 [M − NO_3 − O], 1321.3 [M − NO_3 − 2O], 1290.3 [M − 2 NO_3 + H], 1227.3 [M − 2 NO_3 − 4 O]. − $C_{68}H_{76}O_{17}N_7Eu\cdot 5\ H_2O$ (M_r = 1415.36 + 90.07): calcd. C 54.25, H 5.76, N 6.51; found C 54.11, H 5.62, N 6.42.

*[Tb(**1**)]$(NO_3)_3$:* Yield: 71%. − IR (KBr): ṽ = 3436, 2959, 2865, 1631, 1487, 1383, 1273, 1200, 1164, 1113, 1031, 983, 877, 829 cm^{-1}. − FAB$^+$ (*m*-NBA): *m/z* = 1358 [M − 2 H − NO_3]$^+$, 1296 [M − 2 NO_3 − 2 H], 1235 [M − 2 NO_3 − H], 1281 [M − 2 NO_3 − H − O], 1265 [M − 2 NO_3 − 2 O − H]. − $C_{68}H_{76}O_{17}N_7Tb\cdot 5\ H_2O$ (M_r = 1422.32 + 90.07): calcd. C 54.00, H 5.73, N 6.48; found C 54.12, H 5.82, N 6.42.

*[Gd(**1**)]$(NO_3)_3$:* Yield: 95%. − IR (KBr): ṽ = 3415, 2959, 1631, 1486, 1383, 1271, 1199, 1164, 1110, 1032, 827, 827 cm^{-1}. − FAB$^+$ (*m*-NBA): *m/z* = 1358 [M − NO_3]$^+$, 1296 [M − 2 NO_3], 1234 [M − 3 NO_3], 1264 [M − 2 NO_3 − 2 O]. − $C_{68}H_{76}O_{17}N_7Gd\cdot 5\ H_2O$ (M_r = 1420.65 + 90.07): calcd. C 54.06, H 5.74, N 6.49; found C 53.91, H 5.62, N 6.35.

*[Eu(**2**)]$(NO_3)_3$:* Yield: 78%. − IR (KBr): ṽ = 3417, 2960, 2869, 1728, 1631, 1486, 1384, 1302, 1199, 1120, 1032, 983, 954, 875, 821 cm^{-1}. − FAB$^+$ (*m*-NBA): *m/z* = 1998.1 [M − NO_3]$^+$, 1982.1 [M − NO_3 − O], 1966.1 [M − NO_3 − 2 O], 1934.1 [M − NO_3 − 4 O], 1872.0 [M − 2 NO_3 − 4 O]. − $C_{112}H_{128}O_{21}N_7Eu\cdot 4\ H_2O$ (M_r = 2060.26 + 72.06): calcd. C 63.09, H 6.43, N 4.60; found C 63.05, H 6.32, N 4.31.

*[Tb(**2**)]$(NO_3)_3$:* Yield: 75%. − IR (KBr): ṽ = 3408, 2959, 1631, 1485, 1383, 1301, 1197, 1112, 1032, 875, 821 cm^{-1}. − FAB$^+$ (*m*-NBA): *m/z* = 2004 [M − NO_3]$^+$, 1942 [M − 2 NO_3], 1908 [M − 2 NO_3 − 2 O − H]. − $C_{112}H_{128}O_{21}N_7Tb\cdot 5\ H_2O$ (M_r = 2067.20 + 90.07): calcd. C 62.36, H 6.45, N 4.54; found C 62.23, H 6.30, N 4.38.

*[Gd(**2**)]$(NO_3)_3$:* Yield: 92%. − IR (KBr): ṽ = 3406, 2960, 2868, 1631, 1486, 1384, 1300 (ν_{NO}), 1197, 1115, 1032, 875, 820 cm^{-1}. − FAB$^+$ (*m*-NBA): *m/z* = 2002 [M − NO_3]$^+$, 1940 [M − 2 NO_3], 1878 [M − 3 NO_3]. − $C_{112}H_{128}O_{21}N_7Gd\cdot 5\ H_2O$ (M_r = 2065.55 + 90.07): calcd. C 62.41, H 6.45, N 4.55; found C 62.38, H 6.30, N 4.28.

*[Eu(**3**)]$(NO_3)_3$:* To a solution of ligand **3** (0.040 g, 0.04 mmol) in CD_3CN (5 ml) in a Schlenk tube in a drybox was added $Eu(CF_3SO_3)_3$ (1.1 equiv.). The sealed tube was then heated at 60°C for 3 h. During the course of the reaction, the complex precipitated. When the reaction was complete, an excess of anhydrous, degassed pentane was added to insine precipitation of most of the product, which was then taken up in methanol/ethyl acetate. The resulting solution was filtered through Celite and diffusion of hexane into the filtrate afforded the analytically pure compound. Yield: 65%. − IR (KBr): ṽ = 3473, 2974, 2959, 1632, 1487, 1396, 1271, 1160, 1099, 1045, 880 cm^{-1}. − FAB$^+$ (*m*-NBA): *m/z* = 1529.0 [M − CF_3SO_3]$^+$, 1380.1 [M − 2 CF_3SO_3], 1348.2 [M − 2 CF_3SO_3 − 2 O], 1316.2 [M − 2 CF_3SO_3 − 4 O]. − $C_{71}H_{74}D_2O_{17}N_4S_3F_9Eu\cdot CH_3OH$ (M_r = 1678.551 + 32.042): calcd. C 51.52, H 4.68, N 3.33; found C 51.28, H 4.52, N 3.02.

Spectroscopic Measurements: The solvents employed for photophysical measurements were methanol (Merck UVASOL) and CH_3OD (99.8 atom-% from Fluka), which were used without further purification. Absorption spectra were recorded with a Perkin-Elmer lambda 16 spectrophotometer. Uncorrected emission, corrected excitation spectra, and phosphorescence lifetimes were obtained with a Perkin-Elmer LS 50 spectrofluorimeter.

Luminescence quantum yields (uncertainty ±15%) were determined using quinine sulfate (Φ = 0.546[30] in 1 N H_2SO_4 aqueous solution) for Tb^{3+} and $[Ru(bpy)_3]^{2+}$ (Φ = 0.028 in aerated water[31]) for Eu^{3+} as standards. In order to permit comparisons of emission intensities, corrections for instrument response, inner filter effects, and phototube sensitivity were made.[32] A correction for differences in the refraction indices was introduced where necessary. Emission spectra at 77 K were obtained in a rigid, opaque methanol matrix using quartz tubes immersed in a quartz Dewar vessel filled with liquid nitrogen.

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