Calix[4]arene Podands and Barrelands Incorporating 2,2′-Bipyridine Moieties and Their Lanthanide Complexes: Luminescence Properties

Gilles Ulrich, Raymond Ziessel,* Ilse Manet, Massimo Guardigli, Nanda Sabbatini, Franca Fraternali, and Georges Wipff

Abstract: A new family of cone-shaped podands and barrel-shaped cryptands based on calix[4]arenes incorporating 5,5′-substituted 2,2′-bipyridine subunits were prepared and characterized. The Eu^{3+} and Tb^{3+} complexes of the podands bearing two, three, or four bipyridine chromophores could be isolated. High molar absorption coefficients ($\varepsilon_{max} = 39600\,M^{-1}cm^{-1}$ for **Eu4** and $26700\,M^{-1}cm^{-1}$ for **Eu3**) and high metal luminescence quantum yields (16% for **Eu4** and 15% for **Eu3**) were obtained. Molecular dynamics simulations on **Eu4** showed that the bipyridine arms wrap around the lanthanide cation, efficiently shielding the cation from solvent molecules. In the presence of chloride counterions the fourth bipyridine arms does not coordinate the lanthanide ion. Ligands bearing two bipyridine units and two additional functional groups—ethyl butyrate or *N*-propylpyrrole—did not give stable lanthanide complexes. The barreland containing two calix[4]arene moieties and four bipyridine groups did not form complexes with lanthanide ions, most probably because of the rigidity of the ligand.

Keywords
calixarenes · lanthanides · luminescence · molecular dynamics · N ligands

Introduction

Complexation of Eu^{3+} and Tb^{3+} ions by encapsulating ligands has been extensively studied in the last few years.[1–5] In these complexes metal luminescence can result from a light conversion process consisting of ligand absorption (**A**), ligand-to-metal energy transfer (**ET**), and metal luminescence (**E**) (Figure 1). The main interest in these studies is due to the fact that the Eu^{3+} and Tb^{3+} ions possess long-lived luminescent states and exhibit line-like emission in the visible region. As a result, their complexes can act as valuable labels in bioaffinity assays based on time-resolved luminescence measurements, since they can enhance the sensitivity of the assay by minimizing interference of the short-lived, background luminescence in the UV region of the biological species.[6, 7]

Among the encapsulating ligands used for Eu^{3+} and Tb^{3+} complexation, functionalized calixarenes constitute an important class. For example, the Eu^{3+} and Tb^{3+} complexes of the *p-tert*-butylcalix[4]arene–tetraacetamide ligand[8] are stable in water. The Tb^{3+} complex is strongly luminescent in aqueous solution, while the Eu^{3+} complex shows only weak emission. In order to obtain more intense metal luminescence,[9] chromophores have been attached to calixarenes to form more strongly absorbing ligands for Eu^{3+} and Tb^{3+} complexation.[10–14] In fact, efficient ligand absorption and a high quantum yield for metal luminescence are necessary to obtain high metal luminescence intensity, which is the quantity of interest for the above-mentioned application. The Eu^{3+} and Tb^{3+} complexes of a calix[4]arene bearing four pyridine-*N*-oxide units as chromophores have been shown to exhibit metal luminescence upon ligand excitation in methanol.[10] The same is true for almost all Eu^{3+} and Tb^{3+} complexes of calixarenes with phenyl and diphenyl substituents as chromophores.[11, 12]

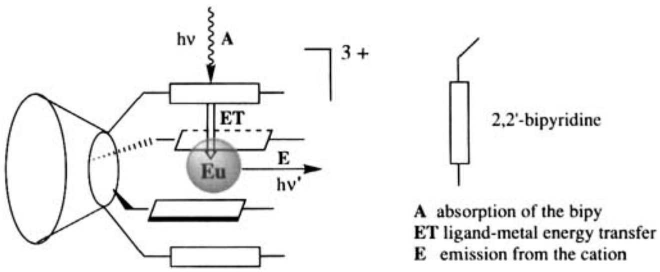

Figure 1. Luminescence process in a Eu^{3+}–podand complex.

Despite the important opportunities offered by appropriately functionalized oligopyridine ligands in metal complexation, calix[4]arene substituted with 2,2′-bipyridine (bipy) molecules have

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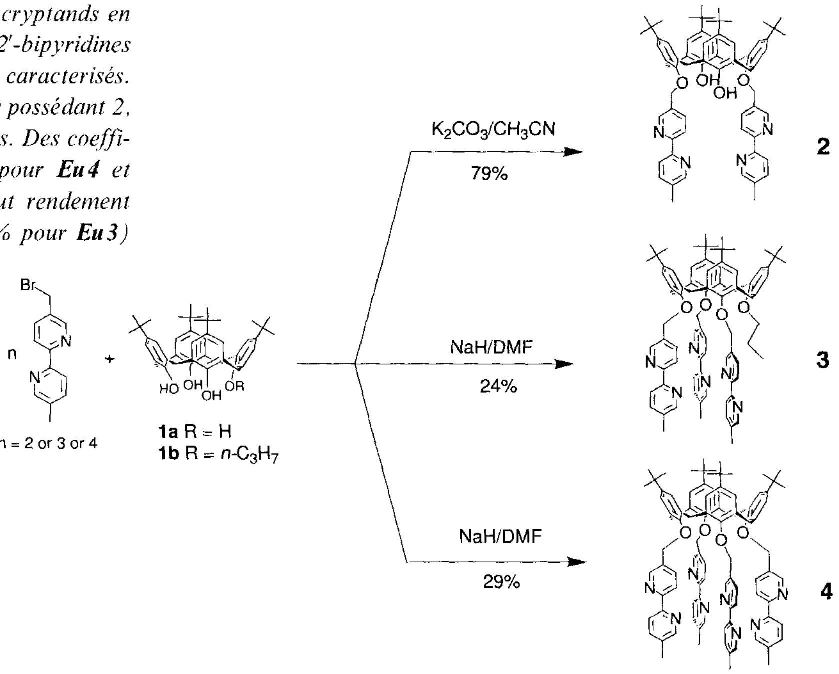
only recently been synthesized.[13–18] Ligands containing two bipy's and two amides or four bipy's, with the bipy's ligated to the calix[4]arene moiety through C^6 (*ortho* position of the pyridine nitrogen), have been prepared.[13, 14] These ligands form 1:1 complexes with Eu^{3+} and Tb^{3+} ions in acetonitrile, and metal luminescence is obtained upon bipy excitation. The syntheses of ligands with 2,2'-bipyridine units attached to the calixarene moiety through C^5 (*meta* position of the pyridinic nitrogen) have recently been reported in a preliminary communication.[19] In this case, the bipyridine was attached in the *meta* position to the calixarene to avoid steric hindrance around the complexed lanthanide ion, and kinetically inert complexes were produced as a result. Here we give a full account of the synthesis of these new ligands and of the luminescence properties of their corresponding lanthanide complexes together with some molecular dynamics calculations.

Abstract in French: *Une nouvelle famille de podands dérivés du calix[4]arène en conformation cône ainsi que des cryptands en forme de tonnelet, tous possédant des sous-unités 2,2'-bipyridines substituées en position 5 et 5' ont été synthétisés et caracterisés. Les complexes d'Eu^{3+} et de Tb^{3+} avec des podands possédant 2, 3 ou 4 chromophores (bipyridines) ont pu être isolés. Des coefficients d'extinction molaire élevés ($\varepsilon_{max} = 39600$ pour* ***Eu4*** *et $26700\,M^{-1}cm^{-1}$ pour* ***Eu3****), ainsi qu'un très haut rendement quantique de luminescence (16% pour* ***Eu4*** *et 15% pour* ***Eu3****) ont été obtenus. Les ligands possédant des unités bipyridine et deux groupes fonctionnels supplémentaires (éthylbutyrate ou propyl-N-pyrrole) ne forment pas de complexes stables avec des ions lanthanides. La présence de deux plate-formes calix[4]arène et de quatre groupes bipyridines dans le calixbarreland impose une grande rigidité, ce qui empêche la diffusion du lanthanide dans la cavité de l'hôte. Des calculs de dynamique moléculaire pour* ***Eu4*** *ont montré que les bras bipyridines enveloppent les cations de lanthanide, ce qui les protègent efficacement des interactions avec le solvant. En présence d'un anion, seulement trois bras bipyridines attachés sur la sous-unité calixarène participent à la complexation du cation.*

Abstract in Italian: *Sono stati preparati e caratterizzati nuovi podandi e criptandi basati su calix[4]areni in conformazione a cono, contenenti come cromofori unità 2,2'-bipiridile sostituite in 5 e 5'. I complessi di Eu^{3+} e Tb^{3+} dei podandi contenenti 2, 3 e 4 cromofori sono stati isolati. Essi mostrano elevati coefficienti di estinzione molare ($\varepsilon_{max} = 39600\,M^{-1}cm^{-1}$ per* ***Eu4*** *e $\varepsilon_{max} = 26700\,M^{-1}cm^{-1}$ per* ***Eu3****) e alti rendimenti quantici di luminescenza del metallo (16% per* ***Eu4*** *e 15% per* ***Eu3****). Simulazioni di dinamica molecolare per il complesso* ***Eu4*** *indicano che nei complessi i cromofori bipiridilici circondano lo ione lantanide proteggendolo dall'interazione con il solvente. In presenza di anioni, soltanto tre unità bipiridilici partecipano alla complessazzione dello ione lantanide. I leganti contenenti due unità bipiridile e due gruppi etilbutirrato o propil-N-pirrolo non formano complessi stabili con gli ioni lantanidi. Lo stesso accade per il criptando contenente due unità calix[4]arene e quattro gruppi bipiridilici, probabilmente a causa della rigidità del legante.*

Results and Discussion

Podands **2**–**4** were prepared by adapting the synthesis for 1,3-disubstituted calix[4]arene ethers or tetrasubstituted calix[4]arene ethers in a cone conformation (Scheme 1).[20] For the synthesis of the compound bearing three bipy subunits, a monopropylcalix[4]arene was used in order to fix the cone conformation of the resulting polysubstituted compound.[21]

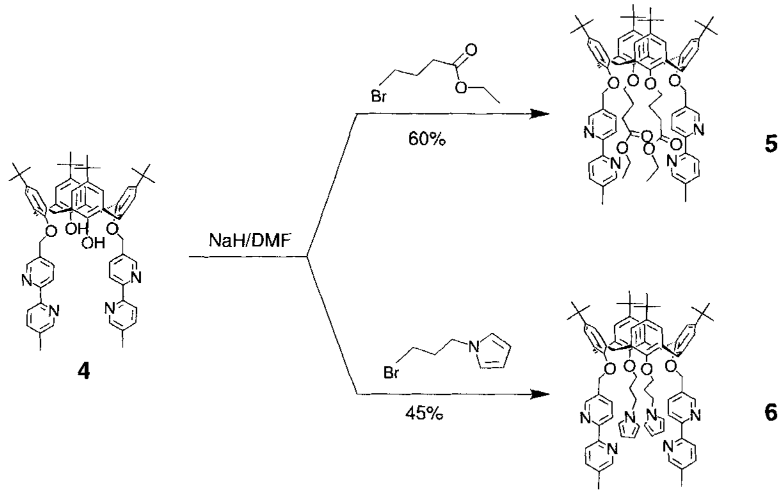


Scheme 1.

The reaction of tetra(*tert*-butyl)calix[4]arene **1a**[22] with 2.2 equiv of 5-bromomethyl-5'-methyl-2,2'-bipyridine in anhydrous acetonitrile, in the presence of K_2CO_3 (5 equiv) as the base, afforded ligand **2** in 79% yield. The ^1H NMR spectrum of **2** shows the characteristic single AB system for the bridging methylene groups, a singlet for the OCH_2bipy moieties, and two singlets for the phenyl protons. In the $^{13}C\{^1H\}$ NMR spectrum, the signal for the bridging methylene groups appears at $\delta = 31.8$, clearly indicating a cone structure and a 1,3-distal substitution pattern of the calix[4]arene.[23, 24]

Reaction of **1a** with NaH in anhydrous dimethylformamide and then with 5-bromomethyl-5'-methyl-2,2'-bipyridine resulted in the formation of ligands **3** in 24% yield. An analogous reaction starting from propoxycalix[4]arene **1b**[16] led to **4** in 29% yield. The ^1H NMR spectra show two AB systems for ligand **3** and a single AB system for **4**, corresponding to the bridging methylene groups; two singlets for **3** and one singlet for **4**, assigned to the OCH_2bipy moieties; and three singlets for **3** and one singlet for **4**, corresponding to the phenyl protons. In the $^{13}C\{^1H\}$ NMR spectra, the bridging methylene groups appear as two signals at $\delta = 31.5$ and 31.4 for **3** and as one signal at $\delta = 31.4$ for **4**. Both spectra clearly indicate a cone conformation of the calix[4]arene moiety and its substitution with three and four bipy's in ligands **3** and **4**, respectively.

Hybrid podands **5**–**6** were prepared in a similar manner to that described above (Scheme 2) by treating ligand **2** with NaH in anhydrous DMF and then with ethyl 4-bromobutyrate or *N*-(3-bromopropyl)pyrrole.[25] The ^1H NMR spectra of ligands **5** and **6** exhibit a single AB system for the bridging methylene groups, one singlet for the OCH_2bipy moieties, and two singlets for the phenyl protons. The $^{13}C\{^1H\}$ NMR spectra of **5** and **6** each show one signal (at $\delta = 31.5$ and 31.9, respectively) for the bridging methylenes. The spectroscopic data unambigously indicate that the cone conformation is retained during alkylation in both cases.



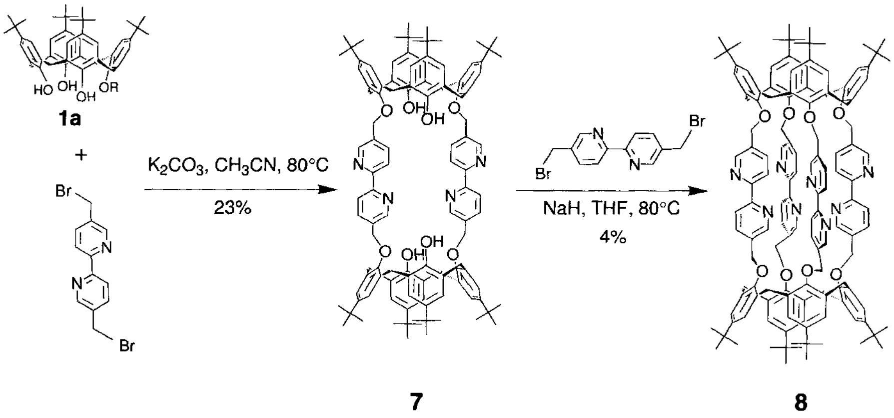
Scheme 2.

Cage-type molecules, commonly named calixbarrelands,[19] were synthesized as depicted in Scheme 3. Reaction of **1a** with 1.1 equiv of 5,5′-bis(bromomethyl)-2,2′-bipyridine[26] in anhydrous acetonitrile with K_2CO_3 (5 equiv) as base afforded ligand **7** in 23% yield. Reaction of semibarreland **7** with NaH in anhydrous THF and then with 5,5′-bis(bromomethyl)-2,2′-bipyridine (2.2 equiv) gave calix[4]barreland **8** in low yield (4%). Compound **8** could not be prepared directly from the sodium tetraanion of *p-tert*-butylcalix[4]arene. High-dilution conditions are not required for the synthesis of molecules **7** and **8**. A template effect of potassium could not be excluded in the case of **7**, even though cryptands free of alkali metals were isolated at the end of the reaction. The yield for the bifunctional alkylation process leading to **8** is low because side-reactions (polymerization, cross-linking, etc.) compete with the intramolecular closure. To the best of our knowledge, calixbarreland **8**, obtained from the semibarreland **7**, is the first tetrabridged cage molecule based on biscalix[4]arenes connected through the lower rims. The appropriate choice of spacer module (methylene groups attached to the 5,5′ positions of the 2,2′-bipyridine) is crucial for the success of cyclizations connecting the lower rims, as recently reviewed in the literature.[27]

The ^1H NMR spectra of **7** and **8** show the characteristic single AB system for the bridging methylene groups, a singlet for the OCH_2bipy moieties, and two singlets in **7** and one singlet in **8** for the phenyl protons. The $^{13}C\{^1H\}$ NMR spectra of **7** and **8** each show one signal for the bridging methylenes at $\delta = 31.9$ and 33.6, respectively. Both spectra clearly indicate a symmetrical environment of the bipyridine subunit, a cone conformation, and a 1,3-distal substitution pattern of the calix[4]arenes in **7** and complete alkylation of the phenol groups in **8**.

The Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes of ligands **2**–**4** and **7** were prepared by reaction of equimolar quantities of the ligands and the lanthanide salts in a methanol/dichloromethane mixture. The complexes decomposed in water and methanol, but were stable in anhydrous acetonitrile, with the exception of the lanthanide complexes of semibarreland **7**, which slowly decomposed in most solvents. The photophysical properties were therefore studied in acetonitrile for lanthanide complexes of ligands **2**–**4**.

Surprisingly, solid samples of lanthanide complexes of ligands **5**, **6**, and **8** could not be isolated. This might be explained by the fact that the appended ethyl butyrate or *N*-propylpyrrole substituents in **5** and **6**, respectively, force the chelating bipy subunits apart,[28] thus markedly decreasing the complexation ability of the latter. In ligand **8** the two calix[4]arene moieties and the four bridging bipy's produce a rigid system, which inhibits diffusion of the lanthanide ion into the cavity. Molecular dynamics simulations on the Eu^{3+} complex of calixbarreland **8** show that it is thermodynamically stable, and that the complexation does not induce significant strain in the ligand, which wraps perfectly around the metal ion, while the counterions are situated in its second coordination shell (Figure 2, top). However, diffusion of the cation into the cavity to form the complex is probably prevented by a high kinetic barrier, related to the separation of the cation from the counterions and to the rigidity of the ligand. Some flexibility, absent in calixbarreland **8**, may be required to lower this energetic barrier so as to allow complex formation.



Scheme 3.

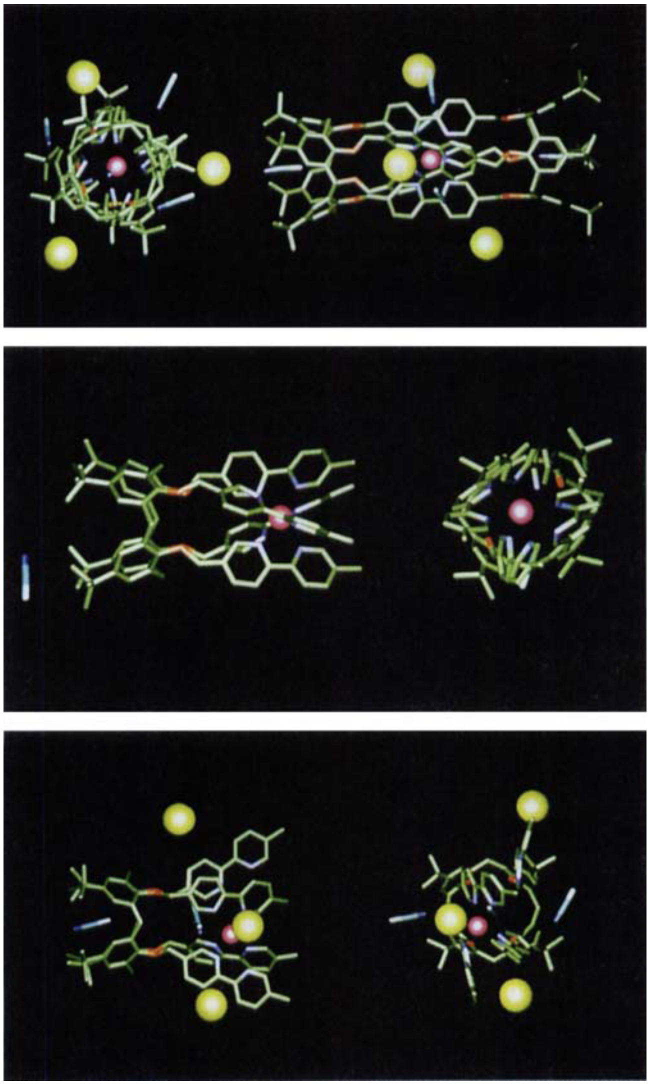


Figure 2. The $EuCl_3$ complex of **8** (top), and the Eu^{3+} (middle) and $EuCl_3$ (bottom) complexes of **4**, after 200 ps of MD simulation in acetonitrile (orthogonal views are shown in each case).

The absorption spectra of **2** (Figure 3), **3**, and **4** (Figure 4) are dominated by the typical features of the π→π* transitions of the bipy chromophore, characterized by high molar absorption coefficients proportional to the number of bipy units. Complexation of the lanthanide ion by these ligands results in a red shift of the absorption maxima and in a decrease of the molar absorption coefficients, as has been observed previously for lanthanide complexes of other encapsulating ligands containing the bipy chromophore.[1] For each ligand, the absorption spectra of the Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes coincide completely and are characterized by high molar absorption coefficients. Comparison of the absorption spectra of the complexes of these ligands shows that the spectra of **2** differ from those of **3** and **4**. In particular, the absorption spectra of **2** show a single band with maximum at 310 nm, typical for the complexed bipy moiety. The presence of a multicomponent band centered at 300 nm in the absorption spectra of **3** and **4** suggests that the bipy units interact differently with the metal ion, probably because of steric hindrance. For the complexes of each ligand, the absorption spectra and metal luminescence excitation spectra obtained upon ligand excitation are similar (Figures 3 and 4). This indicates that all the bipy units are involved in the ligand-to-metal energy transfer.

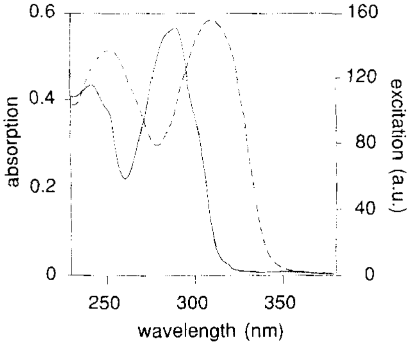


Figure 3. Absorption spectra of ligand **2** (——) and **Eu2** (·····), and metal luminescence excitation spectrum of **Eu2** (-·-·-) in anhydrous acetonitrile.

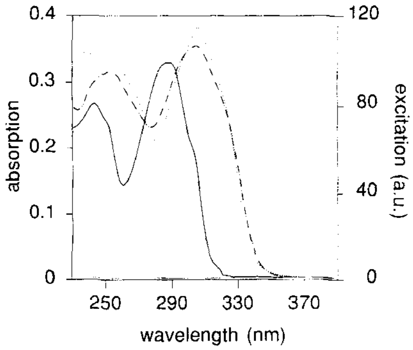


Figure 4. Absorption spectra of ligand **4** (——) and **Eu4** (·····), and metal luminescence excitation spectrum of **Eu4** (-·-·-) in anhydrous acetonitrile.

The lifetimes of the metals emitting from the $^5D_4$ state of the Tb^{3+} complexes of ligands **2**–**4** (Table 1) are rather short, and the metal luminescence quantum yields obtained upon bipy excitation are very low. The decay curves of the metal emitting state of these complexes at 300 K are nonexponentional and

Table 1. Photophysical data in anhydrous acetonitrile [a].

	Absorption		Emission [b]		
Complex	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	τ (ms)	τ^{77K} (ms)	Φ
Eu2	310	22500	1.20	1.30	0.03
Tb2	310	23400	0.15 0.70	1.07	0.001
Eu3 [c]	305	26700	1.60	1.00	0.15
Tb3	305	31500	0.15 0.80	1.07	0.002
Eu4	305	39600	1.60	1.30	0.16
Tb4	305	42800	0.25 0.80	0.98	0.007

[a] Data were obtained at 300 K, unless otherwise noted. [b] Excitation of the ligand was performed at the λ_{max} values indicated in this table; the lifetimes were measured from the $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_5$ emissions for Eu^{3+} and Tb^{3+}, respectively. [c] Values were obtained in the presence of tetraethylammonium nitrate added to dissolve the complex completely.

give a satisfactory fit with a biexponential equation. The nonexponential decay may be due to the presence of a small amount of free Tb^{3+} in solution. Even though the free Tb^{3+} ions have very low molar absorption coefficients at the excitation wavelength, their luminescence could interfere with the lifetime measurement of the Tb^{3+} complexes, owing to the very low metal luminescence quantum yield of these complexes. In analogy with previous studies, we investigated whether the low quantum yield and lifetime values are due to nonradiative deactivation of the Tb^{3+} $^5D_4$ emitting state by means of back-energy transfer to the lowest ligand triplet excited states. To this end, the ligand phosphorescence spectra of the Gd^{3+} complexes were recorded; the lowest energy values obtained for the ligand triplet excited states are about 22200 cm^{-1}. Considering that the energy of the Tb^{3+} $^5D_4$ emitting state is 20400 cm^{-1}, this value seems too high to allow efficient metal-to-ligand back-energy transfer. However, in these cases, the 77 K value may not be appropriate because the energies of the ligand excited states depend on the mode of complexation. Considering the flexible nature of ligands **2**–**4**, complexation at 300 K may be different from that at 77 K. The presence of ligand-to-metal back-energy transfer cannot therefore be excluded.

In contrast to the Tb^{3+} complexes, the Eu^{3+} complexes are characterized by rather high lifetime and quantum yield values. It is interesting that the lifetimes of **Eu3** and **Eu4** are similar to and their quantum yields greater than the corresponding values observed for **Eu2**. The higher complexation constants for **2**, suggested by spectral data, should result in a more efficient metal–ligand interaction, which is a determining factor for the metal luminescence quantum yield. Therefore, nonradiative deactivation by vibronic coupling with the high-energy OH oscillators present in **2** may be responsible for the lower values of **Eu2**. Interestingly, the lifetimes of **Eu3** and **Eu4** are very similiar to those of other Eu^{3+} complexes with encapsulating ligands containing the bipy chromophore, studied in solvents that do not contain high-energy oscillators.[1] Further, the similarity of the quantum yields of **Eu3** and **Eu4** is in agreement with the complexation characteristics of **3** and **4** deduced from the spectral data.

Molecular dynamics simulations on the **Eu4** complex in presence and absence of chloride counterions in acetonitrile solution show that the bipyridine arms wrap around the cation thereby shielding it efficiently from the solvent (Figure 2, middle and bottom). The role of the calix[4]arene moiety is to bring together the bipy subunits in order to form a kinetically stable complex. When **4** complexes the Eu^{3+} ion in absence of counterions, all four bipy's are coordinated to the cation. However, in the presence of counterions, the complex spontaneously relaxes to a form in which only three bipy's are coordinated; one bipy is forced apart from the Eu center and one anion coordinates directly the cation (Figure 2, bottom). Thus, interaction between cation and anion also contributes towards preventing direct solvent coordination to the cation. The MD simulations suggest that the introduction of the fourth bipy unit should not improve the complexation ability of **4** with respect to **3**. The MD simulations are in agreement with the experimental results, which show that the Eu^{3+} complexes of ligands **3** and **4** have similar properties, such as lifetime and quantum yield values.

Conclusion

In comparison with the Eu^{3+} and Tb^{3+} prototype complexes of *p-tert*-butylcalix[4]arene–tetraacetamide, the present Eu^{3+} complexes show luminescence intensities enhanced by up to four orders of magnitude, as a result of their higher molar absorption coefficients and quantum yields. Conversely, for the Tb^{3+} complexes, luminescence intensities (and corresponding emission quantum yields) are low, in spite of the high molar absorption coefficients. Analysis of the metal luminescence intensity as a function of the chromophores attached to the calix[4]arene moiety reveals that the highest molar absorptions are obtained for complexes of **4** containing four bipy units. With regard to the quantum yields, there was no difference between complexes of ligands containing three or four bipy units. It is worthwhile noting that Eu^{3+} complex of **4** is characterized by one of the highest values for metal luminescence intensity among the Eu^{3+} and Tb^{3+} complexes of encapsulating ligands containing the bipy chromophore.

The trapping of a lanthanide cation during the synthesis of the barrel-shaped cryptand (by a template effect) before the cavity is locked is expected to lead to a kinetically inert and thermodynamically stable complex, which may have outstanding luminescence properties.

Experimental Section

General: UV/Vis spectra: Shimatzu UV-260 or Perkin-Elmer Lambda 5 spectrophotometer. FT-IR spectra: Bruker IFS25 spectrometer; KBr pellets. NMR spectra: at RT unless otherwise noted; Bruker-SY-200 or AC-200 [200.1 MHz (^1H) or 50.3 MHz (^{13}C)]; δ(H) in ppm rel. to the solvent $CDCl_3$ ($\delta = 7.25$); δ(C) in ppm rel. to the solvent $CDCl_3$ ($\delta = 77.0$). MS: fast-atom bombardment (FAB, positive mode ZAB-HF-VG-Analytical apparatus in a *m*-nitrobenzyl alcohol (*m*-NBA) matrix unless otherwise specified.

Materials: NBS (Fluka), AIBN (Janssen), SiO_2 (Merck), alumina (Merck), potassium carbonate (Prolabo), NaH (Fluka), europium(III) nitrate hexahydrate (Janssen), europium(III) chloride hexahydrate (Janssen), terbium(III) nitrate hexahydrate (Ventron), terbium(III) chloride hexahydrate (Janssen), gadolinium(III) nitrate pentahydrate (Janssen), gadolinium(III) chloride hexahydrate (Janssen), ethyl 4-bromobutyrate (Aldrich).

Spectroscopic measurements: The solvents used for the photophysical measurements were acetonitrile (99.8%, Merck UVASOL) and anhydrous acetonitrile (99.9%, ROMIL). Tetraethylammonium nitrate was obtained from FLUKA (99%). The UV/Vis absorption spectra were measured with a Perkin-Elmer Lambda 6 spectrophotometer. The luminescence spectra were obtained with a Perkin-Elmer LS 50 spectrofluorimeter. The decay of the metal emitting state was recorded with a Perkin-Elmer LS 50 spectrofluorimeter and analyzed with a least-squares fitting program. The luminescence quantum yields were obtained by the method described by Haas and Stein[29] with the standards $[Ru(bipy)_3]^{2+}$ ($\Phi = 0.028$ in aerated water[30]) for the Eu^{3+} complex and quinine sulfate ($\Phi = 0.546$ in H_2SO_4 1 N[31]) for the Tb^{3+} complex. The measured values were corrected for the refraction index.[32]

Molecular dynamics calculations: MD simulations were performed on the Eu^{3+} and $EuCl_3$ complexes of **4** and **8** with the AMBER 4.0 package and the AMBER force field,[33] with Eu^{3+} represented as described in ref. [34]. The noncovalent interactions were calculated by using a 1–6–12 potential with a residue based cut-off of 10 Å. The atomic charges on the ligand were taken from previous studies on calixarenes[35] and on bipyridine-containing helicate molecules.[36] The acetonitrile molecules were represented with the OPLS parameters,[37] in a cubic box of about 30 Å in length, using periodic boundary conditions. The MD simulations were performed at 300 K, with a time step of 1 fs and SHAKE on solvent molecules and X–H bonds. The starting structures were modelled with Eu^{3+} equidistant from the bipyridine nitrogen atoms. Counterions were added at 6–7 Å from Eu^{3+}, in a plane perpendicular to the C_4 symmetry axis. After immersion in solution followed by a conjugate gradient energy minimization, MD simulations were run first for 20 ps keeping the solute rigid in order to allow for the solvent relaxation around the complex. This was followed by 200 ps of free MD simulations.

5,11,17,23-Tetra(*tert*-butyl)-26,28-bis[5-methyl-2,2′-bipyridine-5′-yl)methoxy]-calix[4]arene-25,27-diol (2): A solution of *tert*-butylcalix[4]arene (**1a**) (0.5 g, 0.77 mmol) and potassium carbonate (0.532 g, 3.85 mmol) in dry acetonitrile (30 mL) was heated at 80 °C during 30 min, after which 5-bromomethyl-5-methyl-2,2′-bipyridine (0.445 g, 1.69 mmol) was added as a solid. The mixture was heated for one day at 80 °C, and then quenched with water. Extraction with dichloromethane (3 × 50 mL), drying of the organic layers over magnesium sulfate, and chromatography (silica treated with triethylamine, ethyl acetate/toluene, 1:1) gave the analytically pure title compound (0.61 g, 78%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.85 (d, 2H, ^4J = 1.8 Hz), 8.42 (m, 4H), 8.26 (d, 2H, ^3J = 8.1 Hz), 8.13 (dd, 2H, ^3J = 8.1 Hz, ^4J = 2 Hz), 7.50 (dd, 2H, ^3J = 8.1 Hz, ^4J = 2.0 Hz), 7.11 (s, 1H, OH calix), 7.08 (s, 1H, OH calix), 7.04 (s, 4H, Ar-H calix), 6.80 (s, 4H, Ar-H calix), 5.16 (s, 4H, bipy-CH_2-O), 3.75 (AB quartet, 8H, J_{AB} = 13.1, $\Delta\nu$ = 193.6 Hz, Ar-CH_2-Ar calix), 2.35 (s, 6H, bipy-CH_3), 1.28 (s, 18H, *t*Bu), 0.96 (s, 18H, *t*Bu); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ = 156.0, 153.4, 150.5, 149.4, 148.4, 147.2, 141.6, 137.3, 136.6, 133.1, 132.5, 132.1, 127.6, 125.7, 125.0, 120.8, 120.7, 75.4, 33.9, 33.8, 31.8, 31.7, 31.4, 30.9, 18.3; IR (KBr): $\tilde{\nu}$ = 3397, 2956, 1655, 1466, 1194, 1123 cm^{-1}; UV (CH_2Cl_2): λ (ε) = 290 (44900), 230 nm (36300 $M^{-1}cm^{-1}$); FAB$^+$ (*m*-NBA): *m/z* = 1013 $[M+H]^+$, 831 $[M - CH_2bipyCH_3 + 2H]$, 647 $[M - 2(CH_2bipyCH_3) + H]$; Anal. calcd for $C_{68}H_{76}O_4N_4$ (M_r = 1013.38): C, 80.60; H, 7.56; N, 5.53. Found: C, 80.48; H, 7.38; N, 5.37.

5,11,17,23-Tetra(*tert*-butyl)-26,27,28-tris{(5-methyl-2,2′-bipyridine-5′-yl)-methoxy}-25-propoxycalix[4]arene (3): To a solution of 5,11,17,23-tetra(*tert*-butyl)-25-propoxycalix[4]arene (**1b**) (0.2 g, 0.29 mmol) in freshly distilled DMF (10 mL) was added sodium hydride in its commercial form (55% in oil, 0.063 g). The mixture was heated at 80 °C overnight, after which solid 5′-bromomethyl-5-methyl-2,2′-bipyridine (0.305 g, 1.15 mmol) was added. The mixture was heated 3 d at 80 °C, and then quenched with water. Extraction with dichloromethane, drying of the organic layers over magnesium sulfate, and short chromatography (alumina, ethyl acetate/toluene, 1:9) gave the analytically pure title compound, which was recrystallized in dichloromethane/hexane (0.085 g, 24%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.78 (d, 2H, ^4J = 1.5 Hz), 8.60 (d, 1H, ^4J = 1.6 Hz), 8.45 (s, 3H), 8.25 (dd, 4H, ^3J = 8.1 Hz, ^4J = 3.0 Hz), 8.17 (d, 2H, ^3J = 8.1 Hz), 7.72 (dd, 2H, ^3J = 4.1 Hz, ^4J = 2.0 Hz), 7.54 (d, 4H, ^3J = 8.1 Hz), 6.81 (d, 4H, ^4J = 2.2 Hz, Ar-H calix), 6.72 (d, 2H, ^4J = 2.2 Hz, Ar-H calix), 6.68 (d, 2H, ^4J = 2.2 Hz, Ar-H calix), 5.02 (s, 2H, bipy-CH_2-O), 4.96 (s, 2H, bipy-CH_2-O), 4.91(s, 2H, bipy-CH_2-O), 3.74 (t, 2H, ^3J = 7.8 Hz, O-CH_2-CH_2), 3.66 (AB quartet, 4H, J_{AB} = 12.5 Hz $\Delta\nu$ = 255.7 Hz, Ar-CH_2-Ar), 3.49 (AB quartet, 4H, J_{AB} = 12.6 Hz, $\Delta\nu$ = 236.8 Hz, Ar-CH_2-Ar), 2.36 (s, 9H, bipy-CH_3), 1.87 (sext, 2H, ^3J = 7.7 Hz, CH_2-CH_2-CH_3), 1.12 (s, 9H, *t*Bu), 1.10 (s, 9H, *t*Bu), 1.03 (s, 18H, *t*Bu), 0.80 (t, 3H, ^3J = 7.4 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ = 155.7, 155.5, 153.6, 152.1, 150.4, 149.5, 145.2, 145.0, 144.6, 138.1, 137.9, 137.5, 137.4, 134.2, 134.1, 133.7, 133.5, 133.3, 133.2, 133.0, 125.4, 125.3, 125.1, 120.8, 120.0, 119.9, 76.5, 74.2, 73.7, 33.9, 31.5, 31.4, 23.5, 16.4, 10.2; IR (KBr): $\tilde{\nu}$ = 2960, 1599, 1466, 1194, 1122 cm^{-1}; UV (CH_2Cl_2): λ (ε) = 284 (64700), 223 nm (57100 $M^{-1}cm^{-1}$); FAB$^+$ (*m*-NBA): *m/z* = 1237 $[M+H]^+$, 1055 $[M - CH_2bipyCH_3 + 2H]$, 871 $[M - 2(CH_2bipyCH_3) + H]$; Anal. calcd for $C_{83}H_{92}O_4N_6$ (M_r = 1237.64): C, 80.55; H, 7.49; N, 6.79. Found: C, 80.38; H, 7.30; N, 6.59.

5,11,17,23-Tetra(*tert*-butyl)-25,26,27,28-tetra(5-methyl-2,2′-bipyridine-5′-methoxy)calix[4]arene (4): To a solution of 5,11,17,23-tetra(*tert*-butyl)-calix[4]arene (**1a**) (0.1 g, 0.154 mmol) in freshly distilled DMF (10 mL) was added sodium hydride in its commercial form (55% in oil, 0.035 g). The mixture was heated at 80 °C overnight, after which 5-bromomethyl-5-methyl-2,2′-bipyridine (0.185 g, 0.693 mmol) was added. The subsequent mixture was heated 3 d at 80 °C, and then quenched with water. Extraction with dichloromethane, drying of the organic layers over magnesium sulfate, removal of the solvent under vacuum, followed by chromatography (silica treated with triethylamine, ethyl acetate/toluene, 2:8) gave the analytically pure title compound, which was recrystallized in dichloromethane/hexane (0.63 g, 29%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.75 (s, 4H), 8.41 (s, 4H), 8.18 (d, 8H, ^3J = 8.1 Hz), 7.61 (d, 4H, ^3J = 9.5 Hz), 7.54 (d, 4H, ^3J = 8.1 Hz), 6.78 (s, 8H, Ar-H calix), 4.92 (s, 8H, bipy-CH_2-bipy), 3.51 (AB quartet, 8H, J_{AB} = 12.3 Hz, $\Delta\nu$ = 242.7 Hz, Ar-CH_2-Ar), 2.36 (s, 12H, bipy-CH_3), 1.07 (s, 36H, *t*Bu); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ = 155.4, 153.5, 151.8, 150.3, 149.3, 145.2, 137.7, 137.3, 133.9, 133.1, 125.2, 120.7, 119.8, 74.1, 33.8, 31.4, 31.1, 18.3; IR (KBr): $\tilde{\nu}$ = 2959, 1600, 1469, 1194, 1123 cm^{-1}; UV (CH_2Cl_2): λ (ε) = 290 (69500), 230 nm (56200 $M^{-1}cm^{-1}$); FAB$^+$ (*m*-NBA): *m/z* = 1377 $[M+H]^+$, 1195 $[M - CH_2bipyCH_3 + 2H]$, 1013 $[M - 2(CH_2bipyCH_3) + 3H]$); Anal. calcd for $C_{92}H_{96}O_4N_8$ (M_r = 1377.842): C, 80.20; H, 7.02; N, 8.13. Found: C, 80.06; H, 6.96; N, 7.99.

General Procedure for the Synthesis of the lanthanides complexes of ligands 2, 3, and 4: To a solution of ligand (0.10 g, 1 equiv) in CH_2Cl_2 (3 mL) was added a lanthanide solution (1.1 equiv) in MeOH (3 mL). The mixture was stirred at 60 °C overnight and then cooled to room temperature. The solvent was removed under vacuum, and the solid was twice recrystallized from ethyl acetate/pentane for the nitrate salts and ethanol/ether for the chloride salts. The analytically pure complexes were obtained in 51 to 91% yields for the nitrate and 60 to 70% yields for the chloride.

[{5,11,17,23-Tetra(*tert*-butyl)-26,28-bis{(5-methyl-2,2′-bipyridine-5′-yl)-methoxy}calix[4]arene-25,27-diol}europium(III)]$(NO_3)_3$ (Eu2): Yield: 91%; IR (KBr): $\tilde{\nu}$ = 2959, 1653, 1482, 1384, 1313, 1030 cm^{-1}; FAB$^+$ (*m*-NBA): *m/z* = 1288 $[M - NO_3]^+$, 1227 $[M - 2NO_3]$; Anal. calcd for $C_{68}H_{76}O_{13}N_7Eu \cdot 4H_2O$ (M_r = 1351.636 + 72.061): C, 57.38; H, 5.95; N, 6.89. Found: C, 57.19; H, 5.72; N, 6.71.

[{5,11,17,23-Tetra(*tert*-butyl)-26,28-bis{(5-methyl-2,2′-bipyridine-5′-yl)-methoxy}calix[4]arene-25,27-diol}terbium(III)]$(NO_3)_3$ (Tb2): Yield: 83%; IR (KBr): $\tilde{\nu}$ = 2953, 1637, 1483, 1384, 1047 cm^{-1}; FAB$^+$ (*m*-NBA): *m/z* = 1295 $[M - NO_3]^+$, 1233 $[M - 2NO_3]$, 1169 $[M - 3NO_3 - 2H]$; Anal. calcd for $C_{68}H_{76}O_{13}N_7Tb \cdot 5H_2O$ (M_r = 1358.328 + 90.076): C, 56.39; H, 5.98; N, 6.77. Found: C, 56.25; H, 5.74; N, 6.62.

[{5,11,17,23-Tetra(*tert*-butyl)-26,28-bis{(5-methyl-2,2′-bipyridine-5′-yl)-methoxy}calix[4]arene-25,27-diol}gadolinium(III)]$(NO_3)_3$ (Gd2): Yield: 71%; IR (KBr): $\tilde{\nu}$ = 2963, 1637, 1483, 1384, 1047 cm^{-1}; FAB$^+$ (*m*-NBA): *m/z* = 1294 $[M - NO_3]^+$, 1168 $[M - 3NO_3 - 2H]$; Anal. calcd for $C_{68}H_{76}O_{13}N_7Gd \cdot 4H_2O$ (M_r = 1356.653 + 72.061): C, 57.17; H, 5.93; N, 6.86. Found: C, 56.92; H, 5.74; N, 6.59.

[{5,11,17,23-Tetra(*tert*-butyl)-26,27,28-tris{(5-methyl-2,2′-bipyridine-5′-yl)-methoxy}-25-propoxy-calix[4]arene}europium(III)](Cl)$_3$ (Eu3): Yield: 63%; IR (KBr): $\tilde{\nu}$ = 1963, 1603, 1478, 1092, 1047 cm^{-1}; FAB$^+$ (*m*-NBA): *m/z* = 1459 $[M - Cl]^+$, 1424 $[M - 2Cl]$; Anal. calcd for $C_{83}H_{92}O_4N_6EuCl_3 \cdot 4H_2O$ (M_r = 1496.015 + 72.061): C, 63.58; H, 6.43; N, 5.36. Found: C, 63.41; H, 6.29; N, 5.21.

[{5,11,17,23-Tetra(*tert*-butyl)-26,27,28-tris{(5-methyl-2,2′-bipyridine-5′-yl)-methoxy}-25-propoxy-calix[4]arene}terbium(III)]$(NO_3)_3$ (Tb3): Yield: 75%; IR (KBr): $\tilde{\nu}$ = 2964, 1604, 1480, 1384, 1090, 1047 cm^{-1}; FAB$^+$ (*m*-NBA): *m/z* = 1519 $[M - NO_3]^+$; Anal. calcd for $C_{83}H_{92}O_{13}N_9Tb \cdot 4H_2O$ (M_r = 1582.636 + 72.061): C, 60.25; H, 6.09; N, 7.62. Found: C, 60.03; H, 5.86; N, 7.41.

[{5,11,17,23-Tetra(*tert*-butyl)-26,27,28-tris{(5-methyl-2,2′-bipyridine-5′-yl)-methoxy}-25-propoxycalix[4]arene}gadolinium(III)](Cl)$_3$ (Gd3): Yield: 70%: IR (KBr): $\tilde{\nu}$ = 2963, 1603, 1480, 1198, 1089, 1047 cm^{-1}; FAB$^+$ (*m*-NBA): *m/z* = 1464 $[M - Cl]^+$; Anal. calcd for $C_{83}H_{92}O_4N_6GdCl_3 \cdot 4H_2O$ (M_r = 1501.305 + 72.061): C, 63.36; H, 6.41; N, 5.34. Found: C, 63.18; H, 6.23; N, 5.12.

[{5,11,17,23-Tetra(*tert*-butyl)-25,26,27,28-tetra{(5-methyl-2,2′-bipyridine-5′-yl)methoxy}calix[4]arene}europium(III)]$(NO_3)_3$ (Eu4): Yield: 51%; IR (KBr): $\tilde{\nu}$ = 2973, 1639, 1479, 1384, 1088, 1047 cm^{-1}; FAB$^+$ (*m*-NBA): *m/z* = 1653 $[M - NO_3]^+$, 1591 $[M - 2NO_3]$; Anal. calcd for $C_{92}H_{96}O_{13}N_{11}Eu \cdot 3H_2O$ (M_r = 1715.817 + 54.046): C, 62.44; H, 5.81; N, 8.71. Found: C, 62.38; H, 5.41; N, 8.62.

[{5,11,17,23-Tetra(*tert*-butyl)-25,26,27,28-tetra{(5-methyl-2,2′-bipyridine-5′-yl)methoxy}calix[4]arene}terbium(III)]$(NO_3)_3$ (Tb4): Yield: 63%; IR (KBr):

$\tilde{\nu}$ = 2974, 1636, 1479, 1384, 1089, 1047 cm^{-1}; FAB$^+$ (*m*-NBA): m/z = 1659 [M − NO$_3$ − H]$^+$; Anal. calcd for $C_{92}H_{96}O_{13}N_{11}Tb \cdot 4H_2O$ (M_r = 1722.782 + 72.061): C, 61.57; H, 5.84; N, 8.58. Found: C, 61.53; H, 5.49; N, 8.51.

[{5,11,17,23-Tetra(*tert*-butyl)-25,26,27,28-tetra{(5-methyl-2,2′-bipyridine-5′-yl)methoxy}calix[4]arene} gadolinium(III)] Cl$_3$ (Gd4): Yield: 60%; IR (KBr): $\tilde{\nu}$ = 2975, 1638, 1479, 1261, 1088, 1048 cm^{-1}; FAB$^+$ (*m*-NBA): m/z = 1604 [M − Cl]$^+$; Anal. calcd for $C_{92}H_{96}O_4N_8GdCl_3 \cdot 3H_2O$ (M_r = 1641.451 + 54.046): C, 65.17; H, 6.06; N, 6.61. Found: C, 64.93; H, 5.91; N, 6.43.

5,11,17,23-Tetra(*tert*-butyl)-26,28-bis(5-methyl-2,2′-bipyridine-5′-methoxy)-25,27-diethoxycarbonylbutoxycalix[4]arene (5): A solution of **2** (0.1 g, 0.098 mmol) in dry DMF (5 mL) was heated overnight at 80 °C with sodium hydride in its commercial form (55% in oil, 0.01 g). Ethyl 4-bromobutyrate (0.058 g, 0.29 mmol) was then added. The solution slowly turned brown and was quenched one day later with water. All the solvent was removed, and the residue extracted with dichloromethane. The organic layers were dried over magnesium sulfate and chromatographed on alumina (toluene/ethyl acetate, 95/5) to give the expected product (0.076 g, 60%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 8.76 (d, 2H, ^4J = 1.6 Hz), 8.49 (s, 2H), 8.30 (dd, 4H, ^3J = 8.0 Hz, ^4J = 2.7 Hz), 7.81 (dd, 4H, ^3J = 8.1 Hz, ^4J = 2.1 Hz), 7.60 (dd, 4H, ^3J = 8.0 Hz, ^4J = 1.9 Hz), 6.90 (s, 4H, Ar-H), 6.62 (s, 4H, Ar-H), 4.96 (s, 4H, bipy-CH_2-O), 4.03 (quat, 4H, ^3J = 7.1 Hz, CH$_3$-CH_2-O-but), 3.80 (t, 4H, ^3J = 6.9 Hz, -CH$_2$-CH_2-O-Ar), 3.63 (8H, J_{AB} = 12.5 Hz, $\Delta\nu$ = 249.9 Hz, Ar-CH_2-Ar), 2.38 (s, 6H, bipy-CH_2-O), 2.16 (m, 8H), 1.17 (m, 24H), 0.95 (s, 18H); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 25 °C): δ = 173.7 (COO), 155.7, 153.7, 153.6, 151.7, 150.4, 149.5, 144.9, 144.8, 138.1, 137.4, 134.5, 133.3, 132.9, 125.2, 124.9, 120.7, 120.5, 120.1, 74.5, 73.9, 60.1, 33.9, 33.7, 31.5, 31.3, 31.0, 30.6, 25.2, 18.4, 14.2; FAB$^+$ (*m*-NBA): m/z = 1241 [M+H]$^+$, 1127 [M − C$_3$H$_6$COOC$_2$H$_5$ + H], 1059 [M − CH$_2$bipyCH$_3$ + H]; Anal. calcd For $C_{80}H_{96}O_8N_4$ (M_r = 1241.68): C, 77.39; H, 7.79; N, 4.51. Found: C, 77.25; H, 7.61; N, 4.45.

5,11,17,23-Tetra(*tert*-butyl)-26,28-bis(5-methyl-2,2′-bipyridine-5′-methoxy)-25,27-bis(3-(pyrrol-1-yl)propoxy)calix[4]arene (6): A mixture of **2** (0.108 g, 0.106 mmol) in dry DMF (5 mL) was heated overnight at 80 °C with sodium hydride (55% in oil, 0.024 g). *N*-(3-Bromopropyl)pyrrole (0.08 g, 0.4 mmol) was then added. The solution turned slowly brown, and was quenched one day later with water. All the solvent was removed. The residue was extracted with dichloromethane. The organic layers were washed with water, dried over magnesium sulfate, and chromatographed on alumina (toluene/ethyl acetate, 95/5) to give the expected product (0.058 g, 43%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 8.85 (d, 2H, ^4J = 1.4 Hz), 8.55 (s, 2H), 8.40 (t, 4H, ^3J = 7.7 Hz), 7.65 (m, 4H), 6.97 (s, 4H, Ar-H), 6.63 (s, 4H, Ar-H), 6.54 (t, 4H, ^4J = 2.0 Hz, H$_{3,5}$-pyrrole), 6.09 (t, 4H, ^4J = 2.0 Hz, H$_{3,4}$-pyrrole), 4.88 (s, 4H, O-CH_2-bipy), 3.80 (t, 4H, ^3J = 7.6 Hz, CH_2-pyrrole), 3.68 (t, 4H, ^3J = 6.9 Hz, CH_2-O), 3.65 (8H, J_{AB} = 12.4 Hz, $\Delta\nu$ = 238.5 Hz, Ar-CH_2-Ar), 2.41 (s, 6H, bipy-CH$_3$), 2.20 (q, 4H, ^3J = 7.4 Hz, CH$_2$-CH_2-CH$_2$-O), 1.24 (s, 18H, *t*Bu), 0.98 (s, 18H, *t*Bu); ^{13}C{^{1}H} NMR JMod (CDCl$_3$): δ = 156.0 (C$_{quat}$), 153.5 (C$_{quat}$), 153.3 (C$_{quat}$), 151.1 (C$_{quat}$), 150.3 (CH), 149.7 (CH), 145.0 (C$_{quat}$), 144.9 (C$_{quat}$), 137.9 (CH), 137.5(CH), 134.5 (C$_{quat}$), 133.5 (C$_{quat}$), 132.7 (C$_{quat}$), 132.6 (C$_{quat}$), 125.4 (CH), 124.9 (CH), 120.7 (CH), 120.5 (CH), 120.2 (CH), 107.9 (CH), 74.4 (CH$_2$), 72.1 (CH$_2$), 46.5 (CH$_2$), 33.9 (C$_{quat}$), 33.7 (C$_{quat}$), 31.9 (CH$_2$), 31.5 (CH$_3$), 31.2 (CH$_3$), 31.1 (CH$_2$), 29.7 (CH$_2$), 18.3 (CH$_3$); FAB$^+$ (*m*-NBA): m/z = 1227 [M]$^+$, 1045 [M − CH$_2$bipyCH$_3$ + H]; Anal. calcd for $C_{82}H_{94}O_4N_6$ (M_r = 1227.70): C, 80.22; H, 7.72; N, 6.85. Found: C, 80.09; H, 7.64; N, 6.74.

Calix[4]semibarreland (7): A mixture of *tert*-butylcalix[4]arene (1.000 g, 1.54 mmol) with potassium carbonate (0.82 g) in dry CH$_3$CN (100 mL) was heated for 30 min at 80 °C and then cooled. 5,5′-Dibromomethyl-2,2′-bipyridine (0.580 g, 1.69 mmol) was poured into the solution, and then heated overnight at 80 °C. The solvent was removed under vacuum, and the organic products extracted with dichloromethane. The pure product was obtained after chromatography on alumina (toluene/ethyl acetate, 8:2) (0.29 g, 23%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 9.07 (d, 4H, ^4J = 1.3 Hz, H$_{6,6'}$-bipy), 8.92 (d, 4H, ^3J = 8.1 Hz, H$_{3,3'}$-bipy), 8.27 (dd, 4H, ^3J = 8.2 Hz, ^4J = 1.9 Hz, H$_{4,4'}$-bipy), 7.37 (s, 4H, OH), 7.09 (s, 8H, Ar-H), 6.88 (s, 8H, Ar-H), 5.17 (s, 8H, O-CH_2-bipy), 3.87 (AB quartet, 16H, J_{AB} = 13.0, $\Delta\nu$ = 184.7 Hz, Ar-CH_2-Ar), 1.32 (s, 36H, *t*Bu), 1.01 (s, 36H, *t*Bu); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 25 °C): δ = 156.1, 150.7, 149.9, 147.9, 147.4, 141.5, 136.0, 132.7, 132.5, 127.4, 125.7, 125.0, 121.6, 75.5, 34.0, 33.8, 31.9, 31.7, 31.0; IR (KBr): $\tilde{\nu}$ = 3401, 2959, 1656, 1599, 1483, 1203, 1124 cm^{-1}; UV (CH$_2$Cl$_2$): λ (ε) = 290 (68400), 231 nm (66900 M^{-1}cm^{-1}); FAB$^+$ (*m*-NBA): m/z = 1657 [M+H]$^+$; Anal. calcd for $C_{112}H_{128}O_8N_4$ (M_r = 1658.29): C, 81.12; H, 7.78; N, 3.38. Found: C, 81.01; H, 7.53; N, 3.21.

Calix[4]barreland (8): A solution of **7** (0.2 g, 0.13 mmol) and NaH in oil (0.024 g, 0.5 mmol) in dry THF (15 mL) was heated for 2 h at 80 °C. A solution of 5,5′-dibromomethyl-2,2′-bipyridine (0.09 g, 0.27 mmol) in dry THF (20 mL) was then added dropwise to the mixture. After a 1 d heating, the solution was quenched with water, evaporated to dryness, and then extracted with toluene. Chromatography on alumina (toluene/ethyl acetate, 95:5), followed by recrystallization from a CH$_2$Cl$_2$/hexane mixture enabled us to obtain the pure title compound as a white powder (0.01 g, 4%). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 8.52 (s, 8H, H$_{6,6'}$-bipy), 8.05 (d, 8H, ^3J = 8.3 Hz, H$_{3,3'}$-bipy), 7.60 (d, 8H, ^3J = 8.2 Hz, H$_{4,4'}$-bipy), 6.82 (s, 16H, Ar-H), 4.67 (s, 16H, bipy-CH_2-O), 4.00 (AB quartet, 16H, J_{AB} = 12.9, $\Delta\nu$ = 230.1 Hz, Ar-CH_2-Ar), 1.10 (s, 72H, *t*Bu); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 25 °C): δ = 156.7, 155.0, 151.9, 146.5, 139.7, 134.8, 134.3, 127.4, 122.7, 75.7, 35.6, 33.6, 33.0, 31.5; IR (KBr): $\tilde{\nu}$ = 2957, 1656, 1600, 1477, 1192, 1124 cm^{-1}; UV (CH$_2$Cl$_2$): λ (ε) = 284 (63100), 230 nm (72100 M^{-1}cm^{-1}); FAB$^+$ (*m*-NBA): m/z = 2019 [M+H]$^+$; Anal. calcd for $C_{136}H_{144}O_8N_8$ (M_r = 2018.712): C, 80.91; H, 7.19. Found: C, 81.28; H, 7.01.

[{Calix[4]semibarreland (7)}europium(III)](NO$_3$)$_3$ (Eu7): To a solution of **7** (0.02 g, 0.012 mmol) in dichloromethane (3 mL) was added a methanolic solution (2 mL) of Eu(NO$_3$)$_3 \cdot$6H$_2$O (0.0059 g, 0.013 mmol). The mixture was then heated at 80 °C during 5 h. After evaporation of the solvents, the complex was recrystallized from a diethyl ether/hexane mixture to give the desired complex (0.02 g, 76%). FAB$^+$ (*m*-NBA): m/z = 1933 [M − NO$_3$]$^+$, 1871 [M − 2NO$_3$]; Anal. calcd for $C_{112}H_{128}O_{17}N_7Eu \cdot 6H_2O \cdot CH_2Cl_2$ (M_r = 1996.266 + 108.092 + 84.933): C, 62.00; H, 6.54: N, 4.48. Found: C, 62.05; H, 6.27; N, 4.52.

Acknowledgements: This work was supported by the Centre National de la Recherche Scientifique, by the Engineer School of Chemistry (ECPM), by MURST (Ministero dell'Università e della Ricerca Scientifica e Tecnologica), and by the Progetto Strategico "Tecnologie Chimiche Innovative (Sottoprogetto A)" of CNR (Consiglio Nazionale delle Ricerche). F. F. and W. G. thank the EU (CHRX-CT94-0484) for a grant and IDRIS for allocation of computer resources.

Received: April 28, 1997 [F679]

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