Biscalix[4]arene Ligands for *Dinuclear* Lanthanide Ion Complexation

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Three types of *lower-lower rim* linked biscalix[4]arenes that contain carboxylic ester (**1**) and/or amide functions (**2** and **3**) at their remaining phenolic oxygen atoms were synthesized. The homo- and heterodinuclear lanthanide ion complexes based on these ligands were used to study the energy transfer between different lanthanide ions. Photophysical studies comparing the luminescence properties of the homodinuclear Eu^{3+} complex and the heterodinuclear Eu^{3+}-Nd^{3+} complex of **2** indicated that energy transfer is likely to occur from Eu^{3+} to Nd^{3+} with an efficiency of > 50%. The luminescence properties turned out to be strongly solvent dependent, which is attributed to structural changes leading to different positions of the lanthanide ions in the cavities provided by the biscalix[4]arene.

Introduction

The research concerning luminescence properties of lanthanide ion complexes is mainly focused on the shielding of lanthanide ions from effective quenchers in the first coordination sphere[1]. Recently, we have shown that also the encapsulating ligand can contribute significantly to luminescence quenching[2]. The absorption coefficients of lanthanide ions are low compared to organic molecules and efficient excitation is therefore not possible[1a]. This problem can be overcome by making use of organic sensitizers that are efficiently excited and that transfer the excitation energy to the lanthanide ions[3]. The same principle is applied in lasers and optical amplifiers by making use of Yb^{3+} ions as a codopant. The broad absorption band of Yb^{3+} with a high absorption coefficient relative to other lanthanide ions renders more efficient excitation of Yb^{3+} possible. The excited Yb^{3+} ions transfer their energy to another lanthanide ion, which emits light in a wavelength region that is of interest for certain applications, e.g. Er^{3+} can be used for optical amplification at 1.55 μm[4]. The excitation efficiency is largely increased by making use of organic sensitizers, since the absorption coefficients of organic sensitizers are 3–4 orders of magnitude larger than the absorption coefficient of Yb^{3+}. However, the use of this energy transfer process in the current telecommunication network renders energy transfer studies from one lanthanide ion to another important. Until now inorganic matrices were used for optical amplifiers, but organic molecules may provide more versatile systems. For that reason heterodinuclear organic complexes were designed in which the intra-lanthanide ion-ion distance is relatively short (< 13 Å). To perform energy transfer studies, the direct excitation of exclusively the donor ion is preferred over sensitized excitation via the ligand. The energy transfer studies can be performed by either detection of the luminescence of the acceptor lanthanide ion after excitation of the donor ion[5], or by a decrease in lifetime of the luminescent excited state of the donor ion due to the presence of the acceptor ion[6]. The latter method is most frequently used because it is easy. The ultimate goal of this study is the application of organic lanthanide ion complexes in optical amplifiers that are compatible with polymeric waveguides. Despite the commonly used Yb^{3+}-Er^{3+} combination in optical amplifiers, in our work the combination Eu^{3+}-Nd^{3+}, that can serve as a model for Yb^{3+}-Er^{3+}, has been used for energy transfer studies because the luminescence properties of Eu^{3+} and Nd^{3+} ions are easier to study[7].

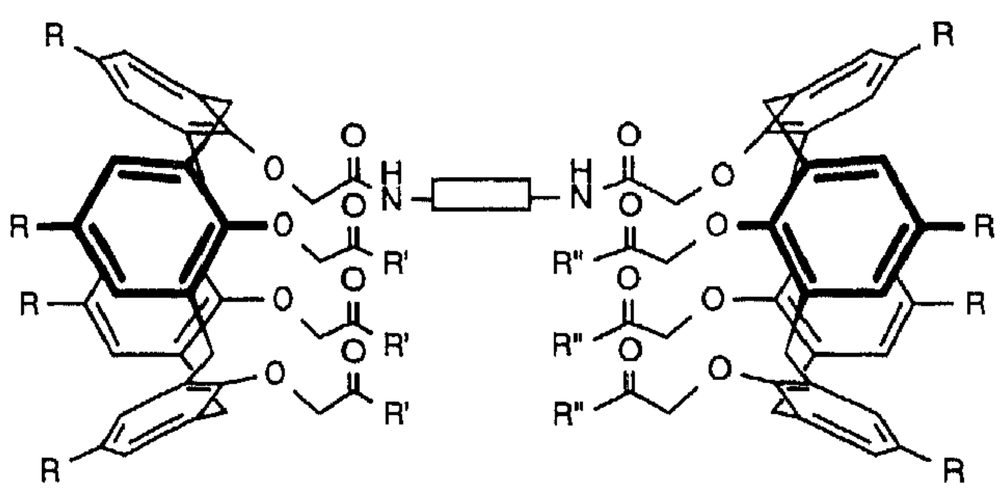
Calix[4]arenes[8] are well-known building blocks in supramolecular chemistry because selective functionalization at the *upper* and/or *lower rim* is possible. These building blocks have been combined with several other building blocks, like resorcinarenes[9], cyclodextrins[10], terphenyls[11], and porphyrins[12]. By combining two or more calix[4]arenes, either by *lower-lower*, *lower-upper*, or *upper-upper rim* linkages, it is also possible to create ligands with more than one cavity for ion encapsulation[13]. The interest in biscalix[4]arenes originates from the presence of two building blocks that can both be used as a molecular platform to introduce functional groups, containing donor atoms that are able to coordinate to lanthanide ions. The hexa-ester[14] biscalix[4]arene

  0947–3440/97/1212–2587 $ 17.50+.50/0

1 synthesized by McKervey et al.[15] is an example that contains a sufficient number of donor atoms and is synthetically easily accessible.

In this paper, the syntheses of hexa-esters linked via amide spacers (**1**) that vary in rigidity and length (Scheme 1), are described. Furthermore, biscalix[4]arenes containing amide groups (**2**) instead of ester functions were synthesized to get further insight in the complexation behavior of the calix[4]arenes. By combining the differently functionalized calix[4]arenes, non-symmetric biscalix[4]arenes (**3**) were synthesized that may complex different lanthanide ions. Molecular modeling was used to get more insight in the structural properties of the biscalix[4]arenes. Photophysical studies were performed with a homodinuclear Eu^{3+} complex and a heterodinuclear Eu^{3+}-Nd^{3+} complex in order to determine whether energy transfer may indeed occur in such organic dinuclear lanthanide complexes.

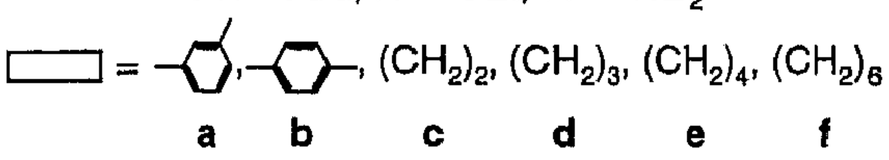
Scheme 1



1 R = *t*-Bu or H, R' = R'' = OEt

2 R = *t*-Bu, R' = R'' = NEt_2

3 R = *t*-Bu, R' = OEt, R'' = NEt_2



a **b** **c** **d** **e** **f**

Results and Discussion

Synthesis

Hexa-Ester Biscalix[4]arenes $\mathbf{1_{tBu}}$ *and* $\mathbf{1_H}$ *(Scheme 2):* The starting material *p-tert*-butylcalix[4]arene was converted to tetraethyl ester **5** (R = *tert*-butyl)[16], and subsequently hydrolyzed to the triethyl ester monoacid derivative **6** (R = *tert*-butyl)[17], both by literature procedures. Coupling of the calix[4]arene to a diamine spacer unit was performed by a slightly modified literature procedure[15]. Triethyl ester monoacid chloride **7** (R = *tert*-butyl) was obtained from **6** by refluxing in oxalyl chloride, and was reacted with 0.5 mol equivalents of the appropriate diamine in dichloromethane, in the presence of triethylamine as a base. In all cases the main product was accompanied by tetraethyl ester **5** (R = *tert*-butyl). The way of formation of this product is not known but the amount of this side product is dependent on the spacer unit, i.e. a larger amount in case of a more rigid and/or a shorter spacer.

Biscalix[4]arenes $\mathbf{1_{tBu}}$ were purified by recrystallization, in most cases from a mixture of dichloromethane and methanol (v/v ca. 95:5), and obtained in high yields (65–76%). Hexa-esters $\mathbf{1_{tBu}}$ were fully characterized by ^{1}H-, ^{13}C-NMR, and IR spectroscopy, FAB mass spectrometry, and elemental analysis. The ^{1}H-NMR spectra all clearly show the amide hydrogen atoms at $\delta = 9.5$ in case of an aromatic spacer, and at $\delta = 8.4$–8.5 for aliphatic spacer units. Furthermore, three AB-q systems were observed; at $\delta \approx 4.9$ and $\delta \approx 4.6$ ($J = 16$ Hz) for the methylene hydrogen atoms of the two opposite pendant ester groups, and at $\delta \approx 4.8$ and $\delta \approx 3.2$ and $\delta \approx 4.7$ and $\delta \approx 3.2$ ($J = 13$ Hz) for the hydrogen atoms of methylene groups connecting the aromatic rings of the calix[4]arenes. The hydrogen atoms of the remaining methylene groups of the pendant ester and amide groups give two singlets at $\delta \approx 4.6$–4.7 and at $\delta \approx 4.5$–4.6, respectively. The integrated peak areas in the ^{1}H-NMR spectrum demonstrate the 2:1 calix[4]arene:spacer ratio. The FAB mass spectra all show the main peak at the calculated value of $[M + H + Na]^+$ and $[M + 2\ H]^+$ or $[M + H]^+$, and elemental analysis indicates the presence of one or two water molecules in the compounds $\mathbf{1_{tBu}}$.

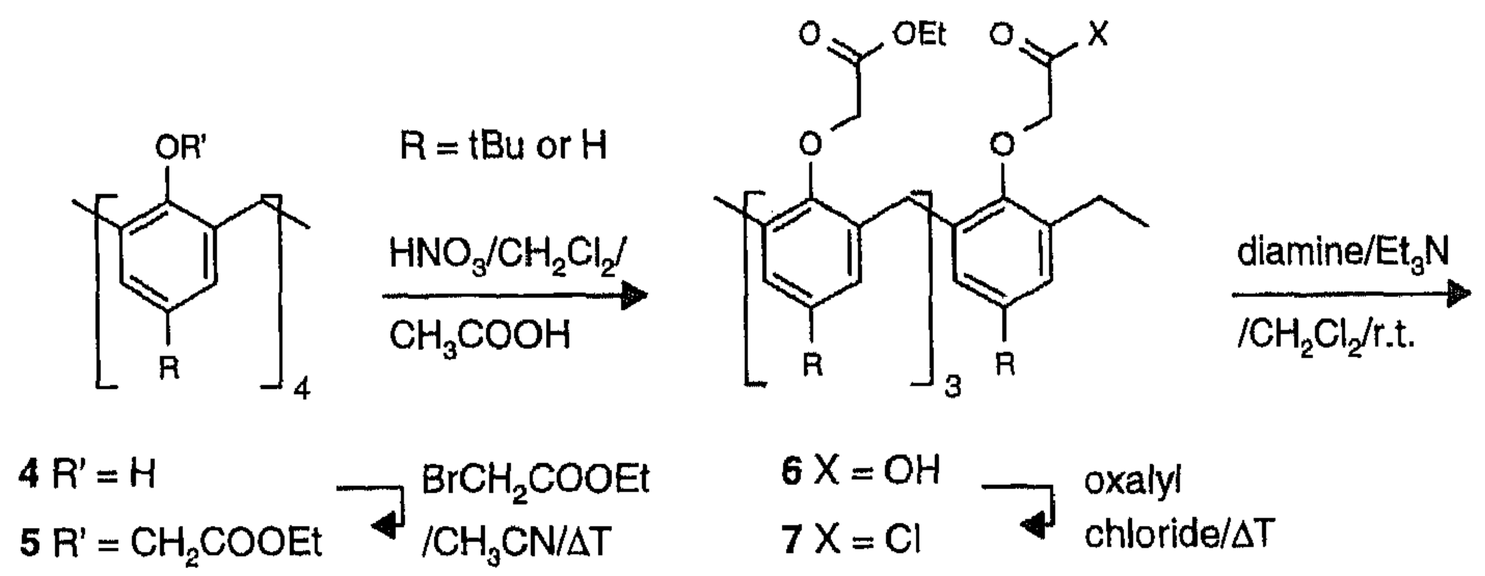
The same type of hexa-esters without substituents at the *upper rim* ($\mathbf{1_H}$) were also prepared by this route starting from de-*tert*-butylated calix[4]arene[18]. The formation of these hexa-esters was fully confirmed by the same characterization methods as used for $\mathbf{1_{tBu}}$. The three AB-q systems in the ^{1}H-NMR spectrum are present at more or less the same positions, whereas the signals attributed to the amide hydrogen atoms are present at $\delta = 9.7$ and at $\delta = 8.4$–8.6 for the aromatic and aliphatic spacers, respectively. The highest peak in the FAB mass spectra correspond to the calculated value of $[M + 2\ H]^+$ or $[M + H + Na]^+$ and the products are pure based on elemental analysis. The *p*-phenylene linked biscalix[4]arene ($\mathbf{1_H b}$) contains one molecule of water.

Recrystallization of $\mathbf{1_H a}$ from a mixture of dichloromethane and methanol (v/v ca. 95:5) resulted in crystals, of which the structure was determined by single X-ray analysis (Figure 1 and Table 3).

The X-ray structure of $\mathbf{1_H a}$ clearly shows the *pinched cone* conformation of the two calix[4]arene units that are connected by a *m*-phenylene spacer. The spacer is positioned more or less in between the two calix[4]arenes, thereby forcing the amide oxygen atoms to rotate away from the possible coordination sphere. Some of the other carbonyl oxygen atoms also point out off the cavity. The molecule has a C_2 symmetry and contains two molecules of water (not shown). Further crystal structural data are collected in Table 3.

Hydrolysis of the hexa-esters in 1 M KOH/MeOH was performed in order to convert the carboxylic ester groups into carboxylic acids, resulting in ligands that can form overall *neutral* complexes. In case of $\mathbf{1_{tBu}b}$, the FAB mass spectrum shows a peak at *m/z* 1856.3 that can be attributed to the mass of the Na^+ complex of the hexa-acid[14]. However, the ^{1}H-NMR spectra were all broad and attempts to isolate overall neutral homodinuclear Eu^{3+} complexes were not successful, due to their low solubility.

Scheme 2



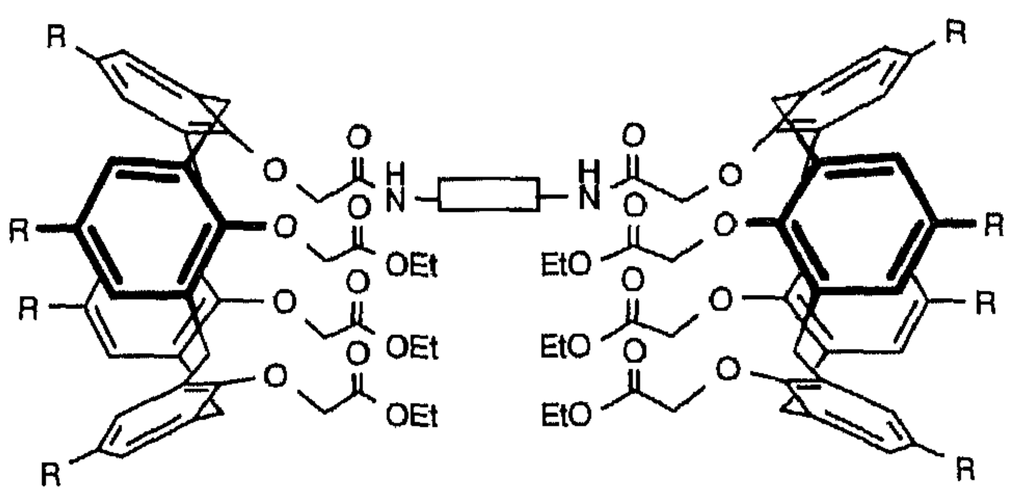
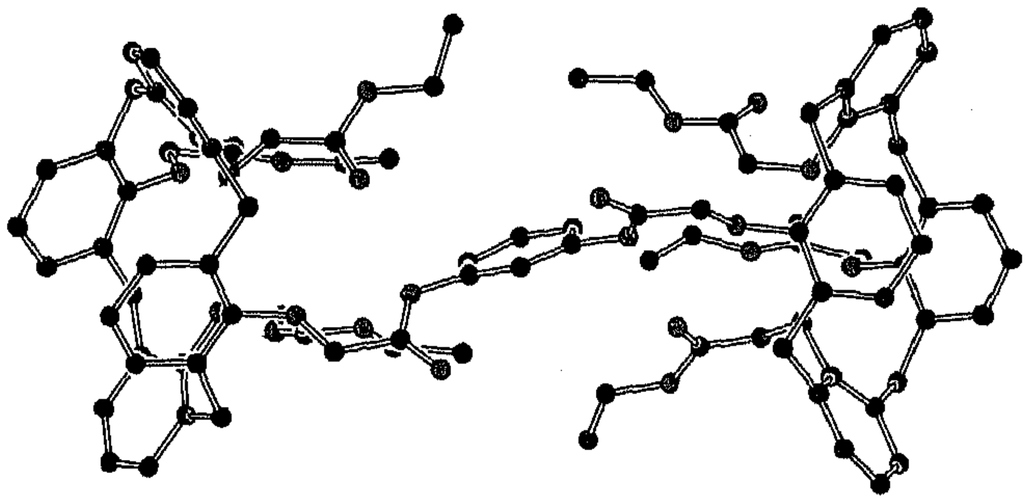
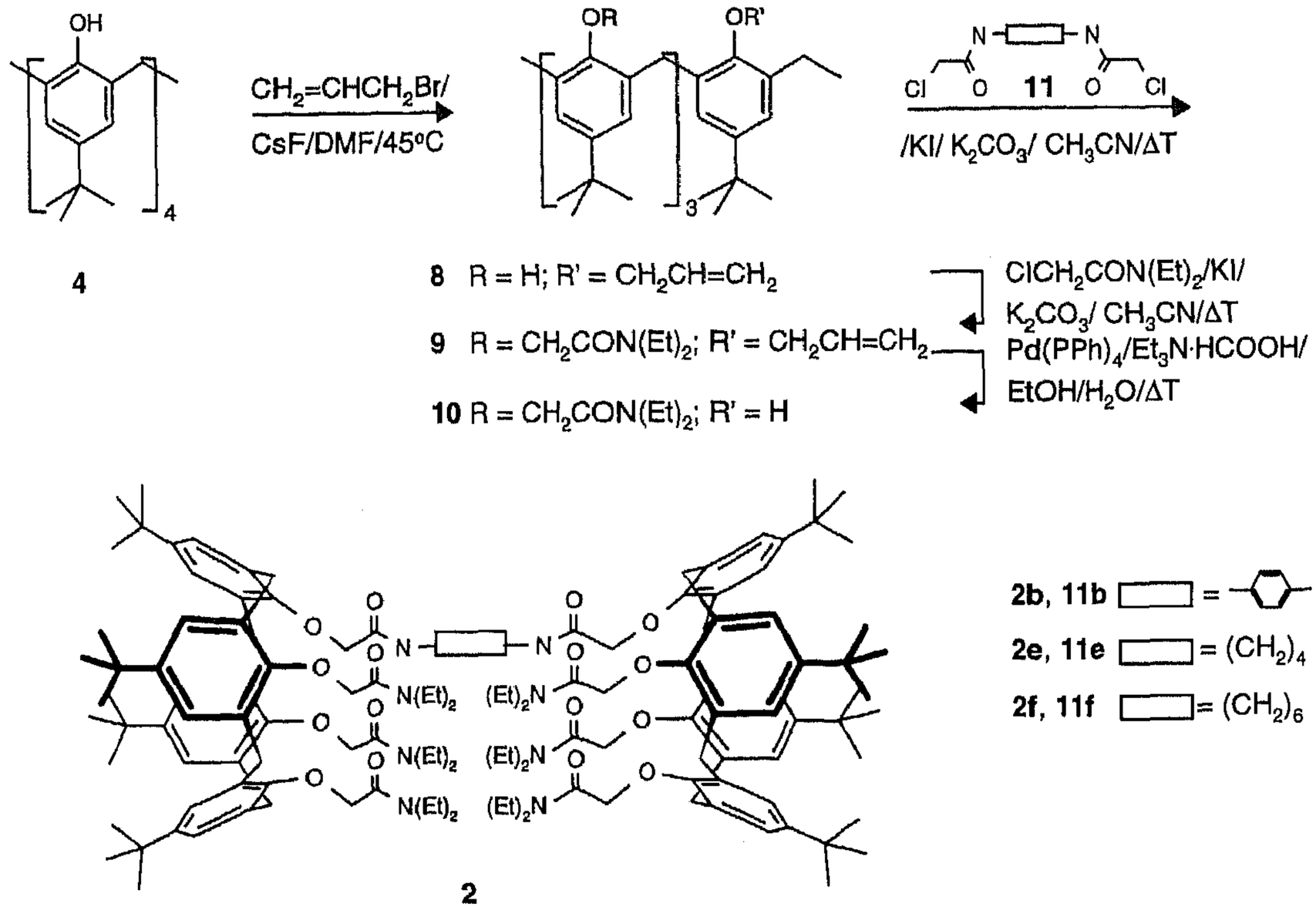


Figure 1. X-ray crystal structure of hexaester $\mathbf{1_H a}$



Hexa-Amide Biscalix[4]arenes **2** *(Scheme 3):* The synthetic route leading to biscalix[4]arene hexa-amides[14] **2** starts with the monoprotection of *p-tert*-butylcalix[4]arene, which was performed by a slightly modified literature procedure[19], using ten equivalents 3-bromo-1-propene in *N,N'*-dimethylformamide using one equivalent of CsF as a base. Calix[4]arene **8** was trialkylated with 2-chloro-*N,N'*-diethylacetamide in acetonitrile in the presence of a catalytic amount of KI and K_2CO_3 as a base. After work up and recrystallization from acetonitrile, compound **9** was obtained in 57% yield. The ^{1}H-NMR spectrum shows two multiplets around $\delta = 5.2$ for the hydrogen atoms of the 2-propenyloxy group, whereas a singlet at $\delta = 5.12$ and an AB-q system at $\delta = 5.05$ and 4.55 ($J = 13.7$ Hz) were observed for the methylene hydrogen atoms of the pendant arms. The highest peak in the FAB mass spectrum is observed at 1050.9 and corresponds to $[M + Na]^+$. Deprotection of **10** was performed with $Pd(PPh_3)_4$ and $Et_3N \cdot HCOOH$ in a mixture of ethanol and water[20]. The product was purified by recrystallization from acetonitrile and obtained in 77% yield. From the ^{1}H-NMR spectrum, it was obvious that the 2-propenyloxy group was removed; a singlet at $\delta = 8.09$ for the phenolic hydrogen atom was observed. The FAB mass spectrum of **10**, which was pure based on elemental analysis, shows the main peak at 1011.0, which corresponds to the Na^+ complex of **10**. Three different spacer units **11b**, **11e**, and **11f** were prepared by reaction of the corresponding diamine with chloroacetyl chloride in a mixture of ethyl acetate and water, using K_2CO_3 as a base. These spacers were obtained in 70−79% yield, and characterized by ^{1}H-NMR spectroscopy. Finally, the hexa-amides **2** were prepared by alkylation of **10** with 0.5 mol equivalents of the spacer unit **11**, a catalytic amount of KI, and K_2CO_3 as a base. Acidic work-up and recrystallization resulted in the biscalix[4]arenes **2**, which were pure according to elemental analysis, in $\geq$ 64% yield.

Scheme 3

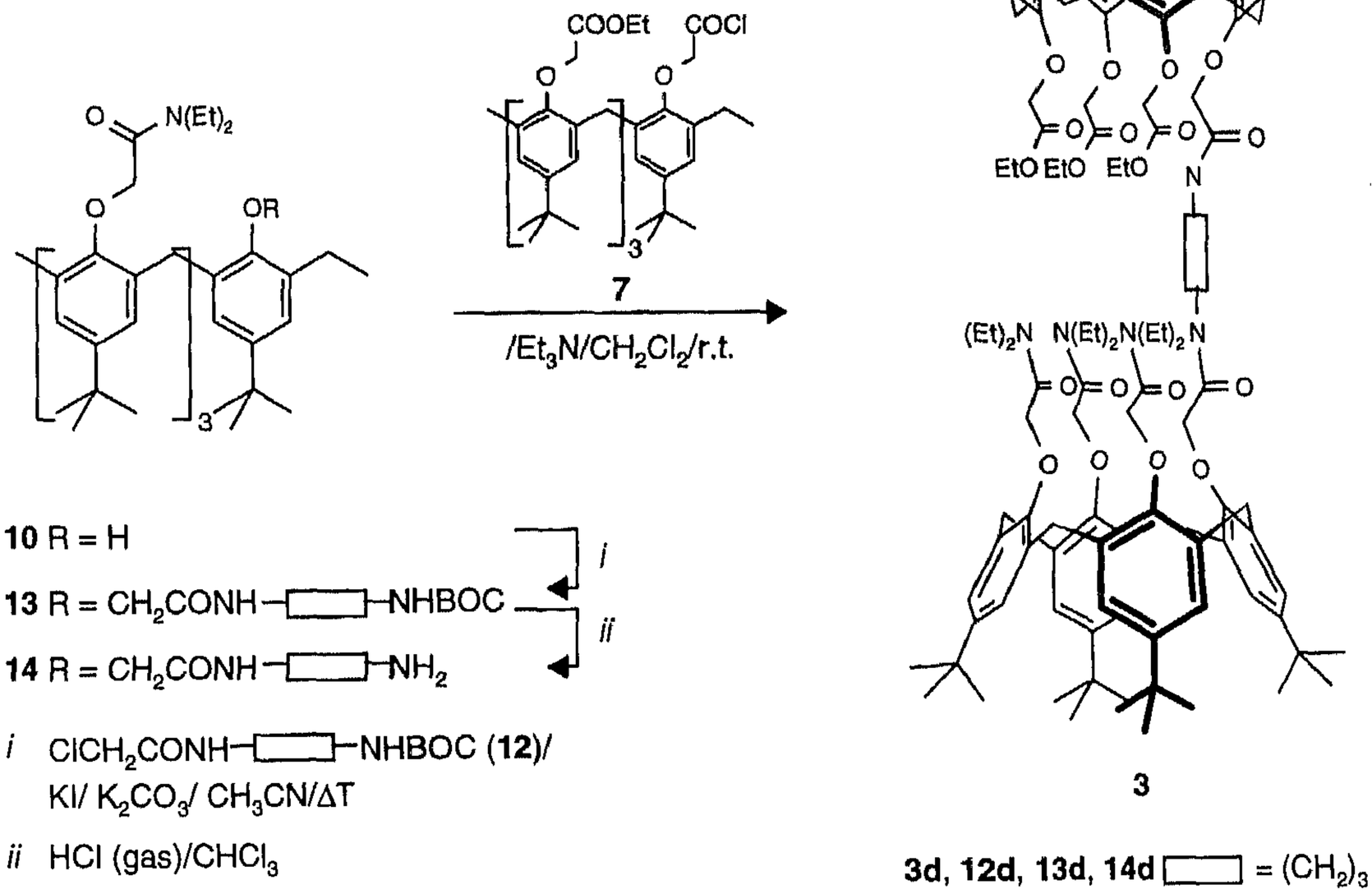


In all cases, the 2:1 calix[4]arene/spacer ratio was obvious from the intensities in the ^{1}H-NMR spectra. For compound **2b** a singlet was observed at $\delta = 7.74$ for the hydrogen atoms of the aromatic spacer. An AB-q system at $\delta = 5.08$ and 4.79 ($J = 15.1$ Hz) and two singlets at $\delta = 4.85$ and 4.80 represent the methylene hydrogen atoms for the pendant arms. The ^{1}H-NMR spectra of the biscalix[4]arenes, **2e** and **2f**, that are linked via aliphatic spacers, show multiplets for the hydrogen atoms of the spacer, whereas the AB-q system and the two singlets for the methylene hydrogen atoms of the pendant arms are situated at $\delta = 5.2$ and 4.8, and at $\delta = 4.8$ and 4.5, respectively. The FAB mass spectra of **2b** and **2f** showed the highest peak at the calculated value of $[M + 2\,H + Na]^+$, i.e. 2188.0 and 2196.2, respectively; for **2e** the main peak was observed at 2167.4 ($[M + H + Na]^+$).

Non-Symmetric Biscalix[4]arenes **3** *(Scheme 4):* By combination of triethyl ester monoacid chloride **7** (R = *tert*-butyl) and tris(diethyl)acetamide functionalized with a primary amine **14**, the non-symmetric biscalix[4]arenes **3** were prepared (Scheme 4). For this synthesis, the BOC-protected spacers **12d** and **12f** were synthesized, in the same way as the spacer units **11**, from a mono-BOC-protected diamine and chloroacetyl chloride in a 1:1 ratio. The products were subsequently purified by flash column chromatography. The spacers **12** were characterized by ^{1}H-NMR spectroscopy, and used in the alkylation of **10**. This alkylation reaction was carried out in a 1:1 ratio, as described for **2**. The 1:1 coupling of the spacer unit to the calix[4]arene was obvious from the ^{1}H-NMR spectra, showing a broad triplet for the amide hydrogen atom at $\delta = 8.9$, and two singlets, corresponding to four hydrogen atoms, at $\delta = 4.8$ and 4.5 for the methylene hydrogen atoms of the pendant arms. Furthermore, a singlet at $\delta = 1.44$, that can be attributed to the *tert*-butyl part of the BOC protective group, was observed. In both cases, FAB mass spectrometry gave the main peak at $[M + Na]^+$; 1225.0 for **13d** and 1266.9 for **13f**. Deprotection of **13** leading to the primary amine was performed by passing HCl gas through a solution of **13** in dichloromethane. The products were obtained as HCl salts in nearly quantitative yields after evaporation of the solvent and purification by trituration with acetonitrile. The absence of the singlet in the ^{1}H-NMR spectrum, and the highest peak in the FAB mass spectra at the calculated value of $[M + H]^+$, show that primary amines **14** were formed. These amines were coupled in a 1:1 fashion to monoacid chloride derivative **7** using the same conditions as were employed for the formation of hexa-esters **1**. These non-symmetric biscalix[4]arenes were recrystallized from dichloromethane and methanol. Derivative **3d**, which is linked via the short spacer, required also Sephadex column chromatography to remove tetraester **5** that was formed as side product.

The ^{1}H- and ^{13}C-NMR spectra of **3** clearly show the presence of ester and amide moieties in a 1:1 ratio, and both show a combination of the signals observed in the corresponding spectra of hexa-esters $\mathbf{1_{tBu}}$ and hexa-amides **2**. The products are pure based on elemental analysis, and the FAB mass spectra show the main peak at the calculated value of $[M + H + Na]^+$, i.e. $m/z = 2072.1$ and 2114.5 for **3d** and **3f**, respectively.

Scheme 4



Complexation of Lanthanide Ions: Different methods were used to complex Eu^{3+} ions by the biscalix[4]arenes (see Experimental Section). In all cases the biscalix[4]arene was dissolved in acetone, acetonitrile, or one of these solvents in combination with dichloromethane. Subsequently, two equivalents of $Eu(NO_3)_3 \cdot 6\ H_2O$ were added followed by stirring overnight either at room or reflux temperature. The white solids were collected either by filtration or evaporation of the solvents. Luminescence studies revealed that hexa-ester $\mathbf{1_{tBu}b}$ does not complex Eu^{3+} ions. After stirring in acetone at room temperature (preparation method 1) only "free" Eu^{3+} ions in solution were detected as was concluded from the luminescence lifetimes. Also the precipitate that was collected after refluxing overnight in acetonitrile (preparation method 2) did not show any detectable luminescence indicating that no Eu^{3+} ions were present. Except preparation method 1a, all preparation methods for Eu^{3+} complexes of the hexa-amide **2b**[21] were successful. However, the formation of the complexes seemed to be slow probably because the ligand is present as its Na^+ complex[22]. The highest yield was achieved in refluxing acetonitrile (preparation method 3).

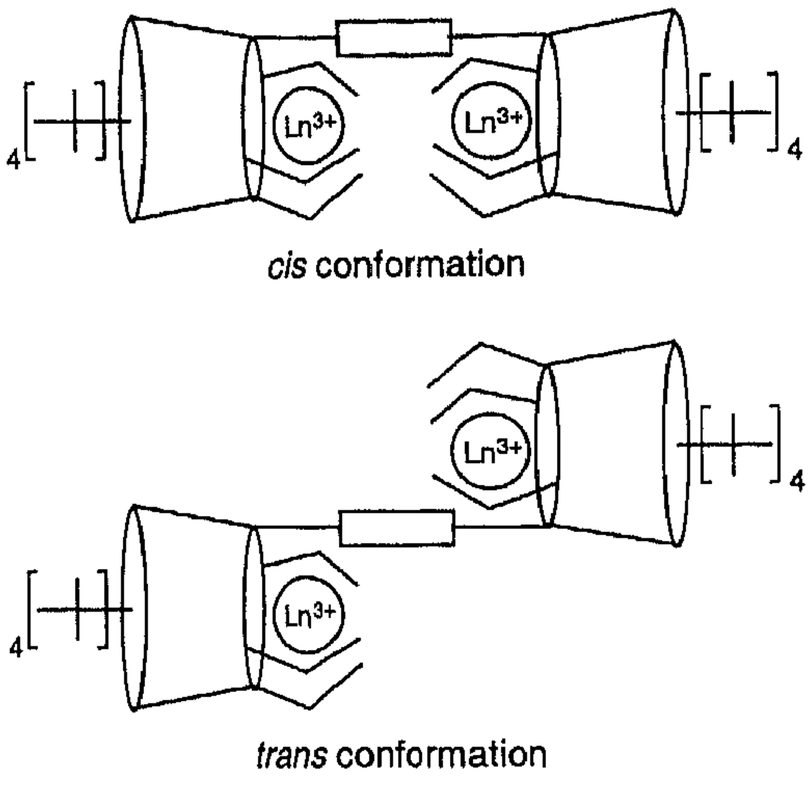
The Eu^{3+} complexes were characterized by mass spectrometry, IR spectroscopy, and elemental analysis. The lanthanide ion content was approximately 4% higher than the calculated value, which might be the result of coordination to the outer sphere of the biscalix[4]arene. Complexation was detected by IR spectroscopy showing two carbonyl stretching vibrations at 1651 and 1623 cm^{-1}, compared to one vibration at 1660 cm^{-1} for the free ligand **2b**. In addition, biscalix[4]arene **2b** was complexed with one equivalent of Eu^{3+} and one equivalent of Nd^{3+} by the same method. This complex also shows two carbonyl stretching vibrations in the IR spectrum at lower wavenumbers compared to the free ligands. The biscalix[4]arene showed a slight preference for Nd^{3+} as was revealed by an ionic distribution Eu^{3+}:Nd^{3+} of 1:1.3 as determined by X-ray fluorescence. Since $\mathbf{1_{tBu}b}$ was not able to complex Eu^{3+} ions, complexation studies with the non-symmetric calix[4]arenes (**3**) were not performed. Apparently the complexation reactions are controlled by thermodynamic aspects.

Molecular Modeling

Molecular simulations[23] were performed to get more insight in the structural properties of the biscalix[4]arenes, and particularly to get an impression of the influence of the type of spacer on the intra-lanthanide ion-ion distance. The dinuclear lanthanide ion complexes of the hexa-ester biscalix[4]arenes with the various spacers that have been synthesized were subjected to molecular mechanics calculations in the gas phase. In case of neutral ligands it was assumed that the nitrate anions do coordinate to the lanthanide ion

complex, and therefore the anions were positioned arbitrarily in the first coordination sphere of the lanthanide ions. An energy minimum and the intra-lanthanide ion-ion distance were calculated for two utmost conformations (Table 1), i.e. the so-called *cis* and *trans* conformations (Figure 2).

Figure 2. *cis* and *trans* conformation of biscalix[4]arene



Subsequently, molecular dynamics calculations with a production phase of 50 ps in an OPLS box of chloroform[23c] were performed with these minimized structures (Table 1). The resulting structures closely resemble the MM minimized structures; the largest deviation in the intra-lanthanide ion-ion distances calculated by MM and MD calculations was 17%. In all complexes the nitrate anions remain coordinated to the lanthanide ions and the number of bidentate coordinated nitrates is increased in all cases relative to the structure calculated from MM simulations. The type of anion coordination seems to be mainly dependent on the conformational properties of the complexing biscalix[4]arene, which determines the degree of coordination of the lanthanide ions. That calix[4]arene cavities are occupied with a molecule of chloroform as was also observed by Wipff et al.[24].

Photophysical Studies

The photophysical properties of the dinuclear complexes **2b·Eu$_2$** and **2b·Eu·Nd** in chloroform, acetonitrile, tetrahydrofuran (THF), and methanol were studied[25]. The luminescence spectra of the chloroform, acetonitrile, and THF solutions show the typical $^5D_0 \rightarrow {}^7F_j$ transitions at 590, 615, 650, and 695 nm, after ligand-mediated excitation at 300 nm (Figure 3a) or after direct excitation of the Eu^{3+} ion at 393 nm (not shown). The relative intensities of the emission after 300 nm and 393 nm are dependent on the solvent and on the concentration. For these complexes, direct Eu^{3+} excitation is more efficient than ligand-mediated excitation, which might be a result of the large distance between the aromatic sensitizing units of the calix[4]arene and the Eu^{3+} ion or the quenching via low-lying LMCT (ligand-to-metal-charge-transfer) bands. Ungaro et al.[22] showed that ligand-mediated excitation of Eu^{3+} complexed by a single calix[4]arene that is functionalized with four diethylamide groups is not efficient. In this complex low-lying LMCT bands are present that significantly deactivate the Eu^{3+} luminescence; this is also likely to occur in our complexes. Moreover, the elemental analysis showed the presence of three water molecules in **2b**. Water molecules are known to coordinate strongly to Eu^{3+} and can consequently have a significant effect on the complexation and luminescence properties of the Eu^{3+} ion. The water molecules might pull the Eu^{3+} ions out of the biscalix[4]arene

Table 1. Calculated energies E (kcal/mol) and intra-lanthanide ion−ion distances d [Å] in the biscalix[4]arenes with various spacers from molecular mechanics and dynamics

	cis conformation					*trans* conformation				
	MM		MD			MM		MD		
	E	d	E[a]	d[b]	Δd[c]	E	d	E[a]	d[b]	Δd[c]
$\mathbf{1}_{tBu}$a	−1006	9.5	−453	9.5	<1%	−997	8.0	−397	8.0	<1%
$\mathbf{1}_{H}$a	−961	9.2	−499	10.3	12%	−984	8.5	−377	8.0	6%
$\mathbf{1}_{tBu}$b	−1010	5.8	−293	5.9	2%	−995	9.5	−464	10.1	7%
$\mathbf{1}_{tBu}$c	−591	6.7	−121	6.9	3%	−572	9.0	−150	8.8	2%
$\mathbf{1}_{tBu}$d	−577	6.9	−119	7.8	12%	−561	11.3	−74	13.3	17%
$\mathbf{1}_{tBu}$e	−1023	6.4	−261	5.7	11%	−994	11.9	−556	12.3	3%
$\mathbf{1}_{tBu}$f	−558	11.8	−117	12.3	5%	−997	13.4	−555	12.2	10%

[a] ± 20 kcal/mol. − [b] ± 0.3 Å. − [c] The difference in the distances calculated by MM and MD relative to the shortest calculated distance.

The lanthanide ions are pulled out of the calix[4]arene cavities by the coordinating nitrate anions. As a consequence, the phenolic oxygen atoms do not coordinate to the lanthanide ions, and the coordination sphere is occupied by the four carbonyl moieties and the nitrate oxygen atoms. One of the carbonyl oxygen atoms directly linked to the spacer does not coordinate to the lanthanide ion in case of the *n*-propyl and *n*-hexyl linked biscalix[4]arenes in the *trans* conformation.

The nitrate anions coordinate to the lanthanide ions via one oxygen atom or in a bidentate fashion. In case of the *cis* conformation of biscalix[4]arene linked via the *p*-phenylene and the *n*-butyl spacer one nitrate anion acts like a bridge between the two lanthanide ions. In most cases the *cis* conformation is the most stable one, except for $\mathbf{1}_{H}$**a** and $\mathbf{1}_{tBu}$**f**. The distance between the lanthanide ions is shorter in the *trans* conformation than in the *cis* conformation when the calix[4]arenes are linked via an aromatic spacer, whereas the aliphatically-linked biscalix[4]arene has a larger intra-lanthanide ion-ion distance in the *trans* conformation.

or expel the nitrate anions out of the first coordination sphere. This might be the reason for the more efficient direct excitation relative to sensitized excitation. Since the water molecules were already present in **2b** prior to complexation we assumed that the effects on complexation and luminescence are quite similar in the solvents chloroform, acetonitrile, and THF.

On the other hand, the complexes behave differently in methanol, as is indicated by the red-shift of the most intense emission band to 624 nm (Figure 3a). This emission band has a shoulder at 614 nm, at which wavelength the peak maximum is usually found. Furthermore, two additional emission bands are present at 570 and 600 nm, whereas the band at 580 nm is broadened. The band around 680 nm is also red-shifted in $[D_4]$methanol. These spectra indicate that the Eu^{3+} ion experiences a different chemical environment in $[D_4]$methanol than in the solvents chloroform, acetonitrile, and THF. This might be the result of the strongly coordinating O−O group present in this solvent. This type of Eu^{3+} emission is not the typical luminescence that is normally observed[2][7] and can completely disappear upon the addition of small amounts of water, resulting in Eu^{3+} luminescence of solvated ions. Probably the water molecules coordinate to the Eu^{3+} ion, thereby expelling the methanol molecules and nitrate anions out of the first coordination sphere of the Eu^{3+}. However, the crystal water molecules that were present prior to complexation are also expected to coordinate to Eu^{3+}.

The presence of Nd^{3+} in **2b·Eu·Nd** was obvious from the typical Nd^{3+} emission band at 1060 nm that was observed after ligand-mediated excitation (Figure 3b). Moreover, luminescence lifetime measurements were performed with the same solutions, and the results are reported in Table 2. The lifetimes of **2b·Eu$_2$** dissolved in chloroform and acetonitrile are equal within the experimental error, whereas the Eu^{3+} luminescence is deactivated slightly more efficiently in THF. This might be an effect of the difference in the chemical environment around the Eu^{3+} ion, because THF contains an oxygen atom that can coordinate to lanthanide ions. Upon addition of small amounts of water, the Eu^{3+} luminescence is extinguished in both acetonitrile and THF, which might indicate that more than three strongly complexing water molecules are required to pull the Eu^{3+} ions out of the biscalix[4]arene. The lifetime of the complex is relatively short in $[D_4]$methanol and the solution contains a large fraction of Eu^{3+} ions that have a long lifetime, 1.9 ms, which probably corresponds to free Eu^{3+} ions in solution[26]. This is supported by the presence of a short-living component in non-deuterated methanol (0.13 ms). In methanol, a different complex seems to exist than in the other solvents. Perhaps the strongly coordinating methanol molecules are more capable of pulling the Eu^{3+} ion out off the cavity resulting in coordination only to the carbonyl oxygens of the amide functions[23b]. The MD simulations showed that the Eu^{3+} ion only coordinates to the four carbonyl oxygens of a hexa-ester in an OPLS box of chloroform. This indicates that also in the less competing solvents the phenolic oxygen atoms do not coordinate to the lanthanide ion, as was supposed for methanol. Another possibility is that the strongly coordinating methanol molecules expel the nitrate anions out off the first coordination sphere of the Eu^{3+} ion. The explanation is supported by the extinction of luminescence upon the addition of water. The number of coordinating O−H high-energy vibrational modes in methanol was estimated to be 2.7 by using *"Horrocks equation"*[27]. However, this value has to be treated with care since the presence of the water molecules has a large effect on the luminescence lifetimes, and hence on the calculated number of O−H oscillators. If the Eu^{3+} ions coordinate only to the carbonyl oxygen atoms in case of methanol as a solvent, the C−H high-energy vibrational modes of the NEt_2 groups and the crystal water molecules might act as efficient deactivators, leading to the short lifetime in $[D_4]$methanol. The present results do not allow a definitive explanation.

The most striking feature of the results reported in Table 2 is the decrease in lifetime of the Eu^{3+} luminescent state after excitation at 300 nm when Nd^{3+} is present. Based on literature data[5][6], it was expected that the decay curve would be biexponential, since the composition of the complex is expected to be statistical. However, only a monoexponential decay curve was observed in all solvents, indicating that the composition of the mixture of complexes is apparently not statistical. The only difference for the Eu^{3+}

Figure 3. Emission spectra after excitation at 300 nm of a) **2b·Eu$_2$** in THF and $[D_4]$methanol and b) **2b·Eu·Nd** in THF in the NIR region of the spectrum

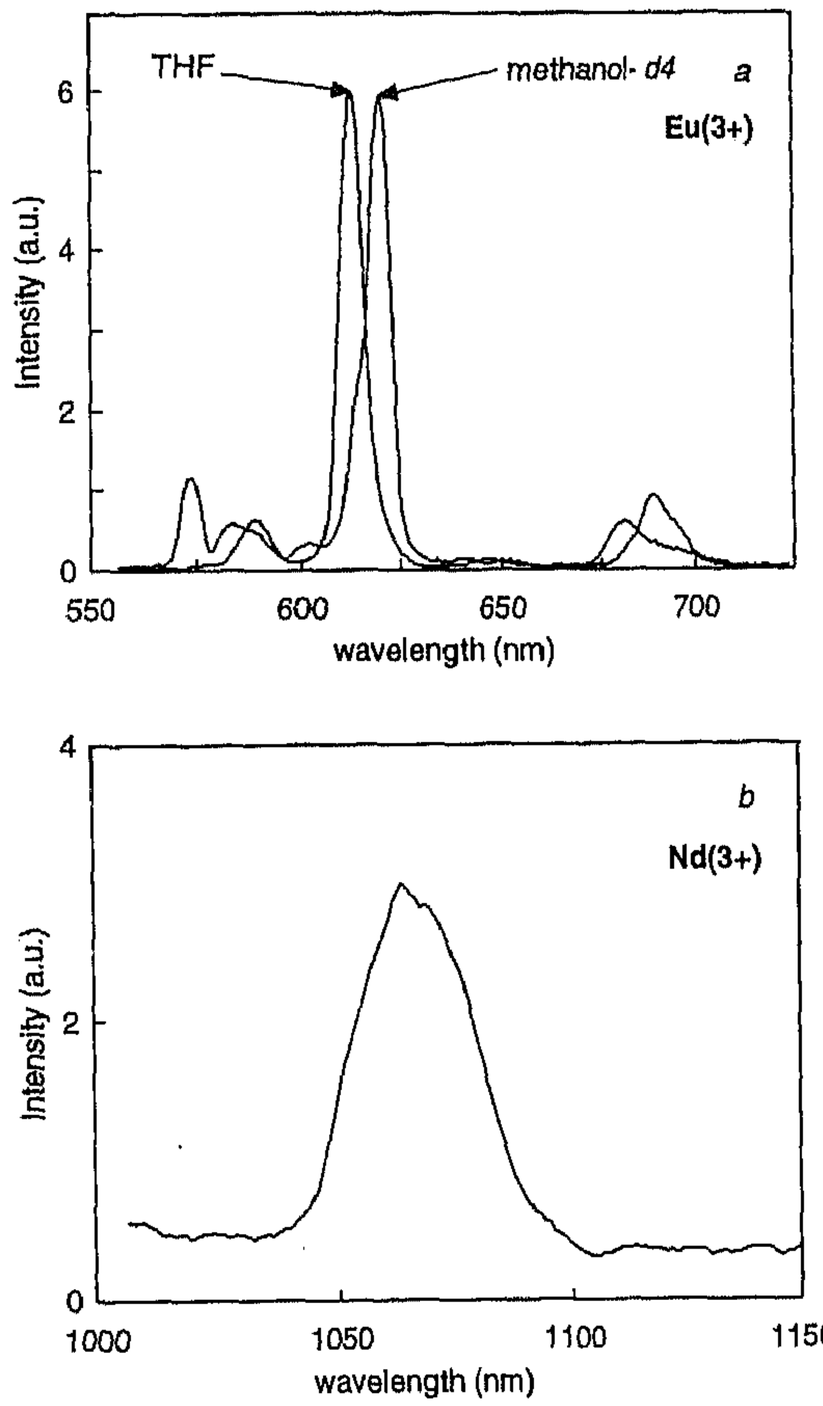


Table 2. Lifetimes [ms] of the $^5D_0$ state of **2b·Eu$_2$** and **2b·Eu·Nd** in different solvents, after excitation at 300 nm and detection at 614 nm, and energy transfer efficiencies (*ET*)[a]

	EuEu $\tau_{Eu^{3+}}$	EuNd $\tau_{Eu^{3+}}$	*ET* [%][b]
$CHCl_3$	1.02	0.50	51
CH_3CN	0.93	0.32	66
THF	0.74	0.29	61
CD_3OD[c]	0.39[d]	0.38	<1
CH_3OH[c]	0.26[e]	—[f]	

[a] Data fitting of the decay curves all show two components, one corresponding to the complex and the other to solid particles present (≈ 0.10 ms). – [b] Relative decrease of the lifetime. – [c] Detected at 624 nm. – [d] Contains a large fraction with a lifetime of 1.9 ms. – [e] Contains a large fraction with a lifetime of 0.1 ms. – [f] Signal too weak.

in the homo- and heterodinuclear complex is the presence of Nd^{3+} instead of another Eu^{3+} ion. Therefore, it is assumed that the Nd^{3+} ion is acting as an energy acceptor. The relative lifetime decrease ET is most pronounced in acetonitrile and the ET values given in Table 2 are equal to the efficiency of energy transfer if this is the only additional deactivation pathway compared to the homodinuclear complex. In this case it is assumed that the symmetry around the Eu^{3+} ion remains essentially the same, thus the radiative decay of Eu^{3+} is equal for both homo- and heterodinuclear complexes. Based on the proposed different structural properties of the complex in methanol, it was expected that the efficiency of energy transfer from $Eu^{3+} \rightarrow Nd^{3+}$ would be different in this solvent compared to chloroform, acetonitrile, and THF. However, the Eu^{3+} lifetime did not decrease at all, which might be a result of the high concentration of high-energy vibrational solvent O–H/C–H or ligand C–H modes around the Eu^{3+} ion, leading to relatively short luminescence lifetimes. The lifetime in the homodinuclear complex is of the same order of magnitude as the lifetime of Eu^{3+} luminescence in the heterodinuclear complex. Therefore, the energy transfer to Nd^{3+} might be obscured by other deactivation pathways. No definitive explanation can be given with the present results[28].

Concluding Remarks

Differently linked (*p-tert*-butyl-)biscalix[4]arenes with six carboxylic ester functions (**1**) were synthesized but it was not possible to isolate dinuclear Eu^{3+} complexes with these ligands. On the other hand, dinuclear Eu^{3+}-Eu^{3+} and Eu^{3+}-Nd^{3+} complexes with the *p*-phenylene linked hexaamide[14] biscalix[4]arene **2** could be isolated. The luminescence properties of these complexes are strongly dependent on the solvent. Solvents that strongly compete with the organic ligand for complexation seem to pull the lanthanide ions out of the cavity.

The lifetime of the Eu^{3+} luminescent state is significantly decreased in the heterodinuclear Eu^{3+}-Nd^{3+} complex compared to the homodinuclear Eu^{3+} complex in chloroform, acetonitrile, and tetrahydrofuran. It is assumed that the Nd^{3+} ion acts as an energy acceptor since no other additional deactivation pathways were introduced. This implies that the $Eu^{3+} \rightarrow Nd^{3+}$ energy transfer is very efficient (> 50%). Further studies using other lanthanide ion combinations are under investigation.

The asymmetric biscalix[4]arene (**3**) was synthesized, however, complexation studies were not performed due to the low complexation ability of the ester functions of **1**.

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Experimental Section

General: Melting point: Reichert melting point apparatus (uncorrected). – NMR: Bruker AC 250 spectrometer spectra, $CDCl_3$ as solvent (unless otherwise stated), TMS as internal standard. – MS: Finnigan MAT 90 spectrometer [*m*-NBA (nitrobenzyl alcohol) as a matrix, unless otherwise stated]. – IR: Biorad 3200 or Nicolet 5SXC FT-IR spectrophotometer. – Elemental analyses[29]: Carlo Erba EA1106. The Eu^{3+} content was determined by destroying the ligand in the presence of concentrated nitric acid and concentrated perchloric acid. The remaining acids were evaporated, the salts dissolved in Q_2 water, followed by the addition of an acetate buffer to keep the pH at 5–5.5, and a drop of pyridine was added. After heating to 60°C a titration with an aqueous solution of 0.01 M EDTA (ethylenediamine tetraacetate) was carried out using xylenol orange as an indicator. CH_2Cl_2 was distilled from $CaCl_2$ and ethyl acetate from K_2CO_3 prior to use. CH_3CN, MeOH, and acetone were dried over molecular sieves (3 Å) for at least 3 d. The complex $Et_3N \cdot HCOOH$ was obtained prior to use by distillation under reduced pressure (17 Torr) of an equimolar mixture of formic acid and Et_3N at 70°C. All other chemicals were of reagent grade and were used without further purification. Column chromatography was performed using silica gel 60 (particle size: 0.040–0.063 mm, 2230–400 mesh) from Merck. All reactions were carried out under an argon atmosphere. 25-[(Carboxylato)methoxy]-26,27,28-tris-[(ethoxycarbonyl)-methoxy]calix[4]arene **6** (R = *tert*-butyl or H) was prepared according to literature procedures[16][17].

General Procedure for the Synthesis of the Biscalix[4]arenes **1$_R$a–f**: Biscalix[4]arenes **1$_R$a–f** were prepared according to a slightly modified literature procedure[15]. Triester-monoacid **6** (R = *tert*-butyl or H) was refluxed in oxalyl chloride (5 ml) for 2 h. After evaporation of the remaining oxalyl chloride, the monoacid chloride was dissolved in dichloromethane (30 ml) under an argon atmosphere. A solution of 0.5 mol equivalents of the corresponding diamine and triethylamine in dichloromethane (12 ml) was slowly added. The reaction mixture was stirred overnight at room temperature and subsequently quenched with an aqueous acetic acid solution (5%, 25 ml). The layers were separated and the organic layer was washed twice with water (50 ml), followed by evaporation of the solvent. The product was recrystallized from CH_2Cl_2/MeOH (v/v = 95:5) unless stated otherwise. Compound **1$_{tBu}$d** was fully characterized by McKervey et al.[15].

1,3-Bis{25-[(aminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]-arene}benzene (**1$_{tBu}$a**): The reaction was performed using **6** (R = *tert*-butyl) (0.50 g, 0.52 mmol), 1,3-phenylenediamine (30 mg, 0.28 mmol), and Et_3N (0.30 ml, 2.1 mmol). A white solid was obtained in 76% yield. m.p: 132–134°C. – ^{1}H NMR: δ = 9.59 (br. s, 2 H, NH), 8.33 (br. s, 1 H, ArH^{spacer}), 7.5–7.4 (m, 2 H, ArH^{spacer}), 7.30 (br. s, 1 H, ArH^{spacer}), 6.87, 6.73, 6.66 (s, 16 H, ArH), 5.01 and 4.68 [AB-q, 8 H, *J* = 16.2 Hz, $OCH_2C(O)$], 4.84, 4.72, 3.25, 3.23 (AB-q, 16 H, *J* = 13.0 Hz, $ArCH_2Ar$), 4.70, 4.66 [s, 8 H,

$OCH_2C(O)$ and $OCH_2C(O)N$], 4.20 (q, 4 H, J = 7.1 Hz, OCH_2CH_3), 4.1−3.9 (m, 8 H, OCH_2CH_3), 1.24, 1.14 [t, 18 H, J = 7.1 Hz, OCH_2CH_3], 1.14, 1.04, 0.98 [s, 72 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 170.6, 170.2 [s, C(O) and C(O)N], 168.3 (s, ArC-N^{spacer}), 153.2, 152.8, 152.6 (s, ArC-O), 145.5, 145.4, 145.3 (s, ArC-*t*Bu), 138.4 (d, ArC^{spacer}), 133.8−132.4 (s, ArC), 125.8−125.4 (d, ArC-H), 74.8, 71.6 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.7 (t, OCH_2CH_3), 33.9, 33.8 [s, $C(CH_3)_3$], 32.0 (t, $ArCH_2Ar$), 31.4, 31.2 [q, $C(CH_3)_3$], 14.1 (q, OCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 1759 ($C=O^{ester}$), 1698 ($C=O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 2024.8 [(M + H + Na)$^+$], 2002.6 [(M + H)$^+$]. − $C_{122}H_{156}N_2O_{22}\cdot H_2O$ (2020.6): calcd. C 72.52, H 7.88, N 1.39; found C 72.27, H 7.93, N 1.48.

1,4-Bis{25-[(aminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]-arene}benzene (**1$_{tBu}$b**): Calix[4]arene **6** (R = *tert*-butyl) (1.00 g, 1.04 mmol) was coupled to 1,4-phenylenediamine (60 mg, 0.57 mmol) in the presence of Et_3N (0.60 ml, 4.2 mmol), and **1$_{tBu}$b** was obtained as a white solid in 72% yield. m.p. 258−260°C. − ^1H NMR: δ = 9.52 (br. s, 2 H, NH), 7.69 (s, 4 H, ArH^{spacer}), 6.86, 6.65, 6.56 (s, 16 H, ArH), 4.99 and 4.63 [AB-q, 8 H, J = 16.2 Hz, $OCH_2C(O)$], 4.78, 4.65, 3.20, 3.18 (AB-q, 16 H, J = 13.0 Hz, $ArCH_2Ar$), 4.57, 4.56 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.18 (q, 4 H, J = 7.1 Hz, OCH_2CH_3), 4.0−3.9 (m, 8 H, OCH_2CH_3), 1.23, 1.10 [t, 18 H, J = 7.1 Hz, OCH_2CH_3], 1.11, 0.96, 0.89 [s, 72 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 170.6, 170.0 [s, C(O) and C(O)N], 168.3 (s, ArC-N^{spacer}), 153.3, 152.6, 152.5 (s, ArC-O), 145.6, 145.5, 145.3 (s, ArC-*t*Bu), 134.5 (d, ArC^{spacer}), 133.9−132.2 (s, ArC), 125.9−125.4 (d, Ar-H), 121.9 (d, ArC-H^{spacer}), 74.9, 71.7, 71.4 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.7 (t, OCH_2CH_3), 34.0, 33.8 [s, $C(CH_3)_3$], 32.0 (t, $ArCH_2Ar$), 31.5, 31.3, 31.2 [q, $C(CH_3)_3$], 14.2, 14.1 (q, OCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 1758 ($C=O^{ester}$), 1638 ($C=O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 2003.0 [(M + 2 H)$^+$], 2025.6 [(M + H + Na)$^+$]. − $C_{122}H_{156}N_2O_{22}\cdot 2\ H_2O$ (2038.6): calcd. C 71.88, H 7.91, N 1.37; found C 71.82, H 7.63, N 1.48.

1,3-Bis{25-[(aminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]-arene}propane (**1$_{tBu}$d**): Compound **6** (R = *tert*-butyl) (0.50 g, 0.52 mmol), 1,3-diaminopropane (22 µl, 0.26 mmol), and Et_3N (0.30 ml, 2.1 mmol) were used as reagents, and recrystallization yielded **1$_{tBu}$d** in 76% yield. m.p. 152−153°C. − ^1H NMR: δ = 8.40 (br. t, 2 H, NH), 6.86, 6.77, 6.73 [s, 16 H, ArH], 4.98 and 4.71 [AB-q, 8 H, J = 16.1 Hz, $OCH_2C(O)$], 4.77, 4.74, 3.23, 3.21 (AB-q, 16 H, J = 13.0 Hz, $ArCH_2Ar$), 4.65, 4.48 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.21, 4.19 (q, 12 H, J = 7.1 Hz, OCH_2CH_3), 3.5−3.4 (m, 4 H, NCH_2^{spacer}), 2.1−1.9 (m, 2 H, CH_2^{spacer}), 1.27, 1.24 (t, 18 H, J = 7.1 Hz, OCH_2CH_3), 1.13, 1.05, 0.96 [s, 72 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 170.7, 170.1, 170.0 [s, C(O) and C(O)N], 153.2, 152.9 (s, ArC-O), 145.4, 145.1 (s, ArC-*t*Bu), 133.6−132.2 (s, ArC), 125.8−125.4 (d, ArC-H), 74.6, 71.5 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.7, 60.6 (t, OCH_2CH_3), 37.4 (t, NCH_2^{spacer}), 33.9, 33.8, 33.7 [s, $C(CH_3)_3$], 32.0 (t, $ArCH_2Ar$), 31.4, 31.3 [q, $C(CH_3)_3$], not observed (CH_2^{spacer}), 14.2 (q, OCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 1759 ($C=O^{ester}$), 1679 ($C=O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 1969.0 [(M + 2 H)$^+$], 1990.6 [(M + H + Na)$^+$]. − $C_{119}H_{158}N_2O_{22}\cdot H_2O$ (1986.6): calcd. C 71.95, H 8.12, N 1.41; found C 71.65, H 7.99, N, 1.51.

1,4-Bis{25-[(aminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]-arene}butane (**1$_{tBu}$e**): Coupling of **6** (R = *tert*-butyl) (1.00 g, 1.04 mmol) and 1,4-diaminobutane (60 µl, 0.57 mmol), in the presence of Et_3N (0.60 ml, 4.2 mmol), yielded **1$_{tBu}$e** after recrystallization from a mixture of chloroform and acetonitrile (4:1) in 65% yield. m.p. 201−203°C. − ^1H NMR: δ = 8.41 (br. t, 2 H, NH), 6.87, 6.77, 6.66 [s, 16 H, ArH], 4.95 and 4.66 [AB-q, 8 H, J = 16.1 Hz, $OCH_2C(O)$], 4.74, 4.69, 3.23, 3.22 (AB-q, 16 H, J = 13.0 Hz, $ArCH_2Ar$), 4.67, 4.50 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.22, 4.21 [q, 12 H, J = 7.1 Hz, OCH_2CH_3], 3.4−3.3 (m, 4 H, NCH_2^{spacer}), 1.8−1.7 (m, 4 H, CH_2^{spacer}), 1.28, 1.27 [t, 18 H, J = 7.1 Hz, OCH_2CH_3], 1.12, 1.07, 0.99 [s, 72 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 170.5, 170.2, 170.1 [s, C(O) and C(O)N], 153.1, 152.9 (s, ArC-O), 145.5, 145.3 (s, ArC-*t*Bu), 133.5−132.5 (s, ArC), 125.8, 125.5 (d, ArC-H), 74.6, 71.7, 71.6 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.7, 60.6 (t, OCH_2CH_3), 39.3 (t, NCH_2^{spacer}), 33.9, 33.8 [s, $C(CH_3)_3$], 32.0 (t, $ArCH_2Ar$), 31.4, 31.3 [q, $C(CH_3)_3$], 27.7 (t, CH_2^{spacer}), 14.2 (q, OCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 1759 ($C=O^{ester}$), 1673 ($C=O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 1982.9 [(M + 2 H)$^+$], 2005.6 [(M + H + Na)$^+$]. − $C_{120}H_{160}N_2O_{22}\cdot 2\ H_2O$ (2018.6): calcd. C 71.40, H 8.19, N 1.39; found C 71.22, H 8.04, N 1.78.

1,6-Bis{25-[(aminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]-arene}hexane (**1$_{tBu}$f**): The double calix[4]arene **1$_{tBu}$f** was obtained in 67% yield from **6** (R = *tert*-butyl) (1.49 g, 1.45 mmol), 1,6-diaminohexane (84 µl, 0.73 mmol), and Et_3N (0.90 ml, 6.3 mmol). m.p. 134−136°C. − ^1H NMR: δ = 8.35 (br. t, 2 H, NH), 6.81, 6.80, 6.71 (s, 16 H, ArH), 4.92 and 4.65 [AB-q, 8 H, J = 16.1 Hz, $OCH_2C(O)$], 4.75, 4.67, 3.25, 3.22 (AB-q, 16 H, J = 13.0 Hz, $ArCH_2Ar$), 4.70, 4.51 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.20 (q, 12 H, J = 7.1 Hz, OCH_2CH_3), 3.4−3.3 (m, 4 H, NCH_2^{spacer}), 1.7−1.6 (m, 4 H, CH_2^{spacer}), 1.4−1.3 (m, 4 H, CH_2), 1.28, 1.27 (t, 18 H, J = 7.1 Hz, OCH_2CH_3), 1.10, 1.09, 1.03 [s, 72 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 170.4, 170.1 [s, C(O) and C(O)N], 153.2, 152.9 (s, ArC-O), 145.5, 145.3 (s, ArC-*t*Bu), 133.3−132.6 (s, ArC), 125.8, 125.5 (d, ArC-H), 74.5, 71.8, 71.4 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.7, 60.5 (t, OCH_2CH_3), 39.5 (t, NCH_2^{spacer}), 33.9, 33.8 [s, $C(CH_3)_3$], 32.0 (t, $ArCH_2Ar$), 31.4 [q, $C(CH_3)_3$], 30.2, 27.3 (t, CH_2^{spacer}), 14.2 (q, OCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 1758 ($C=O^{ester}$), 1680 ($C=O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 2033.5 [(M + H + Na)$^+$], 2011.7 [(M + 2 H)$^+$]. − $C_{122}H_{164}N_2O_{22}\cdot 2\ H_2O$ (2046.7): calcd. C 71.60, H 8.27, N 1.37; found C 71.73, H 8.13, N 1.23.

1,3-Bis{25-[(aminocarbonyl)methoxy]-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]arene}benzene (**1$_H$a**): The reaction of **6** (R = H) (0.51 g, 0.69 mmol) and 1,3-phenylenediamine (40 mg, 0.37 mmol) in the presence of Et_3N (0.40 ml, 2.8 mmol) gave white crystals in 51% yield. m.p. 137−140°C. − ^1H NMR: δ = 9.71 (br. s, 2 H, NH), 8.35 (br. s, 1 H, ArH^{spacer}), 7.5−7.4 (m, 2 H, ArH^{spacer}), 7.29 (br. s, 1 H, ArH^{spacer}), 7.0−6.9 (m, 8 H, ArH), 6.9−6.8 (m, 4 H, ArH), 6.5−6.4 (m, 2 H, ArH), 6.4−6.3 (m, 2 H, ArH), 6.34, 6.19 (d, 8 H, J = 7.6 Hz, ArH^{para}), 5.01 and 4.62 [AB-q, 8 H, J = 16.4 Hz, $OCH_2C(O)$], 4.83, 4.70, 3.28, 3.26 (AB-q, 16 H, J = 13.9 Hz, $ArCH_2Ar$), 4.53, 4.49 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.24 (q, 4 H, J = 7.1 Hz, OCH_2CH_3), 4.1−4.0 (m, 8 H, OCH_2CH_3), 1.29, 1.15 [t, 18 H, J = 7.1 Hz, OCH_2CH_3]. − ^{13}C NMR: δ = 170.7, 169.5 [s, C(O) and C(O)N], 167.8 (s, ArC-N^{spacer}), 157.0, 154.9, 154.6 (s, ArC-O), 138.1 (d, ArC^{spacer}), 135.7−133.1 (s, ArC), 129.4−122.9 (d, ArC-H), 74.3, 71.6, 71.2 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.9, 60.8 (t, OCH_2CH_3), 31.5, 31.0 (t, $ArCH_2Ar$), 14.2, 14.1 [q, OCH_2CH_3]. − IR (KBr): $\tilde{\nu}$ = 1757 ($C=O^{ester}$), 1694 ($C=O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 1554.1 [(M + 2 H)$^+$], 1577.9 [(M + 2 H + Na)$^+$]. − $C_{90}H_{92}N_2O_{22}$ (1553.7): calcd. C 69.57, H 5.97, N 1.80; found C 69.24, H 5.88, N, 2.00.

1,4-Bis{25-[(aminocarbonyl)methoxy]-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]arene}benzene (**1$_H$b**): Compound **1$_H$b** was obtained as a white solid in 76% yield by reaction of **6** (R = H) (0.50 g, 0.67 mmol), 1,4-phenylenediamine (40 mg, 0.37 mmol),

and Et_3N (0.40 ml, 2.8 mmol). m.p. 183–185°C. – ^1H NMR: δ = 9.66 (br. s, 2 H, NH), 7.77 (s, 4 H, ArH^{spacer}), 7.1–7.0 (m, 8 H, ArH), 6.9–6.8 (m, 4 H, ArH), 6.5–6.4 (m, 2 H, ArH), 6.4–6.3 (m, 2 H, ArH), 6.31, 6.14 (d, 8 H, J = 7.6 Hz, ArH^{para}), 5.07 and 4.69 [AB-q, 8 H, J = 16.5 Hz, $OCH_2C(O)$], 4.82, 4.72, 3.29, 3.27 (AB-q, 16 H, J = 13.8 Hz, $ArCH_2Ar$), 4.51, 4.45 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.26 (q, 4 H, J = 7.1 Hz, OCH_2CH_3), 4.2–4.1 (m, 8 H, OCH_2CH_3), 1.31, 1.20 [t, 18 H, J = 7.1 Hz, OCH_2CH_3]. – ^{13}C NMR: δ = 170.8, 169.4 [s, C(O) and C(O)N], 167.6 (s, $ArC\text{-}N^{spacer}$), 157.1, 154.8, 154.2 (s, ArC-O), 135.8–133.0 (s, ArC), 134.3 (d, ArC^{spacer}), 129.4–121.9 (d, ArC-H), 74.4, 71.6, 71.1 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.9 (t, OCH_2CH_3), 31.5, 30.9 (t, $ArCH_2Ar$), 14.2 (q, OCH_2CH_3). – IR (KBr): $\tilde{\nu}$ = 1768 ($C{=}O^{ester}$), 1690 ($C{=}O^{amide}$) cm^{-1}. – MS (FAB); *m/z*: 1554.0 [(M + 2 H)$^+$], 1576.7 [(M + H + Na)$^+$]. – $C_{90}H_{92}N_2O_{22}\cdot H_2O$ (1571.7): calcd. C 68.78, H 6.03, N 1.78; found C 68.42, H 5.94, N 1.97.

1,2-Bis{25-[(aminocarbonyl)methoxy]-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]arene}ethane ($\mathbf{1_H}$**c**): The coupling was performed using **6** (R = H) (0.50 g, 0.67 mmol), 1,2-diaminoethane (22 µl, 0.33 mmol), and Et_3N (0.40 ml, 2.8 mmol). Recrystallization led to $\mathbf{1_H}$**c** in 59% yield. m.p. 175–177°C. – ^1H NMR: δ = 8.58 (br. s, 2 H, NH), 6.9–6.7 (m, 12 H, ArH), 6.5–6.4 (m, 2 H, ArH), 6.4–6.3 (m, 2 H, ArH), 6.38, 6.26 (d, 8 H, J = 7.3 Hz, ArH^{para}), 5.01 and 4.61 [AB-q, 8 H, J = 16.5 Hz, $OCH_2C(O)$], 4.76, 4.72, 3.29, 3.25 (AB-q, 16 H, J = 13.7 Hz, $ArCH_2Ar$), 4.53, 4.37 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.22 (q, 12 H, J = 7.1 Hz, OCH_2CH_3), 3.66 (br. s, 4 H, CH_2^{spacer}), 1.25 (t, 18 H, J = 6.9 Hz, OCH_2CH_3). – ^{13}C NMR: δ = 170.7, 169.8, 169.5 [s, C(O) and C(O)N], 156.7, 155.2 (s, ArC-O), 135.3–133.4 (s, ArC), 129.2–122.9 (d, ArC-H), 74.1, 71.4 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 61.0, 60.8 (t, OCH_2CH_3), 38.6 (t, NCH_2^{spacer}), 31.6, 31.0 (t, $ArCH_2Ar$), 14.2 (q, OCH_2CH_3). – IR (KBr): $\tilde{\nu}$ = 1759 ($C{=}O^{ester}$), 1678 ($C{=}O^{amide}$) cm^{-1}. – MS (FAB); *m/z*: 1506.5 [(M + 2 H)$^+$], 1528.2 [(M + H + Na)$^+$]. – $C_{86}H_{92}N_2O_{22}$ (1505.7): calcd. C 68.60, H 6.16, N 1.86; found C 68.35, H 6.26, N 2.07.

1,3-Bis{25-[(aminocarbonyl)methoxy]-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]arene}propane ($\mathbf{1_H}$**d**): Reaction of **6** (R = H) (0.50 g, 0.67 mmol) with 1,3-diaminopropane (27 µl, 0.32 mmol) in the presence of Et_3N (0.40 ml, 2.8 mmol) gave $\mathbf{1_H}$**d** as a white solid in 61% yield. m.p. 173–174°C. – ^1H NMR: δ = 8.42 (br. s, 2 H, NH), 7.0–6.9 (m, 8 H, ArH), 6.9–6.8 (m, 4 H, ArH), 6.5–6.4 (m, 2 H, ArH), 6.4–6.3 (m, 2 H, ArH), 6.30, 6.14 (d, 8 H, J = 7.5 Hz, ArH^{para}), 5.00 and 4.62 [AB-q, 8 H, J = 16.5 Hz, $OCH_2C(O)$], 4.73, 4.71, 3.24 (AB-q, 16 H, J = 13.9 Hz, $ArCH_2Ar$), 4.48, 4.30 [s, 8 H, $OCH_2C(O)$ and $OCH_2C(O)N$], 4.23, 4.18 (q, 12 H, J = 7.1 Hz, OCH_2CH_3), 3.6–3.4 (m, 4 H, CH_2^{spacer}), 2.1–1.9 (m, 2 H, CH_2^{spacer}), 1.28, 1.24 (t, 18 H, J = 7.1 Hz, OCH_2CH_3). – ^{13}C NMR: δ = 170.8, 169.5, 169.3 [s, C(O) and C(O)N], 157.0, 154.9, 154.6 (s, ArC-O), 135.6–133.1 (s, ArC), 129.4–122.8 (d, ArC-H), 74.0, 71.5, 71.2 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.8 (t, OCH_2CH_3), 37.2 (t, NCH_2^{spacer}), 31.5, 30.9 (t, $ArCH_2Ar$), 30.3 (t, CH_2^{spacer}), 14.2 (q, OCH_2CH_3). – IR (KBr): $\tilde{\nu}$ = 1756 ($C{=}O^{ester}$), 1679 ($C{=}O^{amide}$) cm^{-1}. – MS (FAB); *m/z*: 1542.5 [(M + H + Na)$^+$], 1519.9 [(M + H)$^+$].– $C_{87}H_{94}N_2O_{22}$ (1519.7): calcd. C 68.76, H 6.23, N 1.84; found C 68.62, H 6.25, N 1.93.

25,26,27-Tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-28-(2-propenyloxy)calix[4]arene (**9**): A mixture of monoallylated calix[4]arene **8** (5.00 g, 7.26 mmol), K_2CO_3 (5.0 g, 36 mmol), a catalytic amount of potassium iodide, and 2-chloro-*N,N*-diethylacetamide (2.70 ml, 26.2 mmol) in acetonitrile (300 ml) was refluxed overnight. After cooling to room temperature, the salts were filtered off and the acetonitrile was evaporated. The crude product was taken up in CH_2Cl_2 (200 ml), washed twice with a saturated aqueous solution of NH_4Cl (250 ml), twice with water (250 ml), and was subsequently dried over $MgSO_4$. Recrystallization from acetonitrile gave pure **9** in 57% yield. m.p. 93–95°C. – ^1H NMR: δ = 6.94 (d, 4 H, J = 2.3 Hz, ArH), 6.63, 6.57 [d, 4 H, J = 2.4 Hz, ArH], 5.3–5.2 (m, 1 H, $CH{=}CH_2$), 5.2–5.0 (m, 2 H, $CH{=}CH_2$), 5.12 [s, 2 H, $OCH_2C(O)N$], 5.05 and 4.55 [AB-q, 4 H, J = 13.7 Hz, $OCH_2C(O)N$], 4.81, 4.66, 3.20, 3.14 (AB-q, 8 H, J = 13.9 Hz, $ArCH_2Ar$), 4.65 (s, 2 H, $ArOCH_2$), 3.5–3.2 (m, 12 H, NCH_2CH_3), 1.21, 0.94 [s, 36 H, $C(CH_3)_3$], 1.2–1.0 (m, 18 H, NCH_2CH_3). – ^{13}C NMR: δ = 169.4, 168.3 [s, C(O)N], 154.2, 153.7, 153.4 (s, ArC-O), 144.8, 144.4 (s, ArC-*t*Bu), 137.9 (d, $CH{=}CH_2$), 135.2–132.5 (s, ArC), 125.6–124.9 (d, ArC-H), 115.1 (t, $CH{=}CH_2$), 75.7, 72.2, 71.4 [t, $OCH_2C(O)N$], 41.2, 40.6, 40.0, 39.5 (t, NCH_2CH_3), 34.0, 33.9, 33.7 [s, $C(CH_3)_3$], 32.0 (t, $ArCH_2Ar$), 31.6, 31.4, 31.3 [q, $C(CH_3)_3$], 14.5, 13.1 (q, NCH_2CH_3). – MS (FAB); *m/z*: 1050.9 [(M + Na)$^+$], 1029.0 [(M + H)$^+$]. – $C_{65}H_{93}N_3O_7$ (1028.5): calcd. C 75.91, H 9.11, N 4.09; found C 75.57, H 9.10, N 4.30.

25,26,27-Tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene (**10**): A mixture of **9** (3.00 g, 2.92 mmol), $Et_3N\cdot HCOOH$ (0.52 g, 3.50 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.22 mmol) in ethanol (60 ml) and water (12 ml) was refluxed for 2 h. After cooling to room temperature, the solvents were evaporated and the crude product was taken up into chloroform (50 ml). The organic layer was washed twice with a saturated aqueous solution of NH_4Cl (50 ml) and twice with water (50 ml). After drying over $MgSO_4$ and evaporation of the solvent the crude product was recrystallized from acetonitrile (20 ml). Compound **10** was obtained as a white powder in 77% yield. m.p. 225–227°C. – ^1H NMR: δ = 8.09 (s, 1 H, ArOH), 6.93, 6.87 [s, 4 H, ArH], 6.72, 6.69 (d, 4 H, J = 2.4 Hz, ArH), 5.12 and 4.55 [AB-q, 4 H, J = 14.0 Hz, $OCH_2C(O)N$], 5.06, 4.54, 3.24, 3.19 (AB-q, 8 H, J = 13.3 Hz, $ArCH_2Ar$), 5.08 [s, 2 H, $OCH_2C(O)N$], 3.5–3.2 (m, 12 H, NCH_2CH_3), 1.19, 1.17, 0.97 [s, 36 H, $C(CH_3)_3$], 1.2–1.0 (m, 18 H, NCH_2CH_3). – ^{13}C NMR: δ = 169.7, 168.6 [s, C(O)N], 154.4, 153.2 (s, ArC-O), 150.8 (s, ArC-OH), 146.1, 145.3, 140.7 (s, ArC-*t*Bu), 134.3–128.0 (s, ArC), 126.0–125.0 (d, ArC-H), 73.2, 72.0 [t, $OCH_2C(O)N$], 41.2, 40.2, 40.1 (t, NCH_2CH_3), 34.2, 34.1, 33.9 [s, $C(CH_3)_3$], 32.4, 32.1 (t, $ArCH_2Ar$), 31.9, 31.7, 31.5 [q, $C(CH_3)_3$], 14.5, 13.4, 13.3 (q, NCH_2CH_3). – MS (FAB); *m/z*: 1011.0 [(M + Na)$^+$], 989.0 [(M + H)$^+$]. – $C_{62}H_{89}N_3O_7\cdot H_2O$ (1006.4): C 73.99, H 9.11, N 4.18; found C 73.96, H 9.00, N 4.25.

General Procedure for the Preparation of Spacer Units **11**: A solution of chloroacetyl chloride in EtOAc (20 ml) was added dropwise to a mixture of the appropriate diamine and K_2CO_3 in EtOAc and water. The reaction mixture was stirred overnight, and the precipitate was filtered off. The product was washed with cold EtOAc and dried under vacuum. Compounds **11** were used as such.

N,N'-Bis(chloromethyl)carbonyl-1,4-diaminobenzene (**11b**): The reaction was performed using chloroacetyl chloride (8.63 ml, 0.11 mol) 1,4-phenylenediamine (4.05 g, 37 mmol), and K_2CO_3 (25.6 g, 0.18 mmol) in a mixture of ethyl acetate (200 ml) and water (200 ml), and gave product **11b** in 79%. ^1H NMR ([D$_6$]DMSO): δ = 10.33 (s, 2 H, NH), 7.56 (s, 4 H, ArH), 4.25 (s, 4 H, CH_2Cl).

N,N'-Bis(chloromethyl)carbonyl-1,4-diaminobutane (**11e**): Spacer **11e** was synthesized from chloroacetyl chloride (5.28 ml, 68 mmol) 1,4-diaminobutane (2.28 ml, 22.7 mmol), and K_2CO_3 (14.5 g, 0.10 mol) in a mixture of ethyl acetate (150 ml) and water (150 ml), and was obtained in 72% yield. ^1H NMR: δ = 6.69 (br. t, 2 H, NH),

4.06 (s, 4 H, CH_2Cl), 3.4–3.3 (m, 4 H, NCH_2), 1.7–1.6 (m, 4 H, NCH_2CH_2).

N,N'-Bis(chloromethyl)carbonyl-1,6-diaminobutane (**11f**): The reaction was carried out using chloroacetyl chloride (4.28 ml, 55 mmol), 1,6-diaminohexane (2.00 g, 17.2 mmol), and K_2CO_3 (10.5 g, 76 mmol) in ethyl acetate (60 ml) and water (60 ml), leading to **11f** in 70% yield. ^{1}H NMR: δ = 6.65 (br. t, 2 H, NH), 4.06 (s, 4 H, CH_2Cl), 3.4–3.3 (m, 4 H, NCH_2), 1.6–1.5 (m, 4 H, NCH_2CH_2), 1.4–1.3 (m, 4 H, $NCH_2CH_2CH_2$).

General Procedure for the Preparation of Hexa-Amide Biscalix[4]arenes (**2**): A mixture of **10**, K_2CO_3, a catalytic amount of KI, and 0.5 mol equivalents of **11** in acetonitrile was refluxed for 16 h. After cooling to room temperature, the solvent was evaporated and the crude product was taken up into CH_2Cl_2 (50 ml). The resulting mixture was washed with a saturated aqueous NH_4Cl solution (50 ml) and subsequently with water (50 ml). Compounds **2** were dried over $MgSO_4$, and the solvent was evaporated.

1,4-Bis{25-[(aminocarbonyl)methoxy]-26,27,28-tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene}benzene (**2b**): The reaction of spacer unit **11b** (67 mg, 0.25 mmol) with **10** (0.50 g, 0.51 mmol) in the presence of K_2CO_3 (0.09 g, 0.65 mmol) was performed in acetonitrile (25 ml). After work-up and recrystallization from acetonitrile, **2b** was obtained as a white powder in 65% yield. m.p. 293–295°C. – ^{1}H NMR: δ = 10.37 (s, 2 H, NH), 7.74 (s, 4 H, ArH^{spacer}), 6.9–6.8 (m, 8 H, ArH), 6.78, 6.65 (s, 8 H, ArH), 5.08 and 4.79 [AB-q, 8 H, *J* = 15.1 Hz, $OCH_2C(O)N$], 5.00, 4.93, 3.26, 3.23 (AB-q, 16 H, *J* = 12.8 Hz, $ArCH_2Ar$), 4.85, 4.80 [s, 8 H, $OCH_2C(O)N$], 3.5–3.2 (m, 24 H, NCH_2CH_3), 1.12, 1.09, 0.99 [s, 72 H, $C(CH_3)_3$], 1.1–1.0 (m, 36 H, NCH_2CH_3). – ^{13}C NMR: δ = 168.8, 168.6 [s, C(O)N], 153.6, 153.5 (s, ArC-O), 144.8 (s, ArC-*t*Bu), 134.8 (ArC^{spacer}), 133.8–132.8 (s, ArC), 125.7–125.3 (d, ArC-H), 121.6 (d, $ArCH^{spacer}$), 74.5, 71.4 [t, $OCH_2C(O)N$], 40.9, 40.0 (t, NCH_2CH_3), 33.8 [s, $C(CH_3)_3$], 32.1 (t, $ArCH_2Ar$), 31.5, 31.4 [q, $C(CH_3)_3$], 14.2, 13.0 (q, NCH_2CH_3). – IR (KBr): $\tilde{\nu}$ = 1660 (C=O) cm^{-1}. – MS (FAB); *m/z*: 2188.0 [$(M + 2H + Na)^+$], 2165.2 [$(M + 2H)^+$]. – $C_{134}H_{186}N_8O_{16} \cdot CH_3CN \cdot 3\,H_2O$ (2260.1): calcd. C 72.28, H 8.70, N 5.58; found C 72.20, H 8.61, N 5.75.

1,4-Bis{25-[(aminocarbonyl)methoxy]-26,27,28-tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene}butane (**2e**): The reaction was performed using **11e** (68 mg, 0.28 mmol), **10** (0.56 g, 0.57 mmol), and K_2CO_3 (83 mg, 0.68 mmol) in acetonitrile (25 ml). Recrystallization from a mixture of acetonitrile and dichloromethane (20:1) gave **2e** as a white powder in 64% yield. m.p. 263–265°C. – ^{1}H NMR: δ = 9.07 (br. t, 2 H, NH), 6.9–6.8 (m, 8 H, ArH), 6.73, 6.56 (s, 8 H, ArH), 5.18 and 4.80 [AB-q, 8 H, *J* = 15.1 Hz, $OCH_2C(O)N$], 5.00, 4.84, 3.28, 3.22 (AB-q, 16 H, *J* = 12.8 Hz, $ArCH_2Ar$), 4.79, 4.49 [s, 8 H, $OCH_2C(O)N$], 3.5–3.2 (m, 28 H, NCH_2CH_3 and NCH_2^{spacer}), 1.7–1.6 (m, 4 H, CH_2^{spacer}), 1.15, 1.05, 0.94 [s, 72 H, $C(CH_3)_3$], 1.2–1.0 (m, 36 H, NCH_2CH_3). – ^{13}C NMR: δ = 170.2, 168.9, 168.5 [s, C(O)N], 153.7, 153.6, 153.5 (s, ArC-O), 144.7 (s, ArC-*t*Bu), 133.7–132.3 (s, ArC), 125.9–125.4 (d, ArC-H), 74.9, 71.8, 71.3 [t, $OCH_2C(O)N$], 40.8, 40.7, 39.9, 39.8 (t, NCH_2CH_3), 39.6 (t, NCH_2^{spacer}), 33.9, 33.8, 33.7 [s, $C(CH_3)_3$], 32.5, 31.7 (t, $ArCH_2Ar$), 31.5, 31.3 [q, $C(CH_3)_3$], 27.9 (t, CH_2^{spacer}), 14.3, 13.1 (q, NCH_2CH_3). – IR (KBr): $\tilde{\nu}$ = 1658 (C=O) cm^{-1}. – MS (FAB); *m/z*: 2167.4 [$(M + H + Na)^+$]. – $C_{132}H_{190}N_8O_{16} \cdot H_2O$ (2163.0): calcd. C 73.30, H 8.95, N 5.18; found C 73.10, H 8.79, N 5.00.

1,6-Bis{25-[(aminocarbonyl)methoxy]-26,27,28-tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene}hexane (**2f**): The coupling was carried out using **11f** (6.9 mg, 2.9 mmol), **10** (51 mg, 51 mmol), K_2CO_3 (7.5 mg, 54 mmol), and acetonitrile (15 ml). Recrystallization from methanol gave **2f** as a white powder in 68% yield. m.p. 237–239°C. – ^{1}H NMR: δ = 9.02 (br. t, 2 H, NH), 6.87, 6.86, 6.74, 6.60 (s, 16 H, ArH), 5.17 and 4.80 [AB-q, 8 H, *J* = 15.0 Hz, $OCH_2C(O)N$], 5.01, 4.83, 3.28, 3.23 (AB-q, 16 H, *J* = 12.8 Hz, $ArCH_2Ar$), 4.80, 4.50 [s, 8 H, $OCH_2C(O)N$], 3.5–3.2 (m, 28 H, NCH_2CH_3 and NCH_2^{spacer}), 1.7–1.6, 1.4–1.3 (m, 8 H, CH_2^{spacer}), 1.15, 1.06, 0.95 [s, 72 H, $C(CH_3)_3$], 1.1–1.0 (m, 36 H, NCH_2CH_3). – ^{13}C NMR: δ = 170.1, 168.9, 168.5 [s, C(O)N], 153.7, 153.6, 153.5 (s, ArC-O), 144.7 (s, ArC-*t*Bu), 133.8–132.3 (s, ArC), 125.9–125.3 (d, ArC-H), 74.8, 71.9, 71.3 [t, $OCH_2C(O)N$], 40.8, 40.7, 39.9, 39.8 (t, NCH_2CH_3), 39.8 (t, NCH_2^{spacer}), 33.9, 33.8, 33.7 [s, $C(CH_3)_3$], 32.4 (t, $ArCH_2Ar$), 31.5, 31.3 [q, $C(CH_3)_3$], 30.3, 27.4 (t, CH_2^{spacer}), 14.3, 13.1 (q, NCH_2CH_3). – IR (KBr): $\tilde{\nu}$ = 1659 (C=O) cm^{-1}. – MS (FAB); *m/z*: 2196.2 [$(M + 2H + Na)^+$], 2173.5 [$(M + 2H)^+$]. – $C_{134}H_{194}N_8O_{16} \cdot H_2O$ (2191.1): C 73.46, H 9.02, N 5.11; found C 73.17, H 8.97, N 5.01.

N-[(Chloromethyl)carbonyl]-N'-[(1,1-dimethylethoxy)carbonyl]-1,3-diaminopropane (**12d**): The BOC-protected spacers **12** were synthesized as described for spacer units **11**, using chloroacetyl chloride (0.56 ml, 7.2 mmol) in ethyl acetate (3 ml), and a mixture of *N*-BOC-1,3-propanediamine (1.00 g, 5.7 mmol) and K_2CO_3 (3.2 g, 23 mmol) in EtOAc (20 ml) and water (20 ml). The solution was stirred for 3 h at room temperature and the organic layer was separated and dried over $MgSO_4$. After purification by column chromatography (3% MeOH in CH_2Cl_2), **12d** was obtained as a yellow powder in 82% yield. ^{1}H NMR: δ = 7.14 (br. t, 1 H, NH), 4.84 (br. t, 1 H, NH^{BOC}), 4.03 (s, 2 H, CH_2Cl), 3.35, 3.17 (2 q, 4 H, *J* = 6.3 Hz, NCH_2), 1.7–1.6 (quint, 2 H, *J* = 6.3 Hz, CH_2^{spacer}), 1.41 [s, 9 H, $C(CH_3)_3$].

N-[(Chloromethyl)carbonyl]-N'-[(1,1-dimethylethoxy)carbonyl]-1,6-diaminohexane (**12f**): Compound **12f** was prepared in the same way as described for **12d**, using a solution of chloroacetyl chloride (1.55 ml, 20 mmol) in EtOAc (8 ml), and a mixture of *N*-BOC-1,6-hexanediamine (4.00 g, 16 mmol) and K_2CO_3 (8.88 g, 64 mmol) in EtOAc (50 ml) and water (50 ml). Column chromatography (3% MeOH in CH_2Cl_2) gave **12f** in 75% yield. ^{1}H NMR: δ = 6.62 (br. t, 1 H, NH), 4.54 (br. t, 1 H, NH^{BOC}), 4.02 (s, 2 H, CH_2Cl), 3.29, 3.10 (q, 4 H, *J* = 6.3 Hz, NCH_2), 1.5–1.3 (m, 4 H, CH_2^{spacer}), 1.41 [s, 9 H, $C(CH_3)_3$], 1.4–1.3 (m, 4 H, CH_2^{spacer}).

25,26,27-Tris[(N,N-diethylaminocarbonyl)methoxy]-28-{N-[3-(1,1-dimethylethoxy)carbonylamino]propyl(aminocarbonyl)methoxy}-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene (**13d**): The alkylation was carried out in the same way as described for the biscalix[4]arenes **2**, using **9** (2.00 g, 2.02 mmol), **12d** (0.56 g, 2.23 mmol), K_2CO_3 (0.34 g, 2.42 mmol), a catalytic amount of KI, and acetonitrile (100 ml). After evaporation of the solvent, **13d** was obtained as a foam in 58% yield, and was used as such for further reactions. ^{1}H NMR: δ = 8.94 (br. t, 1 H, NH), 6.81, 6.71 (s, 4 H, ArH), 6.8–6.7 (m, 4 H, ArH), 5.76 (br. t, 1 H, NH^{BOC}), 5.05 and 4.73 [AB-q, 4 H, *J* = 14.9 Hz, $OCH_2C(O)N$], 4.99, 4.78, 3.21, 3.19 (AB-q, 8 H, *J* = 12.8 Hz, $ArCH_2Ar$), 4.86, 4.59 [s, 4 H, $OCH_2C(O)N$], 3.5–3.4 (m, 2 H, NCH^2_{BOC}), 3.4–3.1 (m, 14 H, NCH_2CH_3 and NCH_2^{spacer}), 1.8–1.7 (m, 2 H, CH_2^{spacer}), 1.44 [s, 9 H, $C(CH_3)_3^{BOC}$], 1.2–1.1 (m, 18 H, NCH_2CH_3), 1.10, 1.07, 1.04 [s, 36 H, $C(CH_3)_3$]. – ^{13}C NMR: δ = 171.4 [s, $C(O)N^{BOC}$], 168.7 [s, C(O)N], 156.3, 153.7, 153.3 (s, ArC-O), 144.9 (s, ArC-*t*Bu), 133.4–132.7 (s, ArC), 125.8–125.3 (d, ArC-H), 74.4, 71.9, 71.6 [t, $OCH_2C(O)N$], 40.9, 40.0 [t, NCH_2CH_3], 37.1, 36.1 [t, NCH_2^{spacer}], 33.8 [s, $C(CH_3)_3$], 32.2 (t, $ArCH_2Ar$), 31.8 (t, CH_2^{spacer}), 31.5, 31.4 [q, $C(CH_3)_3$], 28.5 [q, $C(CH_3)_3^{BOC}$], 14.3, 13.1 (q, NCH_2CH_3). – MS (FAB); *m/z*: 1225.0 [$(M + Na)^+$], 1203.0 [$(M + H)^+$].

25,26,27-Tris[(N,N-diethylaminocarbonyl)methoxy]-28-{N-[6-(1,1-dimethylethoxy)carbonylamino]hexyl(aminocarbonyl)methoxy}-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene (**13f**): The alkylation was carried out in the same way as described for the biscalix[4]arenes **2**, using **9** (2.00 g, 2.02 mmol), **12f** (0.65 g, 2.22 mmol), K_2CO_3 (0.34 g, 2.42 mmol), a catalytic amount of KI, and acetonitrile (100 ml). Compound **13f** was obtained as a foam in 62% yield and was used for further reactions without purification. ^{1}H NMR: δ = 8.93 (br. t, 1 H, NH), 6.9−6.8 (m, 4 H, ArH), 6.83, 6.77 (s, 4 H, ArH), 5.11 and 4.76 [AB-q, 4 H, J = 15.0 Hz, $OCH_2C(O)N$], 5.01, 4.80, 3.23, 3.21 (AB-q, 8 H, J = 12.7 Hz, $ArCH_2Ar$), 4.82, 4.52 [s, 4 H, $OCH_2C(O)N$], 4.54 (br. t, 1 H, NH^{BOC}), 3.4−3.2 (m, 14 H, NCH_2CH_3 and NCH_2^{spacer}), 3.1−3.0 (m, 2 H, NCH_2^{BOC}), 1.8−1.6 (m, 4 H, CH_2^{spacer}), 1.44 [s, 9 H, $C(CH_3)_3^{BOC}$], 1.4−1.3 (m, 4 H, CH_2^{spacer}), 1.2−1.1 (m, 18 H, NCH_2CH_3), 1.11, 1.07, 0.98 [s, 36 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 170.3 [s, $C(O)N^{BOC}$], 168.7 [s, C(O)N], 156.0, 153.9, 153.7 (s, ArC-O), 145.1 (s, ArC-*t*Bu), 133.7−133.0 (s, ArC), 125.7−125.4 (d, ArC-H), 74.3, 72.3, 71.8 [t, $OCH_2C(O)N$], 40.8, 40.0, (t, NCH_2CH_3), 39.5 (NCH_2^{spacer}), 33.9 [s, $C(CH_3)_3$], 32.1 (t, $ArCH_2Ar$), 31.6 (t, CH_2^{spacer}), 31.4, 31.3 [q, $C(CH_3)_3$], 30.0, 29.8, 26.9, 26.6 (t, CH_2^{spacer}), 28.4 [q, $C(CH_3)_3^{BOC}$], 14.2, 13.1 (q, NCH_2CH_3). − MS (FAB); *m/z*: 1266.9 [$(M + Na)^+$], 1245.0 [$(M + H)^+$].

25-[N-(3-Amino)propyl(aminocarbonyl)methoxy]-26,27,28-tris[(N,N'-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene (**14d·HCl**): HCl gas was led through a solution of **13d** (0.94 g, 0.78 mmol) dissolved in CH_2Cl_2 (45 ml) for 30 minutes. The solvent was evaporated and the white residue was triturated with acetonitrile to give compound **14d·HCl** in nearly quantitative yield. m.p. 127−129°C. − ^{1}H NMR: δ = 9.05 (br. t, 1 H, NH), 8.71 (br. s, 2 H, NH_2), 6.95, 6.89, 6.79 (s, 8 H, ArH), 5.38 [part of AB-q, 2 H, J = 15.0 Hz, $OCH_2C(O)N$], 5.16 (part of AB-q, 2 H, J = 12.6 Hz, $ArCH_2Ar$), 5.11 [s, 2 H, $OCH_2C(O)N$], 4.7−4.5 [m, 6 H, $OCH_2C(O)N$ and $ArCH_2Ar$] 3.6−3.3 (m, 18 H, NCH_2CH_3 and $ArCH_2Ar$), 3.2−3.0 (m, 2 H, NCH_2^{spacer}), 2.2−2.1 (m, 2 H, CH_2^{spacer}), 1.3−1.1 (m, 18 H, NCH_2CH_3), 1.10, 1.07, 1.02 [s, 36 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 169.5, 169.1 [s, C(O)N], 152.6 (s, ArC-O), 146.1, 145.7 (s, ArC-*t*Bu), 134.2−133.1 (s, ArC), 125.7−125.4 (d, ArC-H), 74.2, 72.0, 71.5 [t, $OCH_2C(O)N$], 41.7, 41.4 (t, NCH_2CH_3), 37.0, 35.8 (t, NCH_2^{spacer}), 33.9 [s, $C(CH_3)_3$], not observed ($ArCH_2Ar$), 31.4 (t, CH_2^{spacer}), 31.3 [q, $C(CH_3)_3$], 26.9 (t, CH_2^{spacer}), 13.9, 13.7, 13.0 (q, NCH_2CH_3). − MS (FAB); *m/z*: 1103.3 [$(M + H)^+$], 1125.1 [$(M + H)^+$]. − $C_{67}H_{99}N_5O_8 \cdot HCl \cdot 2\ H_2O$ (1175.1): calcd. C 68.49, H 8.92, N 5.96; found C 68.61, H 8.98, N 6.24.

25-[N-(6-Amino)hexyl(aminocarbonyl)methoxy]-26,27,28-tris[(N,N'-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene (**14f·HCl**): Compound **14f·HCl** was obtained in the same way as described for **13d**, using HCl gas, and **13f** (1.55 g, 1.25 mmol) dissolved in CH_2Cl_2 (35 ml). After trituration with acetonitrile, a white powder was obtained in nearly quantitative yield. m.p. 133−134°C. − ^{1}H NMR: δ = 9.14 (br. t, 1 H, NH), 8.30 (br. s, 2 H, NH_2), 6.87, 6.79, 6.76 (s, 8 H, ArH), 4.98 [part of AB-q, 2 H, J = 15.7 Hz, $OCH_2C(O)N$], 4.9−4.6 [m, 8 H, $OCH_2C(O)N$ and $ArCH_2Ar$], 4.72 (part of AB-q, 2 H, J = 12.9 Hz, $ArCH_2Ar$), 3.6−3.1 (m, 18 H, NCH_2CH_3 and $ArCH_2Ar$), 3.1−3.0 (m, 2 H, NCH_2^{spacer}), 1.9−1.8, 1.7−1.6, 1.6−1.3 (m, 8 H, CH_2^{spacer}), 1.2−1.0 (m, 18 H, NCH_2CH_3), 1.13, 1.07, 1.03 [s, 36 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 170.6, 169.4, 168.8 [s, C(O)N], 153.3, 152.8 (s, ArC-O), 145.7 (s, ArC-*t*Bu), 133.9−133.4 (s, ArC), 125.6 (d, ArC-H), 73.6, 72.2, 72.0 [t, $OCH_2C(O)N$], 41.2, 40.6 (t, NCH_2CH_3), 39.6 (t, NCH_2^{spacer}), 33.9 [s, $C(CH_3)_3$], not observed ($ArCH_2Ar$), 31.4 (t, CH_2^{spacer}), 31.4, 31.3 [q, $C(CH_3)_3$], 28.9, 27.1, 26.2, 25.8 (t, CH_2^{spacer}), 14.3, 13.1 (q, NCH_2CH_3). − MS (FAB); *m/z*: 1145.1 [$(M + H)^+$], 1166.8 [$(M + Na)^+$]. − $C_{70}H_{105}N_5O_8 \cdot HCl \cdot H_2O$ (1199.1): calcd. C 70.12, H 9.08, N 5.84; found C 69.86, H 8.99, N 6.12.

1-{25-[(Aminocarbonyl)methoxy]-26,27,28-tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene}-3-{25-[(aminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]arene}propane (**3d**): The coupling reaction was performed in the same way as described for the hexaesters **1**, using **7** (0.25 g, 0.26 mmol) dissolved in dichloromethane (20 ml), and a solution of **14d·HCl** (0.29 g, 0.26 mmol), and Et_3N (77 µl, 1.0 mmol) in dichloromethane (10 ml). The product was purified by recrystallization from CH_2Cl_2/MeOH, followed by Sephadex (LH20/MeOH) column chromotography. Compound **3d** was obtained as a white solid in 70% yield. m.p. 120−122°C. − ^{1}H NMR: δ = 9.09, 8.38 (br. t, 2 H, NH), 6.9−6.8 (m, 8 H, ArH), 6.8−6.7 (m, 4 H, ArH), 6.61, 6.57 (s, 4 H, ArH), 5.18 [part of AB-q, 2 H, J = 15.2 Hz, $OCH_2C(O)$], 5.0−4.6 [m, 18 H, $OCH_2C(O)N$ and $OCH_2C(O)$ and $ArCH_2Ar$], 4.51, 4.48 [s, 4 H, $OCH_2C(O)N$ and $OCH_2C(O)$], 4.3−4.1 (m, 6 H, OCH_2CH_3), 3.5−3.1 (m, 24 H, NCH_2CH_3, NCH_2^{spacer}, and $ArCH_2Ar$), 2.1−2.0 (m, 2 H, CH_2^{spacer}), 1.3−1.1 (m, 9 H, OCH_2CH_3), 1.15, 1.14, 1.04, 0.96, 0.93 [s, 72 H, $C(CH_3)_3$], 1.1−1.0 (m, 18 H, NCH_2CH_3). − ^{13}C NMR: δ = 170.7−168.5 [s, C(O)N and C(O)], 153.8−152.8 (s, ArC-O), 145.4−144.7 (s, ArC-*t*Bu), 133.8−132.2 (s, ArC), 125.8−125.3 (d, ArC-H), 74.8, 74.6, 71.5, 71.3 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.7, 60.6 (t, OCH_2CH_3), 40.9, 40.0 (t, NCH_2CH_3), 37.4 (t, NCH_2^{spacer}), 33.9, 33.7 [s, $C(CH_3)_3$], 32.5 (t, CH_2^{spacer}), 32.1 ($ArCH_2Ar$), 31.5, 31.4, 31.3 [q, $C(CH_3)_3$], 14.3, 14.2, 13.1 (q, NCH_2CH_3 and OCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 1760 ($C{=}O^{ester}$), 1667 ($C{=}O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 2072.1 [$(M + H + Na)^+$], 2049.9 [$(M + H)^+$]. − $C_{125}H_{173}N_5O_{19}$ (2049.8): calcd. C 73.25, H 8.51, N 3.42; found C 72.97, H 8.46, N 3.59.

1-{25-[(Aminocarbonyl)methoxy]-26,27,28-tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene}-6-{25-[(aminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,27,28-tris[(ethoxycarbonyl)methoxy]calix[4]arene}hexane (**3f**): The non-symmetric, double calix[4]arene was prepared in the same way as described for **3d**, using **7** (0.25 g, 0.26 mmol) dissolved in dichloromethane (20 ml), and a solution of **14f** (0.30 g, 0.26 mmol), and Et_3N (77 µl, 1.0 mmol) in dichloromethane (10 ml). Purification gave a white solid in 68% yield. m.p. 106−108°C. − ^{1}H NMR: δ = 9.01, 8.38 (br. t, 2 H, NH), 6.9−6.8 (m, 4 H, ArH), 6.80, 6.74, 6.70, 6.61 (s, 12 H, ArH), 5.14 [part of AB-q, 2 H, J = 15.0 Hz, $OCH_2C(O)$], 4.99 (part of AB-q, 2 H, J = 12.8 Hz, $ArCH_2Ar$), 4.9−4.6 [m, 16 H, $OCH_2C(O)N$ and $OCH_2C(O)$ and $ArCH_2Ar$], 4.51 [s, 4 H, $OCH_2C(O)N$ and $OCH_2C(O)$], 4.19 (q, 6 H, J = 7.2 Hz, OCH_2CH_3), 3.4−3.1 (m, 24 H, NCH_2CH_3, NCH_2^{spacer}, and $ArCH_2Ar$), 1.7−1.6, 1.4−1.3 (m, 8 H, CH_2^{spacer}), 1.3−1.2 (m, 9 H, OCH_2CH_3), 1.13, 1.09, 1.08, 1.06, 1.02, 0.96 [s, 72 H, $C(CH_3)_3$], 1.2−1.0 (m, 18 H, NCH_2CH_3). − ^{13}C NMR: δ = 170.4−168.6 [s, C(O)N and C(O)], 153.6−152.9 (s, ArC-O), 145.4−144.8 (s, ArC-*t*Bu), 133.7−132.3 (s, ArC), 125.8−125.3 (d, ArC-H), 74.7, 74.5, 71.7, 71.4 [t, $OCH_2C(O)N$ and $OCH_2C(O)$], 60.7, 60.5 (t, OCH_2CH_3), 40.9, 39.9 (t, NCH_2CH_3), 39.6 (t, NCH_2^{spacer}), 33.9, 33.8, 33.7 [s, $C(CH_3)_3$], 32.4 (t, CH_2^{spacer}), 32.0 ($ArCH_2Ar$), 31.5, 31.4, 31.3 [q, $C(CH_3)_3$], 30.3, 27.3 (t, CH_2^{spacer}), 14.3, 14.2, 13.1 (q, NCH_2CH_3 and OCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 1760 ($C{=}O^{ester}$), 1667 ($C{=}O^{amide}$) cm^{-1}. − MS (FAB); *m/z*: 2114.5 [$(M + H + Na)^+$], 2092.6 [$(M + 2\ H)^+$]. − $C_{128}H_{179}N_5O_{19} \cdot 2\ H_2O$ (2127.9): calcd. C 72.25, H 8.67, N 3.29; found C 72.26, H 8.58, N 3.45.

Procedures for Eu^{3+} Complexation Reactions

1_{tBu}b: 1) Dissolve calix[4]arene in acetone, add two equivalents of $Eu(NO_3)_3$ in acetone (stock solution), stir overnight, evaporate solvent, dry under vacuum.

2) Dissolve calix[4]arene in CH_2Cl_2/acetonitrile (1:1), add two equivalents of $Eu(NO_3)_3$ in acetonitrile, reflux overnight, collect precipitate, dry under vacuum.

2b: 1) Dissolve calix[4]arene in acetone/CH_2Cl_2 (3:1), add two equivalents of $Eu(NO_3)_3$ in acetone, stir overnight, a) evaporate solvent or b) remove solvent with pipet, dry under vacuum.

2) As 1) reflux overnight, collect precipitate, dry under vacuum.

3) As 2) in acetonitrile.

{1,4-Bis[25-aminocarbonyl-26,27,28-tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene]benzene}dieuropium(3+) Hexanitrate(−) (**2b·2[Eu(NO$_3$)$_3$]**): Homodinuclear complex **2b·2[Eu(NO$_3$)$_3$]** was prepared by method 3, using biscalix[4]arene **2b** (0.108 g, 49.9 μmol) and a stock solution of 19.9 mM $Eu(NO_3)_3 \cdot 6\ H_2O$ (5.02 ml, 99.9 μmol) in acetonitrile. m.p. >300°C. − IR (KBr): $\tilde{\nu}$ = 1651, 1623 (C=O) cm^{-1}. − MS (MALDI); *m/z*: 2468.2 (M^+), 2189.8 [(M−2Eu + Na + H)$^+$]. − $C_{134}H_{186}Eu_2N_8O_{16}$ (2468.9): calcd. Eu^{3+} 12.3; found Eu^{3+} 16.3.

{1,4-Bis[25-aminocarbonyl-26,27,28-tris[(N,N-diethylaminocarbonyl)methoxy]-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene]benzene}europium(3+)neodymium(3+) Hexanitrate(−) (**2b·[Eu(NO$_3$)$_3$]·[Nd(NO$_3$)$_3$]**): Heterodinuclear complex **2b·[Eu(NO$_3$)$_3$]·[Nd(NO$_3$)$_3$]** was prepared by method 3, using biscalix[4]arene **2b** (58.2 mg, 26.9 μmol), and stock solutions of 6.14 mM $Eu(NO_3)_3 \cdot 6H_2O$ (4.39 ml, 26.9 μmol), and 6.71mM $Nd(NO_3)_3 \cdot 5H_2O$ (4.01 ml, 26.9 μmol) in acetonitrile. m.p. >300°C. − IR (KBr): $\tilde{\nu}$ = 1651, 1621 (C=O) cm^{-1}. − MS (MALDI); *m/z*: 2466.1 [(M + 5)$^+$], 2188.0 [(M − Eu − Nd + Na)$^+$], 2318 [(M − Nd + H)$^+$]. − $C_{134}H_{186}EuN_8NdO_{16}$ (2461.2): calcd. Eu^{3+} + Nd^{3+} 12.0%; found Eu^{3+} + Nd^{3+} 15.9%. − XRF: Eu^{3+}/Nd^{3+} = 1:1.3.

X-ray Crystallographic Study: X-ray crystallographic analysis of **1_Ha**: colorless prism, $C_{90}H_{92}N_2O_{22}$, F.W. = 1553.74, monoclinic, spacegroup $C2_1/c$, a = 36.169(1), b = 15.098(2), c = 16.042(2) Å, β = 111.1(6)°, V = 8170.4(5) Å^3, Z = 4, D_c = 1.26 g/cm^3. The asymmetric unit consists of half a molecule. Data were collected on an Enraf-Nonius diffractometer in the ω-2θ scan mode. Graphite monochromated Mo-K_α radiation, λ = 0.71073 Å. Of the 4001 independent reflections 1817 were taken as observed with $I_o > 2.5\sigma(I_o)$ (2.5° < θ < 20°). The structure was solved by direct methods using SIR92[30] in the Enraf-Nonius software package[31] and was refined by full matrix least square methods with all atoms treated anisotropically except for the two oxygens, which were partly occupied in the water molecules. Hydrogen atoms were not included. The weighting scheme used was $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$ with p = 0.04. The resulting R factors were: R = 8.2%, R_w = 9.9%. Crystal data are given in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. [Fax: (internat.) + 44(0)1223/336033, E-mail: deposit@chemcrys.cam.ac.uk] on quoting the depository number CCDC-100724, the names of the authors, and the journal citation.

Molecular Modeling: The protocol applied for molecular mechanics and dynamics calculations has been described by van Veggel and Reinhoudt[23b].

Table 3. Data of the crystal structure of **1_Ha**[a]

Formula	$C_{90}H_{92}N_2O_{22}$
M_r	1553.74
crystal	prism
crystal size	0.2 × 0.2 × 0.2 mm
color	colorless
crystal system	monoclinic
space group	*C2/c*
a	36.169(3) Å
b	15.098(1) Å
c	16.042(1) Å
β	111.15(1)°
V	8170(1)
Z	4
D_x	1.26 g/cm^3
μ	0.084 cm^{-1}
T	140 K
Nonius CAD4 diffractometer	θ / 2θ scan
Mo-K_α	λ = 0.71073 Å
θ	8−15°
θ_{max}	20°
h, k, l	−34/32, −14/14, 0/15
Absorbtion correction:	none
measured reflections	7963
independent reflections	4001
observed reflections	1817
$[I > 2.5\ \sigma(I)]$	R_{int} = 5.9%
Refinement on F	
$R(F)$ = 8.2%, $wR(F)$ = 9.9%	S = 3.21
$w = 1/[\sigma^2(F)]$; $\sigma(F) = \sigma(F^2)/(2\ F)$	$\sigma(F^2) = [\sigma^2(I)+(p\cdot F^2)^2]^{1/2}$
$(\Delta/\sigma)_{max}$ = 0.24	$\Delta\rho_{max}$ = 0.51 e/Å^3
Extinction correction	$F^* = F_{calcd.} \cdot 1/(1 + g \cdot I_c)$
Extinction coefficient	$4 \cdot 10^{-6}$

[a] Cell parameters from reorientation of matrices during measurement, 3 standard reflections monitored every 200 reflections. intensity variations within statistical fluctuations, atomic scattering factors from: *International Tables for Crystallography* **1992**, vol. C, Tables 4.2.6.8 and 6.1.1.4.

Photophysical Studies: Steady-state luminescence measurements were performed with a PTI (Photon Technology International, Inc.) Alphascan spectrofluorimeter. For excitation a 75-W quartz-tungsten-halogen lamp followed by a SPEX 1680 double monochromator was used. A PTI 0.25 m single monochromator was used for separation of the emitted light, that was detected at an angle of 90° from the excitation light. The signal from the Hamamatsu R928 photomultiplier was fed to a photon counting interface. For measurements in the phase resolved mode, the excitation beam is modulated in intensity at a frequency of 30−400 Hz by means of an optical chopper. The modulated luminescence signal is subsequently analyzed with a Stanford Research SR530 lock-in amplifier. The frequency dependence of the phase shift and of the demodulation of the luminescence signal is fitted to well-known expressions applied to phase-resolved luminescence data[32]. For faster time resolved luminescence measurements, an Edinburgh Analytical Instruments LP900 system was used, which consisted of a pulsed Xe lamp followed by a 0.25-m monochromator for excitation and another 0.25-m monochromator, used for the separation of light, positioned at an angle of 90° with respect to the first one. The photons were transferred into electric signals by means of a North Coast EO817P liquid nitrogen cooled Germanium detector, and fed to a Tektronix fast digital oscilloscope. Because of the sensitivity of the Eu^{3+} luminescence lifetimes and intensities to the water content of the solutions, methanol was dried over molecular sieves (3 Å) prior to use and the lifetimes and luminescence spectra were recorded using freshly prepared samples.

[1] [1a] W. DeW. Horrocks, Jr., M. Albin, *Proc. Inorg. Chem.* **1984**, *31*, 1. – [1b] N. Sabbatini, M. Guardigli, J.-M. Lehn, *Coord. Chem. Rev.* **1993**, *123*, 210.
[2] M. P. Oude Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruël, J. W. Hofstraat, F. A. J. Geurts, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1997**, *119*, 138.
[3] [3a] M. Li, P. R. Selvin, *J. Am. Chem. Soc.* **1995**, *117*, 8132. – [3b] H. Takalo, I. Hemmilä, T. Sutela, M. Latva, *Helv. Chim. Acta* **1996**, *79*, 789. – [3c] F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. van der Tol, J. W. Verhoeven, *J. Am. Chem. Soc.* **1995**, *117*, 9408.
[4] [4a] J. L. Jackel, A. Yi-Yan, E. M. Vogel, A. Von Lehmen, J. Johnson, E. Snitzer, *Appl. Opt.* **1992**, *31*, 3390. – [4b] K. Hsu, C. M. Miller, J. T. Kringlebotn, E. M. Taylor, J. Townsend, D. N. Payne, *Opt. Lett.* **1994**, *19*, 886.
[5] For the combination $Tb^{3+} \rightarrow Eu^{3+}$ see: F. Tanake, T. Ishibashi, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1105.
[6] S. T. Frey, C. A. Chang, J. F. Carvalho, A. Varadarajan, L. M. Schultze, K. L. Pounds, W. DeW. Horrocks Jr., *Inorg. Chem.* **1994**, *33*, 2882.
[7] M. P. Oude Wolbers, F. C. J. M. van Veggel, J. W. Hofstraat, F. A. J. Geurts, D. N. Reinhoudt, *Perkin Trans. 2*, accepted for publication.
[8] The official IUPAC name for calix[4]arene is pentacyclo[19.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene.
[9] [9a] P. Timmerman, W. Verboom, F. C. J. M. van Veggel, W. P. van Hoorn, D. N. Reinhoudt, *Angew. Chem.* **1994**, *106*, 1313; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1292. – [9b] P. Timmerman, W. Verboom, F. C. J. M. van Veggl, J. P. M. van Duynhoven, D. N. Reinhoudt, *Angew. Chem.* **1994**, *106*, 2437; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2345.
[10] E. van Dienst, B. H. M. Snellink, I. von Piekartz, J. F. J. Engbersen, D. N. Reinhoudt, *J. Chem. Soc., Chem. Commun.* **1995**, 1151.
[11] P. J. Dijkstra, J. A. J. Brunink, K.-E. Bugge, D. N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli, E. Ghidini, *J. Am. Chem. Soc.* **1989**, *111*, 7567.
[12] [12a] Z. Asfari, J. Vicens, J. Weiss, *Tetrahedron Lett.* **1993**, *34*, 627. – [12b] T. Nagasaki, H. Fujishima, S. Shinkai, *Chem. Lett.* **1994**, 989. – [12c] D. M. Rudkevich, W. Verboom, D. N. Reinhoudt, *Tetrahedon Lett.* **1994**, *35*, 7131; D. M. Rudkevich, W. Verboom, D. N. Reinhoudt, *J. Org. Chem.* **1995**, *60*, 6585.
[13] [13a] Z. Asfari, J. Weiss, J. Vicens, *Synlett* **1993**, 719, and references cited therein. – [13b] G. Ulrich, R. Ziessel, *Tetrahedron Lett.* **1994**, *35*, 6299. – [13c] R. Milbradt, J. Weiss, *Tetrahedron Lett.* **1995**, *36*, 2999. – [13d] T. Arimura, C. T. Brown, S. L. Springs, J. L. Sessler, *J. Chem. Soc., Chem. Commun.* **1996**, 2293.
[14] 'Hexa' refers to the number of pendant arms.
[15] M. A. McKervey, M. Owens, H.-R. Schulten, W. Vogt, V. Böhmer, *Angew. Chem.* **1990**, *102*, 326; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 280.
[16] F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marques, B. L. Ruhl, M. J. Schwing-Weill, E. M. Seward, *J. Am. Chem. Soc.* **1989**, *111*, 8681.
[17] V. Böhmer, W. Vogt, S. J. Harris, R. G. Leonard, E. M. Collins, M. Deasy, M. A. McKervey, M. Owens, *J. Chem. Soc., Perkin Trans. 1* **1990**, 431.
[18] C. D. Gutsche, J. A. Levine, *J. Am. Chem. Soc.* **1982**, *104*, 2652.
[19] L. C. Groenen, *Conformational Properties of Calixarenes*, PhD Thesis, University of Twente, The Netherlands, **1992**.
[20] H. Hey, H.-J. Arpe, *Angew. Chem.* **1973**, *85*, 986; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 928.
[21] Molecular modelling indicated that the intra-lanthanide ion–ion distance is the shortest for the hexa-esters in case of this spacer unit.
[22] G. Calestani, F. Ugozzoli, A. Arduini, E. Ghidini, R. Ungaro, *J. Chem. Soc., Chem. Commun.* **1987**, 344.
[23] [23a] Quanta/CHARMm 4.1 was bought from Molecular Simulations Inc., Burlington, MA, USA. For CHARMM see: B. R. Brooks, R. E. Bruccoleri, B. D. Olafsen, D. J. States, S. Swaminathan, M. Karplus, *J. Comput. Chem.* **1983**, *4*, 187. – [23b] F. C. J. M. van Veggel, D. N. Reinhoudt, *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 387. – [23c] W. L. Jorgensen, *J. Phys. Chem.* **1986**, *90*, 1276.
[24] N. Muzet, G. Wipff, A. Casnati, L. Domiano, R. Ungaro, F. Ugozzoli, *J. Chem. Soc., Perkin Trans. 2* **1996**, 1065.
[25] The solubility of the complexes is low and therefore the solutions contained some solid particles that resulted in scattering.
[26] Elemental analysis indicated a relatively high Eu^{3+} content. This lifetime is lower than the lifetime of 2.5 ms that was measured for $EuCl_3$ in [D_4]methanol[2]. However, in other experiments also longer lifetimes were measured, strongly indicating the presence of free ions in solution.
[27] R. C. Holz, C. A. Chang, W. DeW. Horrocks, Jr., *Inorg. Chem.* **1991**, *30*, 3270; the number of coordinating methanol molecules should in principle be calculated from the difference in the reciprocal values of the luminescence lifetimes in CH_3OH and CH_3OD.
[28] The Eu^{3+} luminescence of the heterodinuclear complex after direct excitation at 393 nm was very weak. Consequently, energy transfer studies could not be carried out.
[29] The C content of the Eu^{3+} complexes determined by elemental analysis was too low, probably due to the formation of very stable Eu^{3+} carbides or carbonates (T_{dec} > 1800 °C).
[30] M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D, Vitterbo, *J. Appl. Crystallogr.* **1989**, *22*, 389.
[31] C. K. Fair, *MolEN, An Interactive Intelligent System for Crystal Structure Analysis, User Manual*, Enraf-Nonius, **1990**.
[32] J. R. Lakowicz, *Principle of Fluorescence Spectroscopy*, 2nd ed., Plenum, New York, **1989**, p. 52.

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