Calix[4]arene-triacids as Receptors for Lanthanides; Synthesis and Luminescence of Neutral Eu^{3+} and Tb^{3+} Complexes

Dmitry M. Rudkevich,[a] Willem Verboom,[a] Erik van der Tol,[b] Catherina J. van Staveren,[c] Frans M. Kaspersen,[c] Jan W. Verhoeven[b] and David N. Reinhoudt*[,a]

[a] *Laboratory of Organic Chemistry, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands*

[b] *Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands*

[c] *N. V. Organon, Scientific Development Group, PO Box 20, 5340 BH Oss, The Netherlands*

Calix[4]arene triacids (**3a–d**) have been prepared that are able to form neutral complexes with lanthanides. Complexes of **3a–d** with Eu^{3+} and Tb^{3+} have been studied with respect to their luminescent properties in a protic solvent (methanol). In all cases it was found that the luminescent lifetime of the complexed lanthanide ions is significantly enhanced compared with that of the free ions in the same solvent. Solvent deuterium isotope effects confirm that shielding of the lanthanide ion from the solvent in the calixarene complexes is the main mechanism responsible for the lifetime difference between free and complexed ions, however, the calixarene itself also exerts a moderate lifetime-shortening effect. Excitation spectra show that in the complexes efficient energy transfer to the lanthanide ions occurs both from the calixarene aromatic moieties as well as from aromatic (pyridine) chromophores attached to it.

Calix[4]arenes are popular building blocks in supramolecular chemistry.[1,2] The calixarene platform can be selectively functionalized both at the phenolic OH groups (lower rim) and at the *para* positions of the phenol rings (upper rim)[3] which provides unique possibilities to organize several binding sites appropriately for complexation of potential guests. Recently we and others have shown that *highly preorganized* calixcrowns[4] and calixspherands[5] are able effectively to *shield* alkali-metal cations from solvent molecules with formation of kinetically and thermodynamically stable complexes. An arrangement of four or eight amido functionalities [SO_2NH and (or) C(O)NH][6] immobilized on a rigid calix[4]arene platform has been demonstrated to bind hydrophilic anions in organic media.

It is well documented that pendant-type aza-macrocycles such as 1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetic acid (DOTA) and its derivatives form stable neutral complexes with lanthanides. These complexes are highly luminescent species which may be used as probes for a variety of applications.[7–9] Recently it has been described that calix[4]arenes containing four preorganized carboxamido groups at the lower rim effectively encapsulate and shield lanthanide ions from solvent molecules,[10,11] however, the complexes formed are positively charged.

We report now the preparation of calix[4]arene-based receptors which form *neutral* complexes with trivalent lanthanide cations. In these receptors three carboxylic acid groups and an additional carboxamido fragment are potentially organized in an array complementary to a cationic guest and in addition provide eight or nine co-ordination sites which is highly suitable for shielding of trivalent lanthanide ions.[12] Deprotonation of the carboxylic acid groups leads to negatively charged trianions which are able to bind strongly[13] lanthanides with formation of *electroneutral* complexes. Moreover, our approach has the potential for variation of substituents in the carboxamido fragment.

Results and Discussion

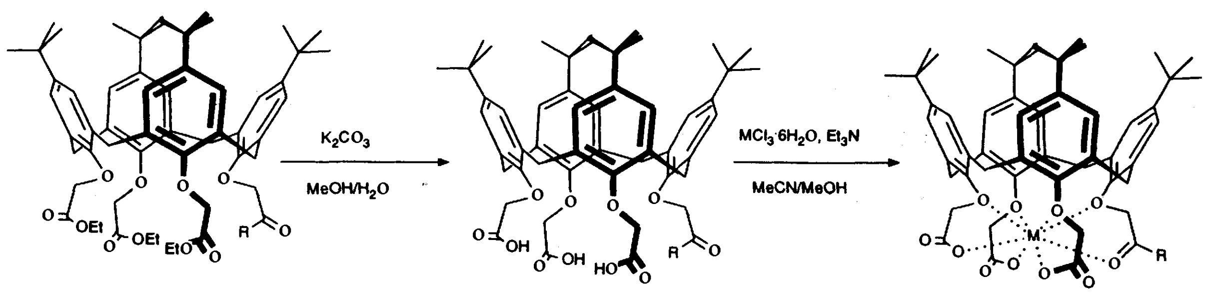
The synthesis of the receptors is depicted in Scheme 1. Reaction of the known calix[4]arene triethyl ester monoacid chloride **1**[14] with an appropriate amine in the presence of Et_3N in CH_2Cl_2 gave the corresponding monoamide triethyl esters **2a–d** in 77–85% yield. Receptors **3a–d** were obtained as white solids in 70–76% yield by mild hydrolysis of **2a–d** with potassium carbonate in refluxing $MeOH–H_2O$, 5:1. In the ^1H NMR spectra of compounds **3a–d** for the aromatic protons as well as for the *tert*-butyl groups three singlets were observed in the ratio 2:1:1, corresponding to the different calix[4]arene aromatic units. Two different types of $Ar–CH_2–Ar$ protons result in two sets of doublets (J = 13.0 Hz) which indicates that the calix[4]arene moiety is still fixed in the 'cone' conformation.

Reaction of ligands **3a–d** with $EuCl_3{\cdot}6H_2O$ or $TbCl_3{\cdot}6H_2O$ in refluxing 1:1 acetonitrile–methanol solution in the presence of Et_3N afforded complexes **4a–d** and **5a–d** as white powders in quantitative yields. The formation of the complexes was confirmed by satisfactory elemental analyses and fast atom bombardment (FAB) mass spectrometry showing an intense signal corresponding to [Ligand + Lanthanide] (Table 1). In order to determine the calix[4]arene conformation we also prepared the non-paramagnetic yttrium complex **6** starting from ligand **3b** and $YCl_3{\cdot}6H_2O$. Analogously to the spectral data of the free ligands **3a–d**, the ^1H NMR spectrum of complex **6** exhibits three singlets in the ratio 2:1:1 for the aromatic protons as well as for the *tert*-butyl groups. In addition, two types of $Ar–CH_2–Ar$ protons result in two sets of doublets (J = 13.1 Hz) which proves that also in the complexes the calix[4]arene moiety is in the cone conformation.

The luminescent nature of the Eu^{3+} and Tb^{3+} lanthanide ions and its known[15,16] sensitivity towards quenching by especially hydroxylic solvents provide an elegant opportunity to investigate the degree to which the present calix[4]arenes are capable of shielding these ions from the environment.

For this purpose the luminescent lifetime was measured in methanol (τ_H) and in perdeuterio-methanol (τ_D) of the compounds **4a–d** and **5a–d** as well as that of 'free' Eu^{3+} and Tb^{3+} in the same solvents. The results of these measurements are compiled in Table 2.

Furthermore, Table 2 compiles the τ_D/τ_H ratios as well as the effective number of solvent molecules (n) coordinated to the lanthanide ions as calculated *via* eqn. (1).[17]



1; R = Cl
2a; R = NHPr^n
2b; R = NH(CH$_2$)$_2$NHC(O)Me
2c; R = NHCH$_2$Py
2d; R = NH(CH$_2$)$_2$Py

3a; R = NHPr^n
3b; R = NH(CH$_2$)$_2$NHC(O)Me
3c; R = NHCH$_2$Py
3d; R = NH(CH$_2$)$_2$Py

4a; R = NHPr^n, M = Eu
4b; R = NH(CH$_2$)$_2$NHC(O)Me, M = Eu
4c; R = NHCH$_2$Py, M = Eu
4d; R = NH(CH$_2$)$_2$Py, M = Eu
5a; R = NHPr^n, M = Tb
5b; R = NH(CH$_2$)$_2$NHC(O)Me, M = Tb
5c; R = NHCH$_2$Py, M = Tb
5d; R = NH(CH$_2$)$_2$Py, M = Tb
6; R = NH(CH$_2$)$_2$NHC(O)Me, M = Y

Scheme 1

Table 1 Yields and mass spectral data of complexes **4a–d**, **5a–d**[a]

Compd.	Yield (%)	FAB-MS m/z (calc. $[M + H]^+$)
4a	94	1072.4[b] (1072.4)
4b	90	1115.5 (1115.1)
4c	89	1121.5 (1121.0)
4d	85	1135.3 (1135.2)
5a	91	1079.0 (1079.1)
5b	94	1121.0[b] (1121.1)
5c	95	1128.7 (1128.1)
5d	87	1141.5[b] (1141.1)

[a] All compounds gave satisfactory elemental analyses. [b] (M^+).

Table 2 Luminescent lifetimes measured in CH_3OH (τ_H) and CD_3OD (τ_D) and the number of coordinated solvent molecules calculated *via* eqn. (1)

Compd.	τ_H/ms	τ_D/ms	τ_D/τ_H	n
Eu^{3+}[a]	0.26	1.9	7.3	7.0 ± 1.0
4a	0.65	1.3	2.0	1.6 ± 0.4
4b	0.69	1.3	1.9	1.4 ± 0.5
4c	0.68	1.1	1.6	1.2 ± 0.5
4d	0.60	1.2	2.0	1.8 ± 0.5
Tb^{3+}[b]	0.65	2.6	4.0	9.7 ± 1.5
5a	0.65	0.67	1.0	0.4 ± 1.5
5b	0.57	0.63	1.1	1.4 ± 1.5
5c	0.65	0.69	1.1	0.7 ± 1.5
5d	0.55	0.61	1.1	1.5 ± 1.5

[a] $EuCl_3{\cdot}6H_2O$ dissolved in CH_3OH or CD_3OD. [b] $TbCl_3{\cdot}6H_2O$ dissolved in CH_3OH or CD_3OD.

$$n = r(1/\tau_H - 1/\tau_D), \qquad (1)$$

$$r = 2.1 \text{ for } Eu^{3+} \text{ and } 8.4 \text{ for } Tb^{3+}$$

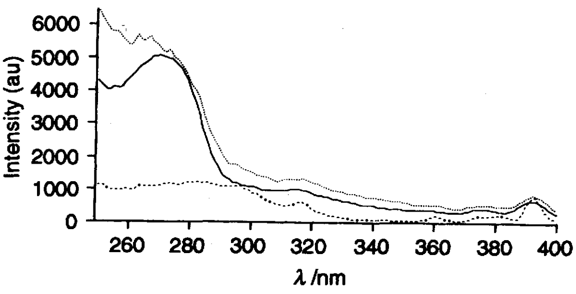


Fig. 1 Corrected excitation spectra of Eu^{3+} (– – –), **4a** (——) and **4d** (· · ·) in CH_3OH at room temperature and normalized on the $^7F_0$–$^5L_6$ lanthanide transition around 394 nm; λ_{em} = 615 nm

It should be stressed that the multiplication factor r is an empirical[17] one and that, especially for Tb^{3+}, this parameter is quite large (because this ion is less sensitive to solvent quenching than Eu^{3+}) thereby leading to a relatively high uncertainty in the calculated n values (see Table 2). However, within the limits of uncertainty, the data obtained for free Eu^{3+} and Tb^{3+} are identical and corroborate the well documented[15,16] quenching of the luminescence of these ions by coordinated hydroxylic solvents thus leading to a dramatic increase of the luminescent lifetime upon transfer from CH_3OH to CD_3OD. This effect is much less pronounced for the calixarene complexes (for the Tb^{3+} complexes the luminescent lifetimes in CH_3OH and CD_3OD are in fact identical within the experimental error of about 10%), thus demonstrating that an effective solvent shielding has been achieved by complexation of the lanthanide ions in the calix[4]arene cage. On the other hand we notice that the calixarene complexation itself also appears to have a (modest) quenching effect since τ_D of the calixarene complexes is significantly shorter than τ_D of the free ions. It seems likely that high frequency vibrational modes of the tightly bound calixarene are involved here as acceptor modes.

It is important to note that for the free ions as well as for all calixarene complexes monoexponential luminescence decay curves were observed. Because of the large differences in lifetimes involved (see Table 2) this implies that—at least in the solvent used—the emission of the complex solutions does not contain a detectable contribution of free lanthanide ions.

Another important conclusion to be drawn from the data in Table 2 is that there appears to be little difference in the efficiency with which the variously substituted calixarenes investigated shield the lanthanides from interaction with the quenching solvent molecules. We may thus conclude that this type of calixarene provides a relatively high degree of solvent shielding of Eu^{3+} and Tb^{3+} ions in an overall neutral complex and at the same time allows one to introduce various substituents in the side chains without disturbing the shielding efficiency. The latter is of particular interest because from the excitation spectra it is evident that—as reported earlier[10]—not only does efficient energy transfer take place from the aromatic calixarene cage to the lanthanide ion, but also from chromophoric substituents in the carboxamido fragment.

This phenomenon is demonstrated in Fig. 1 where the excitation spectra of free Eu^{3+} and of complexes **4a** and **4d** are compared.

In addition to the weak transitions of the lanthanide ion itself the excitation spectrum of the red (615 nm) emission of **4a** displays a pronounced maximum around 270 nm corresponding to the absorption of the aromatic calixarene cage. The excitation spectrum of **4d**, however, features on the short wavelength side of this band some strong shoulders characteristic of the side-chain pyridine chromophore. This demonstrates that efficient energy transfer takes place not only from the calixarene cage[10] but also from the side-chain chromophore, to populate the luminescent energy level of the encapsulated Eu^{3+} ion. Similar observations were made for the other complexes investigated and, together with the relative insensitivity of the encapsulating efficiency for side chain alterations, this suggests that the excitation spectra of these neutral lanthanide complexes can be varied dramatically by introduction of appropriate 'antenna chromophores' in the side chains as demonstrated before in the case of some (positively) charged Ln^{3+}/calix[4]arene complexes.[11]

Experimental

Synthesis.—Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker AC 250 spectrometer for samples in $CDCl_3$ with Me_4Si as an internal standard unless stated otherwise. *J* Values are given in Hz. Positive ion fast atom bombardment (FAB) mass spectra were obtained with a Finnigan MAT 90 spectrometer using *m*-nitrobenzyl alcohol as a matrix. All solvents were purified by standard procedures. Light petroleum refers to the fraction with b.p. 60–80 °C. All other chemicals were analytically pure, and were used without further purification. Compound **1** was prepared according to a literature procedure.[14]

In the work-up procedures the (combined) organic layers were washed with water (2×) and dried with $MgSO_4$, whereupon the solvent was removed under reduced pressure. The presence of solvent in the analytical samples was confirmed by ^1H NMR spectroscopy.

General Procedure for the Preparation of Triester Monoamides **2a–d**.—To a solution of triester monoacid chloride **1**[14] (2.2 g, 2.1 mmol) in CH_2Cl_2 (50 cm^3) was added a solution of an appropriate amine (2.2 mmol) and triethylamine (0.84 g, 8.2 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 3–5 h at room temperature. Subsequently water (50 cm^3) was added and the organic layer was separated and washed with water (2 × 100 cm^3). Evaporation of the solvent and recrystallization from acetonitrile gave compounds **2a–d** as white solids.

Triethyl $1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-7^2-*propylcarbamoylmethoxy*-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetate* (**2a**).—Yield 77%; m.p. 79–80 °C (Found: C, 72.5; H, 8.1; N, 1.6. $C_{61}H_{83}NO_{11}$ requires C, 72.8; H, 8.3; N, 1.4%); δ_H(250 MHz) 8.36 (1 H, br s, NH), 6.89 (2 H, s, Ar), 6.81 (4 H, s, Ar), 6.70 (2 H, s, Ar), 5.0–4.5 (12 H, m, OCH_2, $ArCH_2Ar$), 4.15 (6 H, q, *J* 7.2, OCH_2CH_3), 3.30 (2 H, m, NCH_2), 3.22, 3.19 (4 H, two d, *J* 13.0, $ArCH_2Ar$), 1.7–1.6 (2 H, m, NCH_2CH_2), 1.17 (9 H, t, *J* 7.2, OCH_2CH_3), 1.00 (9 H, s, Bu^t), 0.97 (18 H, s, Bu^t), 0.90 (9 H, s, Bu^t) and 0.87 (3 H, t, *J* 7.0, $NCH_2CH_2CH_3$); *m*/*z* (FAB) 1006.2 ($[M + H]^+$).

Triethyl $1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-7^2-(*2-acetamidoethylcarbamoylmethoxy*)-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetate* (**2b**).—Yield 82%; m.p. 180 °C (Found: C, 70.75; H, 7.85; N, 3.6. $C_{62}H_{84}N_2O_{12}\cdot CH_3CN$ requires C, 70.5; H, 8.0; N, 3.85%); δ_H(250 MHz) 8.63, 7.14 (2 H, two br s, NH), 6.84 (2 H, s, Ar), 6.76 (6 H, s, Ar), 4.90, 4.75, 3.20, 3.17 (8 H, four d, *J* 13.2, $ArCH_2Ar$), 4.79 (4 H, s, OCH_2), 4.61, 4.58 (4 H, two s, OCH_2), 4.17 (6 H, q, *J* 7.0, OCH_2CH_3), 3.60–3.45 (4 H, m, NCH_2CH_2N), 1.97 (3 H, s, Me), 1.27 (t, 9 H, *J* 7.0, OCH_2CH_3), 1.11 (9 H, s, Bu^t), 1.06 (9 H, s, Bu^t) and 1.04 (18 H, s, Bu^t); *m*/*z* (FAB) 1049.5 ($[M + H]^+$).

Triethyl $1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-7^2-(*2-pyridylmethylcarbamoylmethoxy*)-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetate* (**2c**).—Yield 85%; m.p. 81–82 °C (Found: C, 72.2; H, 7.7; N, 3.2. $C_{64}H_{82}N_2O_{11}\cdot 0.5CH_3CN$ requires C, 72.5; H, 7.8; N, 3.25%); δ_H(250 MHz) 8.99 (1 H, br s, NH), 8.59 (1 H, d, *J* 7.0, Py), 7.65 (1 H, t, *J* 7.0, Py), 7.45 (1 H, d, *J* 7.0, Py), 7.14 (1 H, t, *J* 7.0, Py), 6.86 (2 H, s, Ar), 6.83 (2 H, s, Ar), 6.75 (4 H, s, Ar), 5.0–4.5 (14 H, m, OCH_2, $ArCH_2Ar$, CH_2Py), 4.18 (2 H, q, *J* 7.2, OCH_2CH_3), 4.07 (4 H, q, *J* 7.2, OCH_2CH_3), 3.25, 3.22 (4 H, two d, *J* 13.0, $ArCH_2Ar$), 1.20 (3 H, t, *J* 7.2, OCH_2CH_3), 1.14 (6 H, t, *J* 7.2, OCH_2CH_3), 1.13 (9 H, s, Bu^t), 1.10 (9 H, s, Bu^t) and 1.03 (18 H, s, Bu^t); *m*/*z* (FAB) 1055.6 (M^+).

Triethyl $1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-7^2-[*2-(2-pyridyl)ethylcarbamoylmethoxy*]-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetate* (**2d**).—Yield 80%; m.p. 99–100 °C (Found: C, 72.2; H, 7.75; N, 3.5. $C_{65}H_{84}N_2O_{11}\cdot CH_3CN$ requires C, 72.45; H, 7.9; N, 3.75%); δ_H(250 MHz) 8.56 (1 H, br s, NH), 8.49 (1 H, d, *J* 7.0, Py), 7.60 (1 H, t, *J* 7.0, Py), 7.19 (1 H, d, *J* 7.0, Py), 7.10 (1 H, t, *J* 7.0, Py), 6.84 (2 H, s, Ar), 6.77 (6 H, s, Ar), 5.0–4.6 (12 H, m, OCH_2, $ArCH_2Ar$), 4.24 (6 H, q, *J* 7.2, OCH_2CH_3), 3.85–3.80 (2 H, m, CH_2CH_2Py), 3.24, 3.22 (4 H, two d, *J* 13.0, $ArCH_2Ar$), 3.15 (2 H, m, CH_2CH_2Py), 1.24 (9 H, t, *J* 7.2, OCH_2CH_3), 1.12 (9 H, s, Bu^t), 1.07 (9 H, s, Bu^t) and 1.05 (18 H, s, Bu^t); *m*/*z* (FAB) 1070.5 ($[M + H]^+$).

General Procedure for the Preparation of Compounds **3a–d**.—A mixture of calixarene **2a–d** (0.5 mmol) and potassium carbonate (0.69 g, 5 mmol) in 5:1 MeOH–water solution (15 cm^3) was refluxed for 1 h and then poured into water (100 cm^3). Subsequently the pH was adjusted to 4, and the product was extracted with CH_2Cl_2 (2 × 50 cm^3) to give, after evaporation of the solvent **3a–d** as white solids.

$1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-7^2-*propylcarbamoyl*-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetic Acid* (**3a**).—Yield 74%; m.p. 272–273 °C (Found: C, 68.8; H, 7.6; N, 1.4. $C_{55}H_{72}NO_{11}\cdot 2H_2O$ requires C, 68.9; H, 8.0; N, 1.5%); Karl Fischer titration: Found: 3.5. Calc. for 2 H_2O: 3.75; δ_H(250 MHz) 8.60 (3 H, br s, OH), 7.12 (4 H, s, Ar), 6.80 (1 H, br s, NH), 6.62 (2 H, s, Ar), 6.36 (2 H, s, Ar), 4.9–4.1 (12 H, m, OCH_2, $ArCH_2Ar$), 3.4–3.3 (2 H, m, NCH_2), 3.17, 3.15 (4 H, two d, *J* 13.0, $ArCH_2Ar$), 1.7–1.6 (2 H, m, NCH_2CH_2), 1.27 (18 H, s, Bu^t), 0.86 (9 H, s, Bu^t), 0.85 (3 H, t, *J* 7.2, $NCH_2CH_2CH_3$) and 0.67 (9 H, s, Bu^t); *m*/*z* (FAB) 923.0 (M^+).

7^2-(*2-Acetamidoethylcarbamoyl*)-$1^5,3^5,5^5,7^5$-*tetra*-tert-*butyl*-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetic Acid* (**3b**).—Yield 76%; m.p. 251–252 °C (Found: C, 67.6; H, 7.5; N, 2.65. $C_{56}H_{72}N_2O_{12}\cdot 1.5H_2O$ requires C, 67.8; H, 7.6; N, 2.8%); Karl Fischer titration: Found: 2.4. Calc. for 1.5 H_2O: 2.7; δ_H(250 MHz) 8.60 (3 H, br s, OH), 8.15 (1 H, br s, NH), 8.09 (1 H, br s, NH), 7.13 (4 H, s, Ar), 6.66 (2 H, s, Ar), 6.49 (2 H, s, Ar), 5.05, 4.63, 3.20, 3.18 (8 H, four d, *J* 13.0, $ArCH_2Ar$), 4.5–4.1 (8 H, m, OCH_2), 3.7–3.5 (4 H, m, NCH_2CH_2N), 2.16 (3 H, s, Me), 1.31 (18 H, s, Bu^t), 0.99 (9 H, s, Bu^t) and 0.77 (9 H, s, Bu^t); *m*/*z* (FAB) 965.6 ($[M + H]^+$).

$1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-7^2-(*2-pyridylmethylcarbamoylmethoxy*)-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetic Acid* (**3c**).—Yield 73%; m.p. 177–179 °C (Found: C, 67.05; H, 6.9; N, 2.5. $C_{58}H_{70}N_2O_{11}\cdot CH_2Cl_2$ requires C, 67.1; H, 6.9; N, 2.65%); δ_H(250 MHz) 10.36 (3 H, br s, OH), 8.70 (1 H, br s, NH), 8.60 (1 H, d, *J* 7.0, Py), 7.83 (1 H, t, *J* 7.0, Py), 7.56

(1 H, d, *J* 7.0, Py), 7.30 (1 H, t, *J* 7.0, Py), 7.06 (4 H, s, Ar), 6.59 (2 H, s, Ar), 6.45 (2 H, s, Ar), 5.1–4.1 (14 H, m, OCH_2, $ArCH_2Ar$, CH_2Py), 3.18, 3.15 (4 H, two d, *J* 13.0, $ArCH_2Ar$), 1.24 (18 H, s, Bu^t), 0.85 (9 H, s, Bu^t) and 0.73 (9 H, s, Bu^t); *m*/*z* (FAB) 971.4 (M^+).

$1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-7^2-*[2-(2-pyridyl)ethylcarbamoylmethoxy]*-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetic Acid* (**3d**).—Yield 70%; m.p. 182–185 °C (Found: C, 70.1; H, 7.6; N, 2.8. $C_{59}H_{72}N_2O_{11}\cdot1.5H_2O$ requires C, 70.0; H, 7.5; N, 2.8%); Karl Fischer titration: Found: 2.4. Calc. for 1.5 H_2O: 2.7; δ_H(250 MHz) 8.83 (3 H, br s, OH), 8.54 (1 H, d, *J* 7.0, Py), 8.02 (1 H, br s, NH), 7.80 (1 H, t, *J* 7.0, Py), 7.51 (1 H, d, *J* 7.0, Py), 7.35 (1 H, t, *J* 7.0, Py), 7.06 (4 H, s, Ar), 6.58 (2 H, s, Ar), 6.44 (2 H, s, Ar), 5.5–4.1 (8 H, m, OCH_2), 4.71, 4.41, 3.21, 3.15 (8 H, four d, *J* 13.0, $ArCH_2Ar$), 3.8–3.7 (2 H, m, CH_2CH_2Py), 3.38 (2 H, t, *J* 7.1, CH_2CH_2Py), 1.24 (18 H, s, Bu^t), 0.85 (9 H, s, Bu^t) and 0.72 (9 H, s, Bu^t); *m*/*z* (FAB) 985.7 (M^+).

General Procedure for the Preparation of Solid Complexes **4a–d**, **5a–d** *and* **6**.—A solution of $EuCl_3\cdot6H_2O$, $TbCl_3\cdot6H_2O$ or $YCl_3\cdot6H_2O$ (0.11 mmol) in acetonitrile (10 cm^3) was refluxed with a few drops of trimethyl orthoformate for 1 h. Subsequently, a solution of **3a–d** (0.11 mmol) and Et_3N (0.05 g, 0.5 mmol) in MeOH (10 cm^3) was added, and reflux was continued for 3 h. Water (50 cm^3) was added, the solid formed was filtered off, redissolved in CH_2Cl_2 (20 cm^3) and washed with water (5 × 30 cm^3). The solvent was evaporated off *in vacuo* to give complexes **4a–d**, **5a–d** and **6** as white solids (in all cases m.p. > 300 °C). The yields and mass spectral data of compounds **4a–d** and **5a–d** are summarized in Table 1.

$1^5,3^5,5^5,7^5$,*Tetra*-tert-*butyl*-7^2-*(2-acetamidoethylcarbamoylmethoxy)*-1,3,5,7-*tetrabenzenacyclooctophane*-$1^2,3^2,5^2$-*triyltrioxytriacetatoyttrium* (**6**).—Yield 96%; m.p. > 300 °C (Found: C, 63.7; H, 6.5; N, 2.65. $C_{56}H_{69}N_2O_{12}Y$ requires C, 64.0; H, 6.6; N, 2.65%); δ_H[250 MHz; $(CD_3)_2SO$] 8.86 (1 H, br s, NH), 8.61 (1 H, br s, NH), 7.12 (4 H, s, Ar), 6.49 (2 H, s, Ar), 6.40 (2 H, s, Ar), 5.08, 4.74, 3.17, 3.04 (8 H, four d, *J* 13.1, $ArCH_2Ar$), 4.4–4.0 (8 H, m, OCH_2), 3.5–3.1 (4 H, m, NCH_2CH_2N), 1.93 (3 H, s, Me), 1.35 (18 H, s, Bu^t), 0.90 (9 H, s, Bu^t) and 0.76 (9 H, s, Bu^t); *m*/*z* (FAB) 1050.3 ($[M - H]^-$).

Luminescence Measurements.—Continuous excitation spectra (range scanned typically 250–450 nm) and full emission spectra were recorded on a Spex Fluorolog 2 spectrometer. Time resolved emission spectra were obtained using a Lumonics EX700 XeCl excimer laser (308 nm) as the excitation source. Under these conditions both weak local absorptions of the lanthanides and the red edge of the calixarene aromatic absorption are excited. The resulting luminescence was observed by means of a gated diode array detector coupled to an EG & G OMA III data handling system. Spectra were averaged over 100 shots to improve the signal-to-noise ratio. From these spectra luminescent lifetimes were calculated by fitting the integrated signal in time. Monoexponential decay was observed in all cases.

Spectrograde solvents methanol (Merck Uvasol) and perdeuteriomethanol (99.8 atom% D, Aldrich) were used to prepare saturated solutions of the compounds.

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Paper 4/03729D
Received 20*th June* 1994
Accepted 21*st September* 1994