Novel Preorganized Hemispherands To Encapsulate Rare Earth Ions: Shielding and Ligand Deuteration for Prolonged Lifetimes of Excited Eu^{3+} Ions

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Abstract: Quenching of the luminescent excited state of Eu^{3+} ions by C−H high-vibrational modes was studied by deuteration of the encapsulating ligand and the solvent. Novel polydentate hemispherands providing nine donor atoms, which form overall neutral complexes with rare earth ions, were synthesized in nine steps, allowing the easy incorporation of deuterium atoms (**11a−d·Eu^{3+}**). The introduction of *tert*-butyl groups at the aromatic rings of the ligand further increased the solubility of the complexes in organic solvents (**29·Eu^{3+}** and **34·Eu^{3+}**). Photophysical studies, *viz.,* luminescence spectra and lifetime measurements, revealed that significant quenching of the Eu^{3+} excited state is induced by nearby C−H vibrational modes. Substitution of these quenching C−H modes for C−D bonds in the azacrown bridge leads to an enhancement of the luminescent lifetime by a factor of 1.5. C−H high-vibrational modes of the pendant arms which are at a larger distance to the Eu^{3+} ion than the azacrown bridge hydrogen atoms (determined from the MD calculations) are less efficient quenchers. The number of coordinating methanol molecules to **11a·Eu^{3+}**, **29·Eu^{3+}**, and **34·Eu^{3+}** estimated by the "Horrocks equation" is 0.9, 1.2, and 1.9, respectively, as was predicted by MD calculations. Moreover, the experimental data show that quenching of the excited state of well-shielded Eu^{3+} ions by the C−H modes of the ligand is of the same order of magnitude as quenching by one O−H mode.

Introduction

The unique photophysical properties of lanthanide ions and their complexes in solution have been studied for several decades because of their potential application in solid state lasers and in labeling of biomolecular structures.[1] The energy transitions within the 4f shell of the lanthanide ions are Laporte forbidden, leading to low absorptivities and relatively long luminescence lifetimes. It is well known that the excited state of the lanthanide ions is efficiently quenched by interactions with high-energy vibrations like O−H and N−H groups.[2] Especially, the O−H quenching has been thoroughly studied as a consequence of the solvent mainly used, *i.e.,* water, and the relatively large amount of coordinating solvent molecules. This research has led to the well-known "Horrocks equation" which quantifies the number of O−H oscillators positioned in the first coordination sphere of the lanthanide ions Eu^{3+} and Tb^{3+}.[3] Therefore, research has been focused on the encapsulation of lanthanide ions by polydentate ligands, like cryptands,[4] branched macrocyclic ligands,[5] podands,[6] and calix[4]arene derivatives,[7] offering at least 8−9 hard donor atoms, like O and N atoms, which are able to coordinate into the first coordination sphere of the ion.

In this way shielding from any effective quenchers which may be present in their chemical environment can be achieved. Besides O−H vibrations, also C−H groups are able to quench the excited state of the rare earth ions, as was demonstrated by application of deuterated solvents, like (CD$_3$)$_2$C═O and CD$_3$-CN, and by using coordinating deuterated anions like CD$_3$COO$^-$.[8] Especially in the case of small amounts of solvent molecules, the quenching by other high-vibrational modes, like C−H modes frequently present in organic molecules, cannot be neglected.[9]

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Chart 1

11a
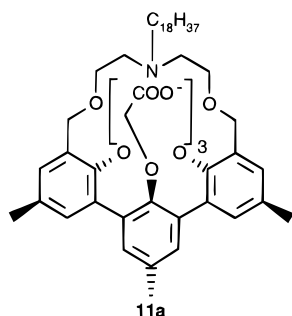
In this paper a novel polydentate ligand, based on a hemispherand, with additional pendant arms at the phenolic oxygen atoms is reported (Chart 1). This ligand is preorganized to deliver nine donor atoms: three carboxylic oxygens, five ethereal oxygens, and one nitrogen atom. Molecular modeling indicates that these nine donor atoms are able to coordinate to the spherical trivalent lanthanide ion and provide efficient shielding. A route for the synthesis of this ligand (depicted in Schemes 1 and 2) has been developed, which allows the incorporation of C−D groups with readily available reagents, without changing either the synthesis route or the coordinating nature of the ligand.[8a] Three ligands with different numbers of C−D groups incorporated in the pendant arms, the azacrown bridge, or both have been synthesized and photophysically studied to assess the extent of quenching caused by various C−H bonds. In addition, two ligands with *tert*-butyl groups substituted at the *para*-positions of the aromatic rings of the hemispherand have been prepared, in order to improve the solubility of the complexes. The present study is focused on the Eu^{3+} ion because the well-documented luminescent properties of this ion allow a critical assessment of the shielding properties of the organic ligand.

The ultimate goal of our research is the development of a polymeric material for an optical amplifier which contains lanthanide ions, like Pr^{3+} and Nd^{3+} for the 1.3 μm wavelength region, or Er^{3+} for the 1.5 μm wavelength region, complexed by organic ligands. In optical telecommunication lanthanide ions dispersed in inorganic glasses are presently used as optical amplifiers.[10] Design criteria for organic rare earth ion complexes which are optimally suited for optical amplification are: (1) a long luminescent lifetime, which requires efficient shielding of the ion from quenching substances, and (2) good solubility in the organic matrix, to prevent aggregation of the complexes.

Results and Discussion

Synthesis. The hemispherands with three pendant carboxylate groups were synthesized starting from the known terphenyl **1**.[11] The dialdehyde **2** was obtained in 70% yield by heating a solution of terphenyl **1** and HMTA in CF$_3$COOH at 90 °C, for 3.5 days, followed by hydrolysis at 60 °C (Scheme 1). The phenolic oxygens were protected in nearly quantitative yield by reacting **2** with 3-bromo-1-propene in acetonitrile with K$_2$CO$_3$ as a base. The dialdehyde **3** was reduced in quantitative yield with NaBH$_4$ in a mixture of methanol and THF (v/v 1:1) at 0 °C. Subsequently, the benzylic alcohol groups were

converted into bromomethyl groups with PBr$_3$, in toluene at 0 °C (83% yield).

The diol **6a**, needed for the subsequent ring closure reaction, was obtained in quantitative yield by the alkylation of diethanolamine with 1-bromooctadecane in refluxing acetonitrile. The macrocyclization of the dibromide **5** and the diol **6a** was performed in THF with NaH as a base under high-dilution conditions (Scheme 2). After purification by column chromatography the cyclic product **7a** was obtained in 58% yield. The ^{1}H NMR spectrum shows an AB-quartet for the benzylic hydrogens at δ = 4.72 and 4.39 (J = 11.7 Hz). The macrocyclic ring of **7a** is further evident from the two *meta*-coupled doublets for the *outer* phenyl rings at δ = 7.05 and 7.01 (J = 2.0 Hz) and a singlet at δ = 7.21 for the *inner* aromatic hydrogen atoms. In principle, two different conformations of the structure are possible: (a) one in which the alkyl chain is pointing toward the *inner* substituent and (b) one in which this group is at the same face of the molecule as the *outer* substituents. The ^{1}H NMR spectrum, however, only shows one set of signals (*vide infra*).

Deallylation of the cyclic product **7a** was accomplished in 86% yield with the Pd(PPh$_3$)$_4$ complex and Et$_3$N·HCOOH in a mixture of ethanol and water (v/v 5:1).[12] The triester **9a·NaClO$_4$** was obtained in quantitative yield by alkylation of the phenolic oxygens with methyl bromoacetate in acetonitrile, with K$_2$CO$_3$ as a base. The base-catalyzed hydrolysis of the triester **9a·NaClO$_4$** was carried out in aqueous methanol in the presence of NaOMe, giving triacid **10a** in almost quantitative yield. Also in the case of the triacid only one conformation is observed in the ^{1}H NMR spectrum. Complexation of Eu^{3+} in the preorganized tricarboxylate was simply achieved by reaction of triacid **10a** with 1 equiv of EuCl$_3$·6H$_2$O in methanol, in the presence of 3 equiv of Et$_3$N as an HCl scavenger. From the FAB mass spectrum of the complex **11a·Eu^{3+}** which shows a peak at *m/z* = 1026.4, corresponding to the (M + H)$^+$ peak (calcd for C$_{51}$H$_{71}$NO$_{11}$Eu 1026.4) and elemental analysis we conclude that a 1:1 Eu^{3+}/**11a** complex is formed. Furthermore, the FAB mass spectrum shows peaks at *m/z* = 968.5 and 908.3 which correspond to [(M − CH$_2$COO)$^+$] and [(M − 2CH$_2$COO)$^+$], respectively; the characteristic isotope pattern of Eu^{3+} is clearly observed for these peaks too. Complete deprotonation is obvious from the peak in the IR spectrum at 1608 cm^{-1} which can be attributed to the COO$^-$ stretching vibration, and, moreover, the absence of the carbonyl stretching mode of the triacid **10a**, located at 1748 cm^{-1}.

MM calculations[13] of the minimal energy of the Eu^{3+} complexes with the alkyl chain pointing at different sides of the molecule (structures *a* and *b*, *vide supra*), in the gas phase, shows that structure *b* in which the alkyl chain is at the same face of the molecule as the outer pendant arms is more stable by 9.3 kcal/mol. Therefore, it is likely that only structure *b* is formed in the cyclization reaction and this structure is used for molecular dynamics (see Figure 1).

The partially deuterated triacids **10b−d** were obtained via the same synthesis route as described above, using the deuterated diol **6b** and/or BrCD$_2$COOMe as reagents.[14] Diol **6b** was obtained in 70% yield by the alkylation in 1-propanol of octadecylamine with ethylene oxide-d_4. The Eu^{3+} complexes

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(14) The base-catalyzed hydrolysis of the triesters which contain deuterated arms (**9c** and **9d**) and the complexation reactions using **10c** and **10d** were carried out in methanol-d_1 in the presence of D$_2$O to prevent the exchange of deuterium atoms by hydrogens.

Scheme 1. Synthetis Route Leading to Dibromide **5**
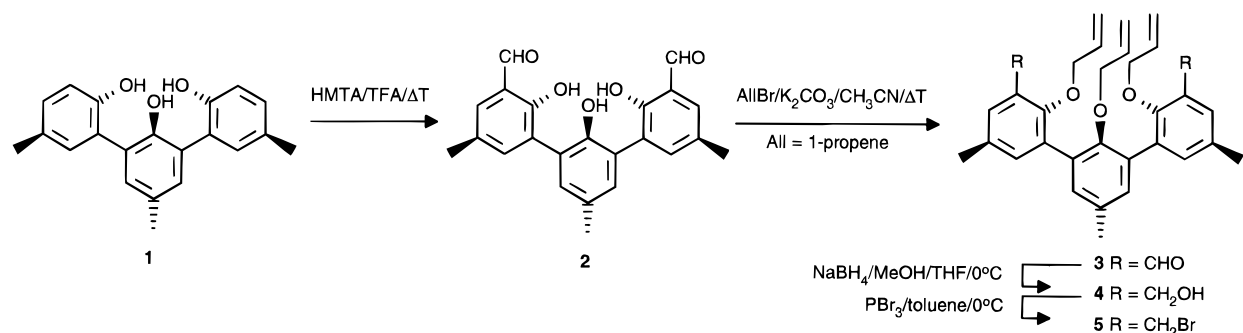
Scheme 2. Synthetis Route Leading to the Eu^{3+} Complexes **11a−d·Eu^{3+}**
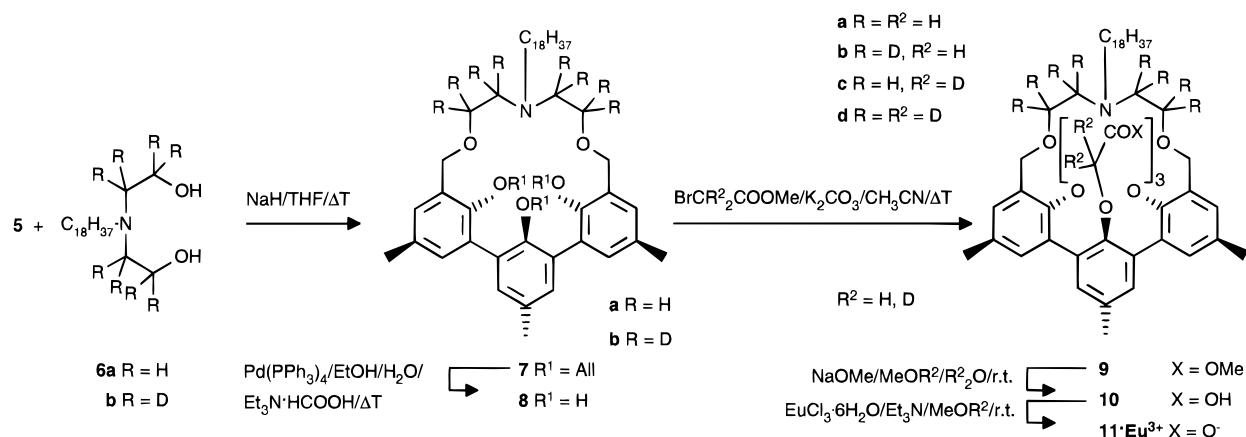
Scheme 3. Synthetis Route Leading to the *tert*-Butyl-Substituted Terphenyl Moiety **19**
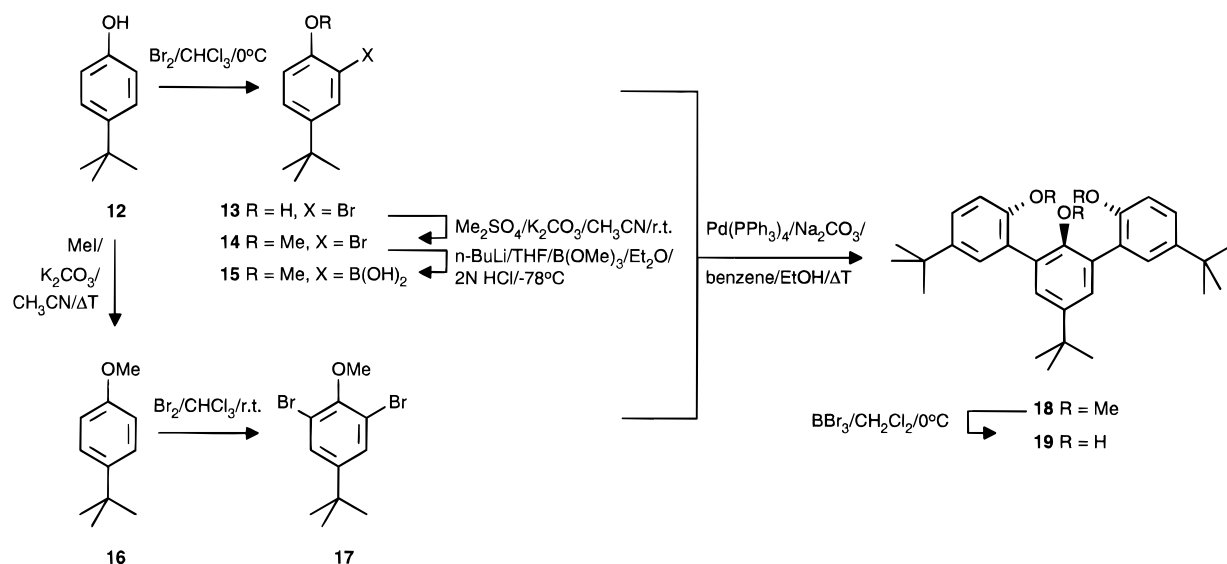
11b·Eu^{3+}, **11c·Eu^{3+}**, and **11d·Eu^{3+}** show peaks in their FAB mass spectra at m/z = 1034.6, 1032.5, and 1040.5, respectively, corresponding to the calculated values of $(M + H)^+$. For these peaks the isotope pattern, characteristic for Eu^{3+}, is clearly observed. The IR spectra of all deuterated complexes show two C−D stretch vibrations at 2097 and 2207 cm^{-1}, whereas pendant arm-deuterated complexes **11c·Eu^{3+}** and **11d·Eu^{3+}** both show an additional absorption at 2156 cm^{-1}.

To increase the solubility of the Eu^{3+} complexes in organic solvents, the methyl groups at the terphenyl ring were replaced by *tert*-butyl groups, starting from *p-tert*-butylphenol (**12**) as depicted in Scheme 3. The compounds **13**,[15] **14**,[15] **15**,[16] and

16[17] were prepared according to literature procedures. Dibromination of **16** with Br$_2$ in chloroform at room temperature gave **17** in 88% yield. Compound **17** was subjected to a double Suzuki coupling[18] in a mixture of benzene, ethanol, and 2 M aqueous sodium carbonate with 2 equiv of boronic acid **15** in the presence of a catalytic amount of Pd(PPh$_3$)$_4$. The terphenyl **18** was obtained in almost quantitative yield and was subse-

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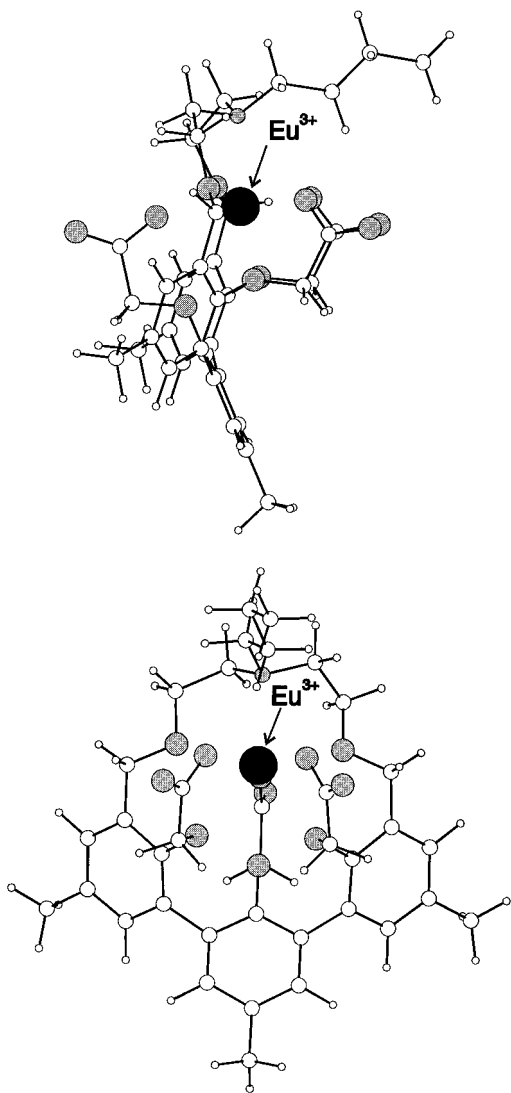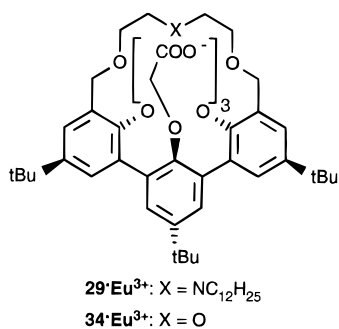
Figure 1. Most stable conformation calculated by MM, with the alkyl chain at the same face of the molecule as the *outer* pendant arms: (a, top) *side* and (b) *front* views.

Chart 2

29·Eu^{3+}: X = NC$_{12}$H$_{25}$
34·Eu^{3+}: X = O

quently demethylated with boron tribromide in dichloromethane at 0 °C, giving **19** in 81% yield. Compound **19** was used as the starting terphenyl moiety in the synthesis route described for **11a−d·Eu^{3+}** (see Scheme 1 and 2), leading to the 1:1 complexes **29·Eu^{3+}** and **34·Eu^{3+}** (Chart 2), as confirmed by FAB mass spectrometry, infrared spectroscopy, and elemental analysis.

Molecular Modeling. The three different structures **11a·Eu^{3+}**, **29·Eu^{3+}**, and **34·Eu^{3+}** [19] were minimized in the gas phase and subjected to molecular dynamics simulations in a cubic OPLS box of methanol.[13] These calculations show that the complexes **11a·Eu^{3+}** and **29·Eu^{3+}** can still accommodate one molecule of

methanol in the first coordination sphere of the Eu^{3+} ion, whereas two molecules of methanol coordinate to **34·Eu^{3+}**, probably due to the absence of the sterically crowded alkyl chain. The solvent molecules all coordinate at the face of the two *outer* pendant arms. Further data extracted from these MD simulations that are relevant for the discussion concerning the photophysical properties of the Eu^{3+} complexes are summarized in Tables 1 and 5.[20]

Photophysical Studies. By studying the luminescent properties of the Eu^{3+} complexes, the influence of (changes in) the chemical environment, like the number and the distance of high-vibrational modes (O−H, C−H) to the Eu^{3+} ion, can be established. The excitation spectra of 10$^{−4}$ M solutions of **11d·Eu^{3+}** and EuCl$_3$·6H$_2$O, detected at 617 nm (the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}) in methanol-d_4, depicted in Figure 2, show the typical excitation bands for Eu^{3+} at 393 and 464 nm. A significant increase in luminescence intensity is observed when excitation is carried out in the UV region of the spectrum due to sensitized emission.[21] Moreover, the spectra for **11d·Eu^{3+}** and **11a·Eu^{3+}** in methanol-d_1 depicted in Figure 2 show that the luminescence intensity is increased upon deuteration of the ligand.[22]

The luminescence spectra of 10$^{−4}$ M solutions of the Eu^{3+} complexes in methanol-d_1 after excitation at 393 nm are depicted in Figure 3, showing the typical $^5D_0 \rightarrow {}^7F_j$ Eu^{3+} transitions.[1a,4a,5a,6a] These spectra also indicate that luminescence enhancement is obtained upon ligand deuteration with the anticipated increase **11d·Eu^{3+}** > **11b·Eu^{3+}** > **11c·Eu^{3+}** > **11a·Eu^{3+}**. This increase can be caused by either the reduced quenching of the Eu^{3+} luminescence of the partially deuterated complex compared to the nondeuterated analogue or a prolonged excited state of the deuterated ligand itself which leads to a more efficient population of the excited state of the Eu^{3+} ion. However, lifetime measurements at 464 nm, exclusively leading to direct excitation of the Eu^{3+} ion, showed effects of ligand deuteration analogous to those of lifetimes measured at 287 and 393 nm, indicating that the increase in lifetime of the excited state of the ligand can be neglected.[23] Furthermore, lifetime measurements after sensitized emission at 77 and 300 K showed that the lifetimes are not temperature dependent to a significant extent; the differences are all within the experimental error of 10%, which would suggest that the lifetime of the triplet state is not significantly affected.

The lifetimes of **11a−d·Eu^{3+}** were determined in 10$^{−4}$ M methanol solutions[24] by excitation at 393 or 287 nm and recording the intensity of the emitted light of the hypersensitive

(19) Computer simulations carried out with the Na$^+$ complex of an analogue of **9a** with triethyl ester groups as pendant arms and an oxygen atom instead of an *N*-alkyl group in the ring have been published. The calculated data are corroborated by ^{1}H NMR spectroscopy and the solid state structure (Veggel, F. C. J. M. van; Duynhoven, J. P. M. v.; Harkema, S.; Oude Wolbers, M. P.; Reinhoudt, D. N. *J. Chem. Soc., Perkin Trans. 2* **1996**, 449−454).

(20) Details of the simulations will be published elsewhere.

(21) The excitation spectrum shows that excitation at 393 nm also gives partly sensitized emission.
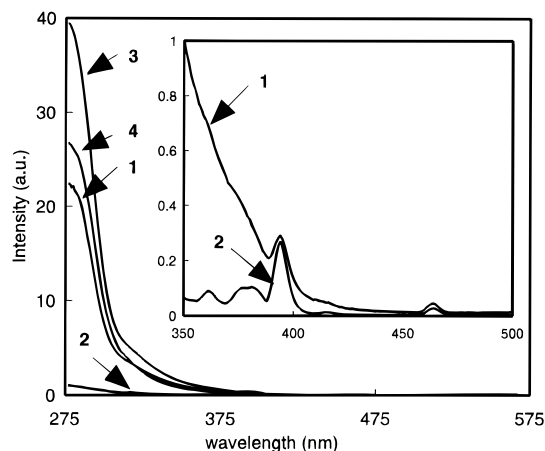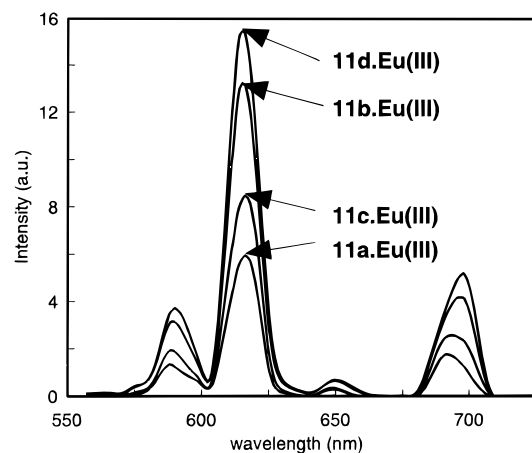
(22) The conditions during the measurements, like slit widths or filters, using solvents which differ in the amount of deuteration (methanol-d_1 vs methanol-d_4) were not exactly the same, leading in this case to a higher intensity in methanol-d_1.

(23) Laser excitation directly at the Eu^{3+} ion at 464 nm using solutions of **11a·Eu^{3+}** and **11d·Eu^{3+}** in methanol-d_4, leads to lifetimes of 0.88 and 1.40 ms, respectively. Upon ligand deuteration the lifetime is increased by a factor 1.6, in full agreement with the lifetime enhancement observed at other excitation wavelengths. Furthermore, it is assumed that the influence of the introduction of deuterium atoms on the positions of the energy levels[8a] or on the background density of the states of the organic ligand can be neglected because the chromophoric system remains essentially the same (Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145−164). Therefore, the energy back-transfer along the series **11a−d·Eu^{3+}** is assumed to be constant.

Table 1. Average Eu^{3+}-Hydrogen Atom Distances (Å) and Standard Deviations (in Parentheses) in the MD Simulations

	O−H^{MeOH}	CH$_2$$^{outer arm}$	CH$_2$$^{outer arm}$	CH$_2$$^{inner arm}$	ArCH$_2$O^a	ArCH$_2$O^a	CH$_2$O^{bridge}	CH$_2$O^{bridge}	CH$_2$X$^{bridge\ b}$	CH$_2$X$^{bridge\ b}$	NCH$_2$^{c}	NCH$_2$CH$_2$^{c}
11a·Eu^{3+}	2.41(0.06)	3.86(0.20)	4.41(0.21)	4.81(0.15)	3.74(0.19)	3.78(0.16)	3.97(0.17)	3.56(0.13)	3.54(0.15)	3.60(0.16)	3.85(0.30)	3.56(0.39)
(as NC$_4$)		4.39(0.11)	4.42(0.17)	4.87(0.14)	4.43(0.11)	4.50(0.11)	4.16(0.12)	4.14(0.09)	4.26(0.08)	4.15(0.10)	4.37(0.26)	4.12(0.46)
29·Eu^{3+}	2.27(0.06)	3.89(0.27)	4.48(0.17)	4.81(0.22)	3.74(0.19)	3.79(0.17)	4.04(0.17)	3.60(0.14)	3.45(0.15)	3.61(0.16)	3.44(0.33)	4.57(0.61)
(as NC$_4$)		4.46(0.17)	4.48(0.22)	4.96(0.18)	4.45(0.10)	4.49(0.12)	4.07(0.16)	4.16(0.09)	4.24(0.09)	4.16(0.09)	4.01(0.42)	5.01(0.43)
34·Eu^{3+}	2.28(0.06)	4.51(0.26)	4.34(0.28)	5.14(0.13)	3.70(0.15)	3.65(0.15)	3.96(0.18)	3.93(0.20)	3.89(0.16)	3.82(0.20)		
	2.29(0.06)	4.73(0.12)	4.70(0.12)	5.15(0.13)	4.45(0.12)	4.46(0.11)	4.14(0.16)	4.06(0.22)	4.06(0.14)	4.04(0.16)		

^{a} The values in the first column correspond to the distance between the axial hydrogen atom and the Eu^{3+} ion, whereas the values in the second column give the distance between the equatorial hydrogen atom and the Eu^{3+} ion. ^{b} With X = N for **11a·Eu^{3+}** and **29·Eu^{3+}** and X = O for **34·Eu^{3+}**. ^{c} Of the long alkyl chain.

Figure 2. Excitation spectra of 10^{-4} M solutions of (1) **11d·Eu^{3+}** in methanol-d_4, and (2) EuCl$_3$ in methanol-d_4, (3) **11d·Eu^{3+}** in methanol-d_1, and (4) **11a·Eu^{3+}** in methanol-d_1, detected at 617 nm.

Figure 3. Emission spectra of 10^{-4} M solutions of **11a−d·Eu^{3+}** in methanol-d_1, excited at 393 nm.

Table 2. Lifetimes (ms) of the $^5D_0$ Excited State Recorded at λ_{em} = 617 nm after Excitation at 393 or 287 nm Using 10^{-4} M Methanolic Solutions of Different Deuterated Complexes **11a−d·Eu$^{3+\ a}$**

	τ_{CH_3OH} (393 nm)	τ_{CH_3OD} (393 nm)	τ_{CD_3OD} (393 nm)	τ_{CH_3OH} (287 nm)	τ_{CH_3OD} (287 nm)	τ_{CD_3OD} (287 nm)
EuCl$_3$	0.26		2.53	0.30		2.55
11a·Eu^{3+}	0.68	0.97	1.04	0.75	1.17	1.33
11b·Eu^{3+}	0.75	1.18	1.54	0.83	1.49	1.91
11c·Eu^{3+}	0.68	0.95	1.11	0.73	1.17	1.29
11d·Eu^{3+}	0.73	1.26	1.57	0.80	1.52	2.00

^{a} The experimental error is ≤10% which was determined from duplicate and triplicate measurements.

$^5D_0 \rightarrow {}^7F_2$ transition (617 nm). In all cases the data could be fitted to monoexponential decay curves, indicating a unique chemical environment. The determined lifetimes are presented in Table 2. These results illustrate that the Eu^{3+} ion is shielded quite well from the quenchers in the chemical environment: the lifetimes of the complexes in methanol, (0.68−0.75 ms) are significantly larger than the lifetime of EuCl$_3$ in this solvent (0.26 ms). The lifetimes measured for the Eu^{3+} complexes in methanol-d_1 are lower (0.95−1.26 ms) than that of EuCl$_3$ (1.45 ms),[3b] which may be explained by the quenching effects of the high-energy vibrational C−H modes of the encapsulating ligand.[25] This hypothesis is supported by the observation that substitution of C-H bonds for C-D bonds in the azacrown bridge

results in an increase of the luminescence lifetime by a factor of about 1.5.[26] Surprisingly, deuteration of the pendant arms does not lead to a significant increase in the lifetime. This observation can be explained when molecular dynamics calculations are taken into account. The quenching of the excited state is mediated by nonradiative transitions, supposed to take place via electromagnetic interactions, referred to as the inductive resonance theory of Förster. The rate constants of such nonradiative transitions are, among others, related to the distance between the quenching high-energy vibration and the emitting ion to the power −6.[2a,3a,27] The molecular dynamics calculations show that the distances of the Eu^{3+} ion to the hydrogen atoms of the pendant arms are significantly longer ((3.86−4.87) ± 0.21 Å) than those to the hydrogen atoms of the azacrown bridge ((3.54−4.26) ± 0.17 Å), and hence the efficiency of quenching by the C−H high-vibrational modes of the pendant arms is smaller.

The quenching of the Eu^{3+} excited state by O−H vibrations is observed by comparison of the lifetimes measured in methanol-d_1 and methanol. In the literature the number of O−H oscillators n in the first coordination sphere of Eu^{3+}, in methanol solutions, has been estimated by the relation $n = 2.1(1/\tau_{CH_3OH} - 1/\tau_{CH_3OD})$, leading to $(0.9−1.2) ± 0.5$ O−H oscillators.[3b] This number was predicted by the molecular dynamics calculations (Table 5). Furthermore, the solvent (methanol) contributes to the C−H quenching as well, as can be seen from the lifetime differences observed in methanol-d_4 and methanol-d_1.[28] In the literature the observed rate constant is defined by eq 1, with k_{obsd} = observed rate constant,[1b] τ_{obsd} = observed lifetime, k_{rad} = radiative rate constant, k_D = rate constant of quenching by

(24) The same lifetimes, within the experimental error of 10%, were observed using 10^{-5} M methanol solutions and an excitation wavelength of 287 nm which means that concentration effects at 10^{-4} M can be excluded.

(25) However, the lifetimes of the luminescent excited state will also be decreased by the reduced symmetry of the coordination sphere around the Eu^{3+} ion, leading to more allowed transitions.

(26) The solvent quenching mechanisms are minimal in the case of methanol-d_4; therefore, the effect of ligand deuteration is determined in this solvent otherwise the effect may be shaded by solvent quenching. However, in methanol-d_1 the lifetimes are still increased by a factor of about 1.3.

(27) Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7−17.

(28) The purity of the methanol used varies from 99.5% to 99.8% which may have a small influence on the lifetimes and on the conclusions drawn according to the importance of the quenching via different pathways. However, molecular modeling also indicates that the CH$_3$ group of the coordinating methanol can have a decreasing effect on the lifetime.

$$k_{\text{obsd}} = 1/\tau_{\text{obsd}} = k_{\text{rad}} + [k_{\text{D}} + k_{\text{O-H}} + k(T) + k_{\text{other}}]_{\text{nonrad}}$$
$$(1)$$

O–D, N–D, and C–D vibrations, $k_{\text{O-H}}$ = rate constant of quenching by O–H vibrations, $k(T)$ = thermal quenching, and k_{other} = rate constant of quenching via other pathways. The quenching by O–D, N–D, or C–D vibrations is usually assumed to be relatively inefficient; however, these quenching modes may not be neglected when the more (>90%) efficient quenching mechanisms are eliminated. The rate constants for nonradiative decay via the O–H groups of the solvent, the C–H groups of the pendant arms and azacrown bridge in the ligand, and the C–H vibrations of the solvent can be expressed by the equations given in Table 3. The calculated rate constants show that the C–H vibrational modes provide efficient quenching of the excited state of the Eu³⁺ ion with an efficiency of the same order of magnitude as that of one O–H vibration; however, the quenching by O–H vibrations is still dominant. The most pronounced effect of substitution of C–D for C–H is observed for deuteration of the bridge (**11b·Eu³⁺** compared to **11a·Eu³⁺**) and excitation at 393 nm, with calculated[1b,3a] rate constants of $k_{\text{O-H}} = 0.49$ ms⁻¹, $k_{\text{C-H}}^{\text{lig}} = 0.31$ ms⁻¹, and $k_{\text{C-H}}^{\text{solv}} = 0.20$ ms⁻¹. Hence, the quenching effect of C–H groups close to the Eu³⁺ ion can be quite significant, if the Eu³⁺ ion is well shielded from the chemical environment by a macrocyclic organic ligand, so that a low concentration of O–H oscillators remains in the first coordination sphere of the Eu³⁺ ion.

The luminescent lifetimes are longer after excitation of the ligand at 287 nm, leading to an enhancement by a factor of about 1.2. On the basis of the present results, no definitive interpretation of the lifetime differences can be given. The present results indicate that the observed rate constant can be expressed by an extended equation with neglect of the thermal quenching:

$$k_{\text{obsd}} = k_{\text{rad}} + [k_{\text{D}} + k_{\text{O-H}} + k_{\text{C-H}}^{\text{lig}} + k_{\text{C-H}}^{\text{solv}} + k_{\text{other}}]_{\text{nonrad}}$$
$$(2)$$

The photophysical properties of Eu³⁺ complexed by the organic ligands with *tert*-butyl groups at the terphenyl moiety, depicted in Chart 2, were studied with the same approach as described above. The luminescence spectra recorded for 10⁻⁴ M solutions in methanol-d_1 after excitation at 393 nm (not shown) show a high increase in intensity for **34·Eu³⁺** by a factor of about 3 when compared to the ligands with an *N*-alkyl chain. This may be due to (a) the decreased quenching upon deuteration of the two coordinating solvent molecules instead of one for **11a·Eu³⁺** and **29·Eu³⁺**, (b) the absence of quenching by the C–H bonds of the two methylene groups of the *N*-alkyl chain, some of which are calculated to be within the "quenching distance" of the Eu³⁺ ion (Table 1), or (c) differences in interaction between the Eu³⁺ ion and the ligand, leading to changes in the symmetry of the chemical environment around the Eu³⁺ ion.[6c,d]

The lifetimes (reported in Table 4) of **29·Eu³⁺** dissolved in methanol and methanol-d_1, and of **34·Eu³⁺** in methanol, excited at both 393 and 287 nm are equal within the experimental error to those of the nondeuterated complex **11a·Eu³⁺**. However, upon solvent deuteration the lifetimes of **34·Eu³⁺** are increased by a factor 2.6 compared to a factor 1.5 for **11a·Eu³⁺**, indicative of a larger number of coordinating solvent molecules in the former complex. The experimentally determined number of coordinating methanol molecules is 1.9 ± 0.5 for **34·Eu³⁺**, whereas the lifetimes detected for **11a·Eu³⁺** and **29·Eu³⁺** lead to estimates of 0.9 ± 0.5 and 1.2 ± 0.5 coordinating MeOH molecules, respectively. Table 5 gives the experimentally

Table 3. Calculated Rate Constants (ms⁻¹) of the Various Quenching Mechanisms

	393 nm[a]	393 nm[b]	287 nm[a]	287 nm[b]
$k_{\text{O-H}}$[c]	0.49	0.58	0.59	0.53
$k_{\text{C-H}}^{\text{lig}}$[d]	0.31	0.32	0.25	0.23
$k_{\text{C-H}}^{\text{solv}}$[e]	0.20	0.16	0.16	0.15

[a] From **11a·Eu³⁺** and **11b·Eu³⁺**. [b] From **11c·Eu³⁺** and **11d·Eu³⁺**. [c] $k_{\text{O-H}} = \tau_{\text{CH}_3\text{OH}}^{-1} - \tau_{\text{CH}_3\text{OD}}^{-1}$. [d] $k_{\text{C-H}}^{\text{lig}} = [\tau_{\text{ND}}^{-1} - \tau_{\text{BD}}^{-1}]_{\text{CD}_3\text{OD}}$ with **ND** = **11a·Eu³⁺** or **11c·Eu³⁺** and **BD** = **11b·Eu³⁺** or **11d·Eu³⁺**. [e] $k_{\text{C-H}}^{\text{solv}} = \tau_{\text{CH}_3\text{OD}}^{-1} - \tau_{\text{CD}_3\text{OD}}^{-1}$.

Table 4. Lifetimes (ms) of the ⁵D₀ Excited State Recorded at λ_{em} = 617 nm after Excitation at 393 or 287 nm Using 10⁻⁴ M Methanolic Solutions of the Complexes with *tert*-Butyl Groups[a]

	$\tau_{\text{CH}_3\text{OH}}$ (393 nm)	$\tau_{\text{CH}_3\text{OD}}$ (393 nm)	$\tau_{\text{CH}_3\text{OH}}$ (287 nm)	$\tau_{\text{CH}_3\text{OD}}$ (287 nm)
29·Eu³⁺	0.62	0.94	0.71	1.20
34·Eu³⁺	0.67	1.76	0.69	1.81

[a] The experimental error is ≤10% which was determined from duplicate and triplate measurements.

Table 5. Calculated Number of Coordinating Methanol Molecules from Lifetime Measurements and MD

	exc 393 nm	exc 287 nm	MD[a]
11a·Eu³⁺	0.9	1.0	0.9
29·Eu³⁺	1.2	1.2	1.2
34·Eu³⁺	1.9	1.9	2.0

[a] The radial distribution function (RDF) can be calculated from the production phase, and the integrated area of the peak around 2.3 Å gives the number of coordinating solvent molecules.

determined number of O–H oscillators and those calculated by molecular dynamics.

From the equal lifetimes for **34·Eu³⁺** and **11a·Eu³⁺** in methanol, despite the decreased shielding from coordinating solvent molecules in the case of **34·Eu³⁺**, it can be concluded that ligand mediated quenching is more important in **11a·Eu³⁺**. Until now, in the literature the research has mainly focused on the shielding of the Eu³⁺ ion from the chemical environment, but the present results indicate that other quenching mechanisms, like by the C–H modes of the ligand or the solvent, are important as well. However, deuteration of the chemical environment of the Eu³⁺ ion increases the relative importance of the shielding of the ion from the solvent again.

Conclusions

A significant lifetime enhancement by a factor of 1.5 is obtained by only partial deuteration of the encapsulating ligand. It has been shown that the quenching efficiency is dependent on the distance between the high-energy vibrational quenching mode and the lanthanide ions, in agreement with the Förster mechanism. Further deuteration of the ligand may lead to even longer lifetimes as can be concluded from the photophysical studies comparing the ligand with the crown bridge and the ligands with the *N*-alkyl chain in the ring. It is obvious from the equal lifetimes in both cases with one and with two coordinating methanol molecules that not only the shielding properties are important, but quenching via other nonradiative mechanisms, like C–H modes, can also play a role. It has been demonstrated that, in the presence of small amounts of the dominating O–H vibrations, the nonradiative deactivation by C–H groups is of the same order of magnitude as quenching via O–H modes. It is expected that in the case of complete shielding of the Eu³⁺ ion from the chemical environment the main quenching mode becomes that of the C–H group because the C–H concentration around a Eu³⁺ ion, encapsulated by an

organic ligand, is relatively high. Excellent agreement between the results of the photophysical studies and the MD calculations is obtained, which allows the use of molecular dynamics as a tool to predict the composition of the coordination sphere.

Experimental Section

Photophysical Studies. Luminescence spectra were recorded for $\lambda_{em} = 550-725$ nm with a PTI (Photon Technology International, Inc.) Alphascan spectrofluorometer after excitation of the Eu^{3+} ion at $\lambda_{exc} = 393$, or 287 nm. Measurements were carried out either in the steady state mode, where the signal from the Hamamatsu R928 photomultiplier was fed to a photon-counting interface and detected, or in the phase-resolved mode. In the latter 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 demodulation of the luminescence signal are fitted to well-known expressions applied for phase-resolved luminescence data.[29] 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.

Synthesis. Melting points were determined with a Reichert melting point apparatus and are uncorrected. Mass spectra were recorded with a Finnigan MAT 90 spectrometer using *m*-NBA (nitrobenzyl alcohol) as a matrix, unless otherwise stated. IR spectra were obtained using a Biorad 3200 or a Nicolet 5SXC FT-IR spectrophotometer. Elemental analysis[30] was performed using a 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 and 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. MeOH was dried over molecular sieves (3 Å) for at least 3 days. $EuCl_3 \cdot 6H_2O$ was of reagent grade and was used after heating under reduced pressure. The synthesis procedures and the analytical evidence for the formation of the compounds **2–10**, **17–28**, and **30–33** are available as Supporting Information.

General Procedure for the Complexation of Eu^{3+}. The corresponding triacid was dissolved in MeOH, after which 3 equiv of Et_3N was added using a microsyringe. Subsequently a solution of $EuCl_3 \cdot 6H_2O$ in a minimal amount of MeOH was added in one portion, upon which the complex precipitated immediately as an almost white solid. The reaction mixture was stirred for an additional 15 min and concentrated (to ~3 mL), after which the complex was filtered off. The product was purified by refluxing it in CH_3CN for 3 h, after which it was concentrated (to ~3 mL) and cooled to 0 °C. The product was filtered off and washed once with cold CH_3CN (~3 mL).

[25,26,27-Tris(carboxylatomethoxy)-4,9,23-trimethyl-16-octade-cyl-13,19-dioxa-16-azatetracyclo[19,3,1,1^{2,6},1^{7,11}]heptacosa-1(25),2,4,6-(27),7,9,11(26),21,23-nonaene(3−)]europium(3+) (11a·Eu^{3+}). The reaction was carried out using triacid **10a** (0.80 g, 0.83 mmol), Et_3N (0.34 mL, 2.47 mol) in MeOH (10 mL), and $EuCl_3 \cdot 6H_2O$ (0.34 g, 0.93 mmol) in MeOH (3 mL). The off-white solid **11a·Eu^{3+}** was obtained in quantitative yield. Mp: >300 °C. IR (KBr): 1608 cm^{-1}. MS (FAB): *m/z* 1026.4 [(M + H)$^+$], 968.5 [(M − CH_2COO)$^+$], 908.3 [(M − 2CH_2COO)$^+$]. Anal. Calcd for $C_{51}H_{70}NO_{11}Eu \cdot 2.75H_2O$: H, 7.08; N, 1.30; Eu^{3+}, 14.1. Found: H, 6.87; N, 1.31; Eu^{3+}, 14.1. Karl-Fisher calcd for 2.75 mol of H_2O: 4.61. Found: 4.63.

(29) Lakowicz, J. R. *Principle of Fluorescence Spectroscopy*, 2nd ed.; Plenum: New York, 1989; pp 52−57.

(30) 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).

[25,26,27-Tris(carboxylatomethoxy)-4,9,23-trimethyl)-16-octade-cyl-13,19-dioxa-16-azatetracyclo[19,3,1,1^{2,6},1^{7,11}]heptacosa-1(25),2,4,6-(27),7,9,11(26),21,23-nonaene-14,14′,15,15′,17,17′,18,18′-d_8(3−)]eu-ropium(3+) (11b·Eu^{3+}). The Eu^{3+} complex **11b·Eu^{3+}** was obtained using bridge-deuterated triacid **10b** (79.4 mg, 0.090 mmol), Et_3N (0.037 mL, 0.27 mmol), and $EuCl_3 \cdot 6H_2O$ (37.9 mg, 0.103 mmol) in MeOH (1.0 and 0.5 mL, respectively). The Eu^{3+} complex was obtained in 94% yield as an off-white solid. Mp: >300 °C. IR (KBr): 2207, 2097, 1611 cm^{-1}. MS (FAB): *m/z* 1034.6 [(M + H)$^+$], 976.4 [(M − CH_2COO)$^+$], 916.6 [(M − 2CH_2COO)$^+$]. Anal. Calcd for $C_{51}H_{62}$-$D_8NO_{11}Eu$: H, 6.05; N, 1.36; Eu^{3+}, 14.7. Found: H, 6.07; N, 0.94; Eu^{3+}, 15.6.

[25,26,27-Tris(carboxylatomethoxy-31,31′-32,32′-33,33′-d_6)-4,9,-23-trimethyl-16-octadecyl-13,19-dioxa-16-azatetracyclo[19,3,1,1^{2,6},1^{7,11}]-heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene(3−)] europium-(3+) (11c·Eu^{3+}). The synthesis of the Eu^{3+} complex **11c·Eu^{3+}** was carried out using triacid **10c** (0.52 g, 0.59 mmol), Et_3N (0.25 mL, 1.77 mmol), and $EuCl_3 \cdot 6H_2O$ (0.24 g, 0.66 mmol) in MeOD (7 and 3 mL, respectively). The complex was obtained in 86% yield as an off-white solid. Mp: >300 °C. IR (KBr): 2207, 2156, 2097, 1612 cm^{-1}. MS (FAB): *m/z* 1032.5 [(M + H)$^+$], 972.7 [(M − CD_2COO)$^+$], 910.4 [(M − 2CD_2COO)$^+$]. Anal. Calcd for $C_{51}H_{64}D_6NO_{11}Eu$: H, 6.26; N, 1.36; Eu^{3+}, 14.7. Found: H, 6.16; N, 1.02; Eu^{3+}, 15.8.

[25,26,27-Tris(carboxylatomethoxy-31,31′-32,32′,33,33′-d_6)-4,9,-23-trimethyl-16-octadecyl-13,19-dioxa-16-azatetracyclo[19,3,1,1^{2,6},1^{7,11}]-heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene-14,14′,15, 15′,17,17′,18,18′-d_8(3−) europium(3+) (11d·Eu^{3+}). The bridge- and arm-deuterated Eu^{3+} complex **11d·Eu^{3+}** was synthesized using triacid **10d** (0.14 g, 0.16 mmol), Et_3N (0.065 mL, 0.47 mmol), and $EuCl_3 \cdot 6H_2O$ (63.3 mg, 0.173 mmol) in MeOD (2 and 1 mL, respectively). Yield: 94% (off-white solid). Mp: >300 °C. IR (KBr) 2207, 2156, 2097, 1612 cm^{-1}. MS (FAB): *m/z* 1040.5 [(M + H)$^+$], 980.4 [(M − CD_2-COO)$^+$], 918.4 [(M − 2CD_2COO)$^+$]. Anal. Calcd for $C_{51}H_{56}D_{14}NO_{11}$-$Eu$: H, 5.43; N, 1.35. Found: H, 5.82; N, 1.06.[31]

[25,26,27-Tris(carboxylatomethoxy)-4,9,23-tri-*tert*-butyl-16-dode-cyl-13,19-dioxa-16-azatetracyclo[19,3,1,1^{2,6},1^{7,11}]heptacosa-1(25),2,4,6-(27),7,9,11(26),21,23-nonaene(3−)]europium(3+) (29·Eu^{3+}). The reaction was carried out using triacid **28** (0.10 g, 0.11 mmol), Et_3N (46 μL, 0.33 mmol) in MeOH (3 mL), and $EuCl_3 \cdot 6H_2O$ (0.04 g, 0.12 mmol) in MeOH (1 mL). The off-white solid **29·Eu^{3+}** was obtained in 63% yield. Mp: >300 °C. IR (KBr): 1635 cm^{-1}. MS (FAB): *m/z* 1067.4 (M$^+$). Anal. Calcd for $C_{54}H_{76}NO_{11}Eu$: H, 7.18; N, 1.31; Eu^{3+}, 14.2. Found: H, 6.92; N, 1.03; Eu^{3+}, 12.8.

[25,26,27-Tris(carboxylatomethoxy)-4,9,23-tri-*tert*-butyl-13,16,19-trioxatetracyclo[19,3,1,1^{2,6},1^{7,11}]heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene(3−)] europium(3+) (34·Eu^{3+}). The reaction was carried out using triacid **33** (0.20 g, 0.27 mmol), Et_3N (0.11 mL, 0.81 mol) in MeOH (5 mL), and $EuCl_3 \cdot 6H_2O$ (0.12 g, 0.32 mmol) in MeOH (2 mL). The off-white solid **34·Eu^{3+}** was obtained after the addition of diisopropyl ether in 67% yield. Mp: >300 °C. IR (KBr): 1612 cm^{-1}. MS (FAB): *m/z* 899.5 [(M + H)$^+$], 865.6 [(M + Na − CH_2COO)$^+$]. Anal. Calcd for $C_{42}H_{52}O_{12}Eu$: H, 5.71; Eu^{3+}, 16.9. Found: H, 5.47; Eu^{3+}, 17.9.

Supporting Information Available: Synthesis procedures and analytical evidence for the formation of the products **2–10**, **17–28**, and **30–33** (23 pages). See any current masthead page for ordering and Internet access instructions.

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(31) For Eu^{3+} no satisfactory elemental analysis could be obtained.