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). 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 hydrogens (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$^{3+}$ is determined 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 is of the same order of magnitude as quenching by one O-C 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. 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. 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$^{3+}$. Therefore, research has been focused on the encapsulation of lanthanide ions by polydentate ligands, like cryptands, branched macrocyclic ligands, podands, and calix[4]arene derivatives, 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 quencher 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$_3$)$_2$CO and CD$_3$CN, and by using coordinating deuterated anions like CD$_3$COO$^{-}$.

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.

In this paper a novel polynuclear ligand, based on a hemispherand, with additional pendant arms at the phenolic oxygen atoms is reported (Chart 1). This ligand is proorganized 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. As 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 teri-butyli 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 Eu3+ 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 Pr3+ and Nd3+ for the 1.3 μm wavelength region, or Er3+ 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. 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. The dialdehyde 2 was obtained in 70% yield by heating a solution of terphenyl 1 and HMTA in C6H12COOH 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-propane in acetonitrile with K2CO3 as a base. The dialdehyde 3 was reduced in quantitative yield with NaBH4 in a mixture of methanol and THF (v/v 1:1) at 0 °C. Subsequently, the benzyl alcohol groups were converted into bromomethyl groups with PBr3, in toluene at 0 °C (83% yield).

The dial 6a, needed for the subsequent ring closure reaction, was obtained in quantitative yield by the alkylation of diethylamine with 1-bromoacetadecane in refluxing acetonitrile. The macrocyclization of the dibromide 5 and the dial 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 1H NMR spectrum shows an AB-quartet for the benzylic hydrogens at δ = 4.72 and 4.39 (J = 11.9 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 1H NMR spectrum, however, only shows one set of signals (vide infra).

Dealkylation of the cyclic product 7a was accomplished in 85% yield with the Pd(PPh3)4 complex and Et3N·HCOOH in a mixture of ethanol and water (v/v 5:1). The trisester 9a-NaHCO3 was obtained in quantitative yield by alkylation of the phenolic oxides with methyl bromacetate in acetonitrile, with K2CO3 as a base. The base-catalyzed hydrolysis of the trisester 9a-NaHCO3 was carried out in aqueous methanol in the presence of NaOMe, giving trisacid 10a in almost quantitative yield. Also in the case of the triacid only one conformation is observed in the 1H NMR spectrum. Complexation of Eu3+ in the preorganized tricarboxylate was simply achieved by reaction of trisacid 10a with 1 equiv of EuCl3·6H2O in methanol, in the presence of 3 equiv of Et3N as an HCl scavenger. From the FAB mass spectrum of the complex 11a-Eu3+ which shows a peak at m/e = 1026.4, corresponding to the (M + H)+ peak (called for C39H27Na2O12Eu 1026.4) and elemental analysis we conclude that a 1:1 Eu3+·11a complex is formed. Furthermore, the FAB mass spectrum shows peaks at m/e = 968.5 and 908.3 which correspond to [(M - CH2CO2)2] and [(M - 2CH2CO2)] respectively; the characteristic isotope pattern of Eu3+ 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 trisacid 10a, located at 1748 cm−1.

MM calculations of the minimal energy of the Eu3+ 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 triacid 10b-d were obtained via the same synthesis route as described above, using the deuterated diol 6b and/or BrCD2COOMe as reagents. Diol 6b was obtained in 70% yield by the alkylation in l-propanol of octodecylamine with ethylene oxide-d4. The Eu3+ complexes (12) Hey, H.; Arpe, H.-J. Angew. Chem., Int. Ed. Engl. 1973, 12, 928-929.

(13) The calculations were carried out following the protocol described in van Veggel, F. C. J. M.; Reinhoudt, D. N. Reel. Chem. Phys. 1998, 114, 387-394.

(14) The base-catalyzed hydrolysis of the triesters which contain deuterated arms (9e and 9d) and the complexation reactions using 10e and 10d were carried out in methanol-d4 in the presence of D2O to prevent the exchange of deuterium atoms by hydrogen. The Eu3+ complexes...
Scheme 1. Synthesis Route Leading to Dibromide 5

Scheme 2. Synthesis Route Leading to the Eu³⁺ Complexes 11a–d·Eu³⁺

Scheme 3. Synthesis Route Leading to the tert-Butyl-Substituted Terphenyl Moiety 19

11b·Eu³⁺, 11c·Eu³⁺, and 11d·Eu³⁺ 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 Eu³⁺, 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·Eu³⁺ and 11d·Eu³⁺ both show an additional absorption at 2156 cm⁻¹.

To increase the solubility of the Eu³⁺ 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, 14, 15, 16 and 17 were prepared according to literature procedures. Dibromination of 16 with Br₂ in chloroform at room temperature gave 17 in 88% yield. Compound 17 was subjected to a double Suzuki coupling 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(PPh₃)₄. The terphenyl 18 was obtained in almost quantitative yield and was subse-


methanol in the first coordination sphere of the Eu³⁺ ion, whereas two molecules of methanol coordinate to 34-Eu³⁺, 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 Eu³⁺ complexes are summarized in Tables 1 and 2.

Photophysical Studies. By studying the luminescent properties of the Eu³⁺ 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 Eu³⁺ ion, can be established. The excitation spectra of 10⁻⁴ M solutions of 11d-Eu³⁺ and EuCl₂·6H₂O, detected at 617 nm (the hypersensitive 7D₀ → 5F₂ transition of Eu³⁺) in methanol-d₄, depicted in Figure 2, show the typical excitation bands for Eu³⁺ 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. Moreover, the spectra for 11d-Eu³⁺ and 11a-Eu³⁺ in methanol-d₄, depicted in Figure 2 show that the luminescence intensity is increased upon deuteration of the ligand.

The luminescence spectra of 10⁻⁴ M solutions of the Eu³⁺ complexes in methanol-d₄ after excitation at 393 nm are depicted in Figure 5, showing the typical 7D₀ → 5F₂ Eu³⁺ transitions. These spectra also indicate that luminescence enhancement is obtained upon ligand deuteration with the anticipated increase 11d-Eu³⁺ > 11b-Eu³⁺ > 11c-Eu³⁺ > 11a-Eu³⁺. This increase can be caused by either the reduced quenching of the Eu³⁺ 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 Eu³⁺ ion. However, lifetime measurements at 464 nm, exclusively leading to direct excitation of the Eu³⁺ 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.

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-Eu³⁺ were determined in 10⁻⁴ M methanol solutions by excitation at 393 or 287 nm and recording the intensity of the emitted light of the hypersensitive

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

(19) Computer simulations carried out with the Na⁺ complex of an analogous of 9a with triethyl ester groups as pendant arms and an oxygen atom instead of the C₁-Alkyl group in the ring have been published. The calculated data are corroborated with 1H NMR spectroscopy and the solid state structure (Yaghi, F. J. M. W.; Dayshoven, J. P. M. V.; Harkema, S. J.; Otten Wolbers, M. P.; Reinholdt, D. N. J. Chem. Soc., Perkin Trans. 2, 1996, 449–454).

(20) Details of the calculations 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-d₄ vs methanol-d₄) were not exactly the same, leading in this case to a higher intensity in methanol-d₄.

(23) Laser excitation directly at the Eu³⁺ ion at 464 nm using solutions of 11a-Eu³⁺ and 11d-Eu³⁺ in methanol-d₄, leads to lifetimes of 0.88 and 1.40 ns, 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 deuteration atoms on the positions of the energy levels 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. J.; Jortner, J. Mol. Phys. 1974, 18, 145–164). Therefore, the energy level-transfer along the series 11a,d-Eu³⁺ is assumed to be constant.
Table 1. Average Eu(III)-Hydrogen Atom Distances (Å) and Standard Deviations (in Parentheses) in the MD Simulations

<table>
<thead>
<tr>
<th></th>
<th>O-H bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
<th>CH3-C H-bond</th>
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</thead>
<tbody>
<tr>
<td>11a-Eu</td>
<td>2.41(0.06)</td>
<td>3.86(0.20)</td>
<td>4.16(0.20)</td>
<td>4.81(0.15)</td>
<td>3.74(0.19)</td>
<td>3.80(0.16)</td>
<td>3.97(0.17)</td>
<td>3.56(0.13)</td>
<td>3.54(0.16)</td>
<td>3.60(0.16)</td>
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<td>(as NCS)</td>
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</tr>
<tr>
<td>29-Eu</td>
<td>2.27(0.06)</td>
<td>3.89(0.22)</td>
<td>4.46(0.17)</td>
<td>4.71(0.14)</td>
<td>4.80(0.20)</td>
<td>4.36(0.12)</td>
<td>4.34(0.10)</td>
<td>4.16(0.12)</td>
<td>4.10(0.09)</td>
<td>3.44(0.18)</td>
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<tr>
<td>(as NCS)</td>
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</tr>
<tr>
<td>34-Eu</td>
<td>2.28(0.06)</td>
<td>4.11(0.20)</td>
<td>4.46(0.20)</td>
<td>4.96(0.18)</td>
<td>4.50(0.10)</td>
<td>4.10(0.10)</td>
<td>4.20(0.16)</td>
<td>3.90(0.16)</td>
<td>3.80(0.10)</td>
<td>3.70(0.10)</td>
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<tr>
<td></td>
<td>2.29(0.06)</td>
<td>4.73(0.12)</td>
<td>5.15(0.13)</td>
<td>5.17(0.12)</td>
<td>4.50(0.12)</td>
<td>4.46(0.12)</td>
<td>4.10(0.12)</td>
<td>4.05(0.22)</td>
<td>4.06(0.14)</td>
<td>4.00(0.16)</td>
</tr>
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</table>

"The values in the first column correspond to the distance between the atomic hydrogen atom and the Eu(III) ion, whereas the values in the second column give the distance between the equatorial hydrogen atom and the Eu(III) ion. With X = N for 11a-Eu and 29-Eu and X = O for 34-Eu. Of the long alkyl chain.

Figure 2. Excitation spectra of 10−4 M solutions of (1) 11d-Eu(III) in methanol-d6, and (2) EuCl3 in methanol-d6, (3) 11b-Eu(III) in methanol-d6, and (4) 11a-Eu(III) in methanol-d6, detected at 617 nm.

Table 2. Lifetimes (ns) of the D2° Excited State Recorded at λem = 617 nm after Excitation at 393 or 287 nm Using 10−4 M Methanolic Solutions of Different Deuterated Complexes 11a−d-Eu(III)+

<table>
<thead>
<tr>
<th></th>
<th>τ(D393) (393 nm)</th>
<th>τ(D393) (287 nm)</th>
<th>τ(D287) (393 nm)</th>
<th>τ(D287) (287 nm)</th>
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</thead>
<tbody>
<tr>
<td>EuCl3</td>
<td>0.26</td>
<td>0.23</td>
<td>0.30</td>
<td>0.35</td>
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<tr>
<td>11a-Eu</td>
<td>0.68</td>
<td>0.97</td>
<td>0.74</td>
<td>1.17</td>
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<tr>
<td>11b-Eu</td>
<td>0.75</td>
<td>1.18</td>
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<td>11c-Eu</td>
<td>0.68</td>
<td>0.95</td>
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<tr>
<td>11a-Eu</td>
<td>0.73</td>
<td>1.26</td>
<td>1.57</td>
<td>0.80</td>
</tr>
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</table>

"The experimental error is ±10% which was determined from duplicate and triplicate measurements.

The results in an increase of the luminescence lifetime by a factor of about 1.5.200

Figure 3. Emission spectra of 10−4 M solutions of 11a−d-Eu(III) in methanol-d6, detected at 393 nm.

5D2 → 7F2 transition (617 nm). In all cases the data could be fitted to monoeponential decay curves, indicating a unique chemical environment. The determined lifetimes are presented in Table 2. These results illustrate that the Eu(III) 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 EuCl3 in this solvent (0.26 ms). The lifetimes measured for the Eu(III) complexes in methanol-d6 are lower (0.55−1.26 ms) than that of EuCl3 (1.45 ms), 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 1.5.200

(24) The same lifetimes, within the experimental error of 10%, were observed using 10−4 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(III) ion, leading to more allowed transitions.

(26) The solvent quenching mechanisms are minimal in the case of methanol-d6, therefore, the effect of ligand deuteration is determined in this solvent otherwise the effect may be shaded by solvent quenching. However, in methanol-d6 the lifetimes are still increased by a factor of about 1.3.


(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 CH3 group of the coordinating methanol can have a decreasing effect on the lifetime.
Prolonged Lifetimes of Excited Eu²⁺ Ions

\[
k_{\text{obs}} = \frac{1}{k_{\text{deg}} + k_{\text{OH}} + k_{\text{H₂O}} + k_{\text{H₂O,water}} + k_{\text{other,measured}}}
\]

\[\text{O-D, N-D, and C-D vibrations, } k_{\text{H₂O}} \text{ rate constant of quenching by O-H vibrations, } k(\lambda) \text{ thermal quenching, and } k_{\text{deg}} = \text{rate constant of energy transfer by 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 nonadiabatic decay via the O-H groups of the solvent, the C-H groups of the pendant arm 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 Eu²⁺ 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 deuterium of the bridge (11b-Eu³⁺) and excitation at 393 nm, with calculated \( k_{\text{deg}} \) rate constants of \( k_{\text{H₂O}} = 0.49 \text{ ms}^{-1} \), \( k_{\text{OH}} = 0.31 \text{ ms}^{-1} \), and \( k_{\text{deg,water}} = 0.20 \text{ ms}^{-1} \). 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:

\[
k_{\text{obs}} = \frac{1}{k_{\text{deg}} + k_{\text{OH}} + k_{\text{H₂O}} + k_{\text{H₂O,water}} + k_{\text{other,measured}}}
\]

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-d₂ 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 deuterium 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.\footnote{The lifetime (reported in Table 4) of 29-Eu³⁺ dissolved in methanol and methanol-d₂, 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 deuterium 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 determined number of coordinating methanol molecules.}

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

<table>
<thead>
<tr>
<th></th>
<th>393 nm²</th>
<th>393 nm³</th>
<th>287 nm²</th>
<th>287 nm³</th>
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<tr>
<td>( k_{\text{OH}} )</td>
<td>0.49</td>
<td>0.58</td>
<td>0.59</td>
<td>0.53</td>
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<tr>
<td>( k_{\text{H₂O}} )</td>
<td>0.31</td>
<td>0.32</td>
<td>0.23</td>
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<tr>
<td>( k_{\text{deg,water}} )</td>
<td>0.20</td>
<td>0.16</td>
<td>0.16</td>
<td>0.15</td>
</tr>
</tbody>
</table>

\* From 11a-Eu³⁺ and 11b-Eu³⁺, \* From 11c-Eu³⁺ and 11d-Eu³⁺, \* From 11a-Eu³⁺ and 11c-Eu³⁺ with ND = 11a-Eu³⁺ or 11c-Eu³⁺ and BD = 11b-Eu³⁺ or 11d-Eu³⁺.

Table 4. Lifetimes (ns) of the Eu³⁺ Excited State Recorded at \( \lambda_{\text{ex}} = 617 \text{ nm} \) for Excitation at 393 or 287 nm Using 10⁻⁴ M Methanolic Solutions of the Complexes with tert-Butyl Groups

<table>
<thead>
<tr>
<th></th>
<th>393 nm²</th>
<th>393 nm³</th>
<th>287 nm²</th>
<th>287 nm³</th>
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<tr>
<td>( k_{\text{OH}} ) (393 nm)</td>
<td>0.62</td>
<td>0.94</td>
<td>0.71</td>
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<td>( k_{\text{OH}} ) (287 nm)</td>
<td>0.67</td>
<td>1.76</td>
<td>0.69</td>
<td>1.81</td>
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\* The experimental error is ±10% which was determined from duplicate and triplicate measurements.

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

<table>
<thead>
<tr>
<th></th>
<th>exc 393 nm</th>
<th>exc 287 nm</th>
<th>MD</th>
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<tbody>
<tr>
<td>11a-Eu³⁺</td>
<td>0.9</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>29-Eu³⁺</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>34-Eu³⁺</td>
<td>1.9</td>
<td>1.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\* 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 at an 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 λex = 550–725 nm with a PTI (Photon Technology International, Inc.) Alphaplan spectrophotometer after excitation of the Eu** ion at λex = 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** luminescence lifetimes and intensities to the water content of the solutions, methanol was dried over molecular sieves (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 recorded using a Bluestar 3200 or a Nicolet 660 FT-IR spectrophotometer. Elemental analysis30 was performed using a Carlo Erba EA1106. The Eu** 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 water, followed by the addition of an acetone 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 (ethylenediaminetetraacetate) was carried out using xylene orange as an indicator. Methanol was dried over molecular sieves (Å) for at least 3 days. EuCl3·6H2O 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**. The corresponding triacid was dissolved in MeOH, after which 3 equiv of BuN3 was added using a microsyringe. Subsequently a solution of EuCl3·6H2O 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 CH2CN 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 CH2CN (∼3 mL).

[30] The C content of the Eu** complexes determined by elemental analysis was too low due to the formation of very stable Eu** carbides or carbonates (Tm > 1800 °C).

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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. JAS09314

For Eu** no satisfactory elemental analysis could be obtained.