

# Increased Luminescent Lifetimes of Ln<sup>3+</sup> Complexes Emitting in the Near-Infrared as a Result of Deuteration

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The luminescence of lanthanide(III) ions emitting in the near-infrared region is ideally suited for telecommunications applications, and a number of applications have been developed. These are in general based on inorganic matrices, but polymer-based matrices would have advantages in device fabrication. In organic matrices, however, molecular vibrations in the matrix quench the excited state of luminescent lanthanide ions. Replacement of strongly quenching groups such as C–H oscillators by more weakly quenching

groups enhances the luminescence lifetime and hence also the luminescence quantum yield. This article reports a synthesis route developed in order to deuterate all C–H groups that contribute to the quenching in an organic lanthanide complex. The luminescences of three near-infrared emitting lanthanide ions – Nd<sup>3+</sup>, Er<sup>3+</sup>, and Yb<sup>3+</sup> – were measured. The maximum effect achieved upon deuteration is a factor of 2–3, but lifetimes remain in the microsecond region (**1**·Nd<sup>3+</sup>: 5.5 μs; **1**·Yb<sup>3+</sup>: 52.3 μs; **1**·Er<sup>3+</sup>: 5.4 μs).

## Introduction

Lanthanide ions attract a great deal of interest,<sup>[1]</sup> because their luminescence properties are useful in a variety of applications, such as optical amplification for telecommunications, light-emitting diodes,<sup>[2]</sup> and fluoro-immuno assays.<sup>[3]</sup> The luminescence of the lanthanide ions stems from intra-4f transitions, which in principal are forbidden transitions, resulting in relatively long-lived excited states. This makes them (among other compounds) suited for optical amplification and laser applications. Erbium ions are actually being used as the active components in optical amplification in Erbium Doped Fiber Amplifiers (EDFAs)<sup>[4]</sup> in telecommunications devices. Polymer-based materials would have advantages over inorganic materials in devices, because fabrication and integration of polymer waveguide-based optical components, such as splitters, switches, and multiplexers, is relatively easy with standard lithographic techniques. For incorporation of lanthanide ions into organic materials, they must be made soluble in the organic polymer matrix by encapsulation in organic polydentate ligands. Besides solubilizing the ions, the polydentate ligand shields them from luminescence-quenching moieties in the matrix.<sup>[5]</sup> For europium and terbium, with emissions in the visible region of the spectrum, the quenching by oscillating groups such as O–H groups has been studied extensively.<sup>[6]</sup> Ligands that effectively shield the emitter from the solvent have been synthesized and the remaining quenching is mainly due to C–H groups within the ligand itself.<sup>[7]</sup> For lanthanide ions, emitting in the near-infrared, quenching by the ligands is more strongly reflected in their quantum yields in organic

media.<sup>[8,9]</sup> Even with effective shielding of the ion from the solvent the lifetimes remain low relative to those in inorganic materials.<sup>[10]</sup> One strategy to increase the quantum yield of the lanthanide ions is to eliminate the C–H oscillators in close proximity to the lanthanide ion by introduction of deuterium or fluorine in place of hydrogen.<sup>[7,11]</sup> The C–D and C–F bonds oscillate at lower energy, and so quenching of the lanthanide excited state is reduced.

Our strategy was to fully deuterate all C–H groups that contribute to quenching in a lanthanide ligand.<sup>[9]</sup> The ligand (Figure 1) has advantages in terms of solubility, shielding of the ion to solvent molecules, and easy functionalization with chromophores and dyes.<sup>[8,12–14]</sup>

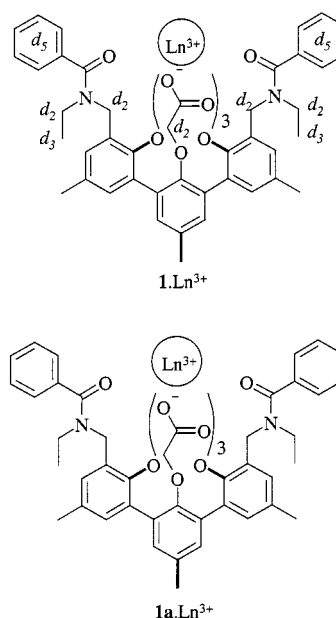


Figure 1. Terphenyl-based lanthanide complexes

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## Results and Discussion

## Molecular Modeling

The quenching rate is exponentially related to the distance between donor and acceptor. C–H groups at 6 Å and further away from the lanthanide ion will not quench significantly and thus do not have to be deuterated. Average distances between hydrogen atoms and the lanthanide ion were determined from molecular dynamics simulations in a box of OPLS methanol.<sup>[15,16]</sup> Figure 2. Eu<sup>3+</sup> was taken as representative for the NIR emitting ions in the simulation.<sup>[17]</sup> The average distances between the lanthanide ion and the hydrogen atoms derived from the MD simulation are presented in Table 1.

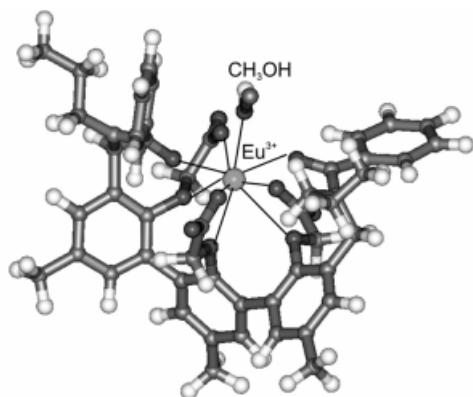
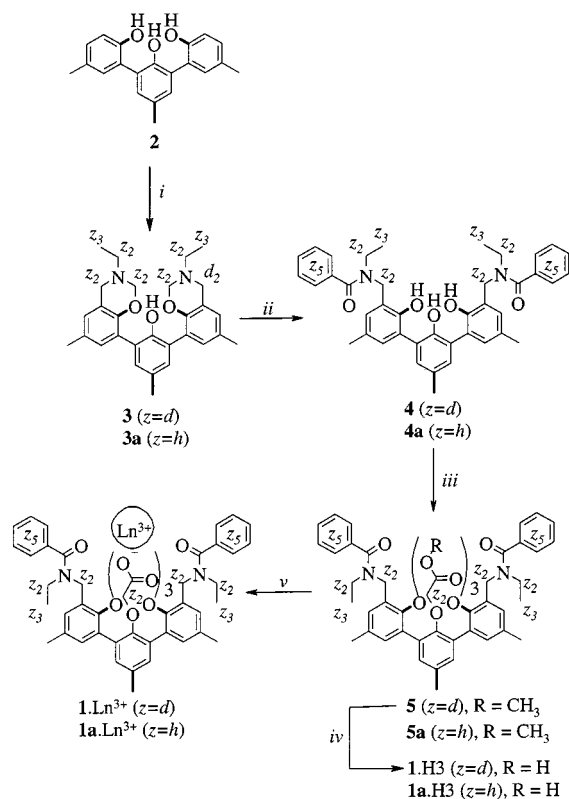


Figure 2. Snapshot of  $1 \cdot \text{Eu}^{3+}$  in OPLS methanol; one  $\text{CH}_3\text{OH}$  molecule is coordinated in the first coordination sphere of the lanthanide ion; instead of ethyl groups, propyl groups were used in the modeling; this has no effect on the complexation behavior of the complexes; for further details on the modeling procedure see refs.<sup>[15,17]</sup>

It is clear from the results that the hydrogen atoms of the *m*-terphenyl moiety are relatively distant from the lanthanide ion compared to the other hydrogen atoms and should not significantly contribute to the luminescence quenching. All the other groups will have to be deuterated to reduce the quenching.

## Synthesis

A new synthesis route, permitting the use of commercially available deuterated reagents, to deuterated lanthanide complexes has been designed. The key step in this route is the Mannich reaction<sup>[18]</sup> between an amine, formaldehyde, and a phenol. The synthesis route is depicted in Scheme 1. The same procedure was used to prepare deuterated ( $1 \cdot \text{Ln}^{3+}$ ) and non-deuterated ( $1\mathbf{a} \cdot \text{Ln}^{3+}$ ) lanthanide complexes.



Scheme 1. i:  $\text{D}_2\text{CO}$ ,  $[\text{D}_5]\text{EtNH}_3\text{Cl}$ ,  $\text{NaOAc}$ , 1,4-dioxane/ $\text{D}_2\text{O}$ , reflux, 70%; ii: aqueous  $\text{HCl}$ ,  $\text{CH}_3\text{OD}$ , reflux;  $[\text{D}_5]\text{BzCl}$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ ;  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_3\text{OD}/\text{D}_2\text{O}$ , reflux, 56%; iii: methyl  $[\text{D}_2]$  bromoacetate,  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_3\text{CN}$ , reflux, 78%; iv:  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_3\text{OD}/\text{D}_2\text{O}$ , reflux, 96%; v:  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_3\text{OD}$ , quantitative

Table 1. Distances (in Å) between C–H groups and  $\text{Eu}^{3+}$  derived from the molecular modeling study<sup>[a]</sup>

$\text{ArH}^{\text{terph},i}$	$\text{ArH}^{\text{terph},o}$	$\text{ArCH}_3$	$\text{ArCH}_2\text{N}$	$\text{CH}^{\text{tail},1[b]}$	$\text{CH}^{\text{tail},2 [b]}$	$\text{ArH}^{\text{Bz},1 [b]}$	$\text{ArH}^{\text{Bz},2 [b]}$	$\text{OCH}_2\text{CO}_2$
$6.3 \pm 0.1$	$6.4 \pm 0.1$	$8.2 \pm 0.3$	$5.3 \pm 0.1$	$3.8 \pm 0.4$	$6.2 \pm 0.1$	$4.8 \pm 0.3$	$4.0 \pm 0.2$	$4.3 \pm 0.2$
$6.2 \pm 0.1$	$6.6 \pm 0.2$	$7.9 \pm 0.2$	$3.8 \pm 0.2$	$4.4 \pm 0.4$	$6.4 \pm 0.1$	$6.8 \pm 0.3$	$6.4 \pm 0.2$	$4.3 \pm 0.1$
	$6.3 \pm 0.1$	$8.0 \pm 0.2$	$5.1 \pm 0.2$	$6.1 \pm 0.4^{[c]}$	$6.7 \pm 0.6^{[c]}$	$7.7 \pm 0.2$	$8.0 \pm 0.2$	$4.3 \pm 0.1$
	$6.3 \pm 0.1$		$5.8 \pm 0.1$			$7.1 \pm 0.2$	$7.9 \pm 0.1$	$3.8 \pm 0.2$
						$5.3 \pm 0.3$	$6.1 \pm 0.1$	$4.2 \pm 0.1$
								$3.7 \pm 0.1$

<sup>[a]</sup> The different hydrogen positions in the ligand are denoted as follows: terphenyl aromatic hydrogen atoms ( $\text{ArH}^{\text{terph}}$ , with <sup>i</sup> as the inner ring and <sup>o</sup> for the outer rings), terphenyl  $\text{CH}_3$  hydrogen atoms ( $\text{ArCH}^{\text{terph}}$ ), benzylic hydrogen atoms ( $\text{ArCH}_2\text{N}$ ), aliphatic hydrogen atoms on the amine tail ( $\text{CH}^{\text{tail}}$ ), aromatic hydrogen atoms of the benzoyl groups ( $\text{ArH}^{\text{Bz}}$ ), and hydrogen atoms on the acetic acid arms ( $\text{OCH}_2\text{CO}_2$ ). Different values in one column represent different hydrogen atoms on this position. – <sup>[b]</sup> Because of the asymmetry in the complex, the different ethyl and benzoyl groups have different separations from the  $\text{Ln}^{3+}$  ion. – <sup>[c]</sup> This value is for all hydrogen atoms at the  $\beta$ -position.

The benzoxazine **3** was prepared by refluxing a solution of the building block **2**,<sup>[19]</sup> deuterated ethylamine, and an excess of formaldehyde in a mixture of 1,4-dioxane and water. The benzoxazine was converted into the amine by refluxing the yellow solid in ethanol with a few drops of concentrated hydrochloric acid. After amidation with per-deuterated benzoyl chloride in dichloromethane with triethylamine, the crude product was refluxed with potassium carbonate in a mixture of water and methanol to hydrolyze the esters of the phenol groups and excess benzoyl chloride. Bis(amide) **4** was subsequently alkylated with 3 equiv. of deuterated methyl bromoacetate in acetonitrile in the presence of potassium carbonate under reflux for 3 h. The methyl esters were hydrolyzed by refluxing terphenyl **5** in water/methanol in the presence of potassium carbonate. Deuteration was confirmed for all intermediates by comparison of spectroscopic data – i.e., NMR and FT-IR – with data from the non-deuterated analogues. In <sup>13</sup>C NMR spectra (<sup>1</sup>H-decoupled, <sup>2</sup>H-coupled) the deuterated carbon atoms showed up as multiplets caused by coupling with the <sup>2</sup>H nuclei. The FT-IR spectra exhibited peaks corresponding to C–D vibrations between 2200 and 2000 cm<sup>-1</sup>.<sup>[20]</sup> After hydrolysis of the ester groups in **5**, the lanthanide complexes were easily obtained by treatment of the lanthanide nitrate salts [Nd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Er(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and Yb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O] with triethylamine in methanol. Complex formation was confirmed by mass spectrometry, which showed the parent mass peaks with the correct isotope pattern for the corresponding lanthanide ion. Absorptions at 1600 cm<sup>-1</sup> for the carboxylates are present in the infrared spectra. The complexes are soluble in most common solvents such as chloroform, dichloromethane, and DMSO.

### Near-Infrared Luminescence

The metal-centered luminescence of the NIR-emitting lanthanide ions was measured by indirect excitation of the ions through the *m*-terphenyl chromophore.<sup>[8]</sup> Figure 3 shows the excitation and emission spectra of the Yb<sup>3+</sup>, Nd<sup>3+</sup>, and Er<sup>3+</sup> complexes measured in [D<sub>6</sub>]DMSO. The excitation spectra closely resemble the absorption spectra (maximum around 300 nm), demonstrating the sensitized emission in which the *m*-terphenyl moiety acts as the sensitizer.

The emission spectra clearly show the typical emission characteristics originating from 4f–4f transitions of Nd<sup>3+</sup> [880 (<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2</sub>, not shown<sup>[21]</sup>), 1064 (<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub>), 1330 nm (<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>13/2</sub>)], Yb<sup>3+</sup> [980 nm (<sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub>)], and Er<sup>3+</sup> [1550 nm (<sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub>)]. Lifetime measurements were performed by excitation of the ions through the *m*-terphenyl moiety with a pulsed nitrogen laser operating at 337 nm and by collection of the decay curves at the appropriate wavelength (1060 nm for Nd<sup>3+</sup>, 980 nm for Yb<sup>3+</sup>, and 1550 nm for Er<sup>3+</sup>). All the decay curves could be fitted with a single exponential curve and the results of the fittings are summarized in Table 2, together with lifetimes obtained from the non-deuterated complexes. For comparison, luminescent lifetimes (τ<sub>0</sub>) of these complexes in the absence of quenchers were taken from the literature.<sup>[14]</sup>

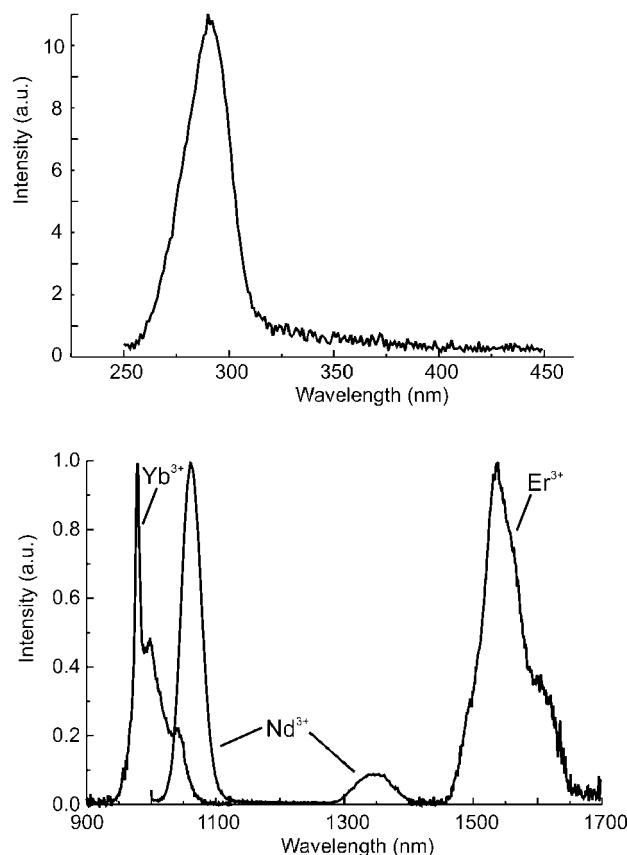


Figure 3. Excitation spectrum (top) of **1**-Nd<sup>3+</sup>, obtained by measuring the emission at 1060 nm; and the (normalized) emission spectra (bottom) of **1**-Yb<sup>3+</sup>, **1**-Nd<sup>3+</sup>, and **1**-Er<sup>3+</sup> by excitation at 300 nm, both measured in [D<sub>6</sub>]DMSO solution

The lifetimes and intrinsic luminescence quantum yields of the ions were increased by a factor of 2–3 relative to the corresponding parameters for the non-deuterated compounds. The radiative lifetime of the ions should not be changed upon deuteration, and quantum yields, calculated by dividing the observed lifetime by the radiative lifetime τ<sub>0</sub>, were increased by the same factors as the lifetimes (φ<sub>1-Nd</sub> = 0.02, φ<sub>1-Er</sub> = 0.0004, φ<sub>1-Yb</sub> = 0.03). This is an important achievement on the way towards our ultimate goal, as longer lifetimes are beneficial in the optical amplification process. However, the lifetimes are still much lower than those in inorganic systems,<sup>[10]</sup> and from this and from other reports<sup>[7,8,11,22]</sup> we conclude that lifetimes in organic complexes are likely to remain in the microsecond region.

### Conclusion

A new synthesis route has been developed, with the goal of reducing the number of C–H quenchers in *m*-terphenyl-based lanthanide ion complexes. Complexes were prepared and the photophysical properties of these deuterated complexes were measured. The lanthanide ions were excited in the UV region through their *m*-terphenyl moieties and emitted the corresponding near-infrared light. The luminescence

Table 2. Luminescence lifetimes of lanthanide ion complexes in [D<sub>6</sub>]DMSO solution

	$\tau$ ( $\mu$ s); Ln <sup>3+</sup> = Nd <sup>3+</sup>	$\tau$ ( $\mu$ s); Ln <sup>3+</sup> = Er <sup>3+</sup>	$\tau$ ( $\mu$ s); Ln <sup>3+</sup> = Yb <sup>3+</sup>
<b>1</b> ·Ln <sup>3+</sup>	5.5	5.4	52.3
<b>1a</b> ·Ln <sup>3+</sup>	2.5	3.3	19.0
$\tau_0$ <sup>[a]</sup>	0.25 ms	14 ms	2.0 ms

<sup>[a]</sup> Radiative lifetimes, from ref.<sup>[14]</sup>

lifetimes, and hence the quantum yields, of the deuterated compounds were increased by a factor 2–3 relative to the nondeuterated analogues. The luminescence lifetimes of the near-infrared emitting lanthanide ions in organic complexes remain in the microsecond region.

## Experimental Section

**General Remarks:** 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 (*m*-nitrobenzyl alcohol) or Magic Bullet (MB)<sup>[23]</sup> as a matrix. – IR spectra were recorded with a Perkin–Elmer Spectrum BX FT-IR System, using KBr pellets as matrix. – Elemental analyses were performed with a Carlo Erba EA 1106 apparatus. – <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with Varian 300 or Varian 400 spectrometers with CDCl<sub>3</sub> as the solvent unless stated otherwise, using residual CHCl<sub>3</sub> ( $\delta$  = 7.26) and CDCl<sub>3</sub> ( $\delta$  = 77.0) as the internal standards, respectively. In the assignments of the protons the <sup>o</sup> and <sup>i</sup> superscripts stand for the protons on the *m*-terphenyl moiety on the outer and inner phenolic rings, respectively. Multiplets in the <sup>13</sup>C NMR spectrum were unresolved and assigned with an *m*. Deuterated reagents, 20% [D<sub>2</sub>]formalin solution in D<sub>2</sub>O, [D<sub>5</sub>]ethylamine hydrochloride, [D<sub>5</sub>]benzoylchloride, and methyl [D<sub>2</sub>]bromoacetate were purchased from Isotec Inc. – Deuterated solvents D<sub>2</sub>O, CH<sub>3</sub>OD, and CD<sub>3</sub>OD were purchased from Merck and all other chemicals were purchased from Aldrich. All chemicals were used as received without further purification. CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and hexane were distilled from CaCl<sub>2</sub>, ethyl acetate was distilled from K<sub>2</sub>CO<sub>3</sub>, Et<sub>3</sub>N was distilled in vacuo and stored over KOH. 1,4-Dioxane and acetonitrile were of analytical grade and were dried over molecular sieves (4 Å) prior to use. Preparative column chromatography separations were performed using Merck silica gel (particle size 0.040–0.063 mm, 230–400 mesh) or Merck LiChroprep RP-18 (particle size 0.025–0.040 mm).

**Compound 3:** A solution of *m*-terphenyl<sup>[18]</sup> (0.5 g, 1.56 mmol) in 10 mL of dioxane was added to a solution of deuterated formalin (20% solution D<sub>2</sub>CO in D<sub>2</sub>O, 1.23 g, 7.8 mmol), deuterated ethylamine·HCl salt (0.32 g, 3.7 mmol), and sodium acetate (0.32 g, 3.9 mmol) in 25 mL of 1,4-dioxane. D<sub>2</sub>O (5 mL) was subsequently added to dissolve all the salts and the solution was refluxed for 3 h. After the mixture had cooled down to room temperature and the solvents had been removed, 100 mL of dichloromethane was added and the solution was washed twice with water and once with brine. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and, after filtration of the salts, the solution was concentrated to dryness under vacuum. The crude product was purified by reversed phase (RP18) column chromatography with methanol as the eluent. A yellow solid was obtained, yield 0.52 g, 70%, m.p. 79–82 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.11 (s, 2 H, ArH<sup>i</sup>), 7.05 (d, *J* = 3.0 Hz, 2 H, ArH<sup>o</sup>), 6.82 (d, *J* = 3.0 Hz, 2 H, ArH<sup>o</sup>), 6.42 (s, 1 H, OH), 2.38 (s, 3 H,

ArCH<sub>3</sub><sup>i</sup>), 2.32 (s, 6 H, ArCH<sub>3</sub><sup>o</sup>). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 149.0, 148.7, 131.3–126.6, 119.6, 81.9 (m), 66.9, 49.0 (m), 44.3 (m), 20.5, 12.3 (m). – MS (FAB, NBA): *m/z* = 476.5 [M]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>16</sub>D<sub>18</sub>N<sub>2</sub>O<sub>3</sub> 476.4. – IR (KBr):  $\tilde{\nu}$  = 2222, 2149, 2126, 2075 cm<sup>-1</sup> (C–D).

**Compound 3a:** The undeuterated compound was synthesized analogously to the deuterated compounds, with the difference that 37% formalin solution in H<sub>2</sub>O containing 25% methanol was used, refluxing was overnight, and purification was by using silica gel with ethyl acetate as eluent.<sup>[24]</sup> Yield: 0.32 g, 45%, m.p. 81–82 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.05 (s, 2 H, ArH<sup>i</sup>), 6.98 (d, *J* = 3.0 Hz, 2 H, ArH<sup>o</sup>), 6.75 (d, *J* = 3.0 Hz, 2 H, ArH<sup>o</sup>), 6.36 (s, 1 H, OH), 4.83 (s, 4 H, ArCH<sub>2</sub>N), 3.94 (s, 4 H, NCH<sub>2</sub>O), 2.77 (q, *J* = 6.7 Hz, 4 H, NCH<sub>2</sub>CH<sub>3</sub>), 2.28 (s, 3 H, ArCH<sub>3</sub><sup>i</sup>), 2.25 (s, 6 H, ArCH<sub>3</sub><sup>o</sup>), 1.05 (t, *J* = 7.3 Hz, 6 H, N–CH<sub>2</sub>–CH<sub>3</sub>). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 149.4, 149.0, 130.5–119.8, 82.3, 49.5, 47.3, 20.3, 12.8. – MS (FAB, NBA): *m/z* = 459.3 [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>35</sub>N<sub>2</sub>O<sub>3</sub> 459.3. – C<sub>29</sub>H<sub>34</sub>N<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O (476.6): calcd. C 73.08, H 7.61, N 5.88; found C 73.17, H 7.50, N 5.68.

**Compound 4:** A solution of **3** (0.2 g, 0.44 mmol) in ethanol with a few drops of concentrated HCl was refluxed for 1 h. After concentration to dryness, the remaining white solid was dissolved in 50 mL of dichloromethane, and Et<sub>3</sub>N (0.26 mL, 1.78 mmol) followed by [D<sub>5</sub>]benzoylchloride (0.13 mL, 1.11 mmol) were added. The solution was stirred overnight, diluted to 100 mL with dichloromethane, and washed twice with 1 N HCl and once with brine. After drying with MgSO<sub>4</sub> and filtration of the salts, the dichloromethane was removed under vacuum. The crude product was dissolved in a mixture of [D]methanol/D<sub>2</sub>O (1:1) with K<sub>2</sub>CO<sub>3</sub> (0.17 g, 1.2 mmol) and refluxed for 1 h. The mixture was extracted three times with dichloromethane and the combined organic layers were washed twice with 1 N HCl and once with brine. After drying with MgSO<sub>4</sub>, filtration, and removal of dichloromethane, the product was purified by column chromatography with ethyl acetate/hexane (40:60) as eluent. Yield: 0.16 g, 56%, m.p. 100–101 °C. – <sup>1</sup>H NMR (CD<sub>3</sub>OD):  $\delta$  = 7.18–6.92 (m, 6 H, ArH), 2.35 (m, 9 H, ArCH<sub>3</sub>). – <sup>13</sup>C NMR (CD<sub>3</sub>OD):  $\delta$  = 175.0, 174.4, 151.7, 151.4, 150.1, 137.9, 137.1, 137.0, 133.3–124.8, 44.1, 40.7, 33.2, 30.8, 30.6, 24.3, 23.8, 20.8, 18.5, 14.5. – MS (FAB, NBA): *m/z* = 667.5 [M + H]<sup>+</sup>, calcd. for C<sub>41</sub>H<sub>19</sub>D<sub>24</sub>N<sub>2</sub>O<sub>5</sub>: 667.9. – IR (KBr):  $\tilde{\nu}$  = 2272, 2227, 2148, 2118, 2070 (C–D), 1587 (C=O) cm<sup>-1</sup>. – C<sub>41</sub>H<sub>18</sub>D<sub>24</sub>N<sub>2</sub>O<sub>5</sub> (666.9): calcd. C 73.83, H 6.35, N 4.20, found C 73.43, H 6.12, N 4.57.

**Compound 4a:** This compound was synthesized in the same way as **4**, but non-deuterated reagents were used. Yield: 0.17 g, 62%, m.p. 99–101 °C. – <sup>1</sup>H NMR (CD<sub>3</sub>OD):  $\delta$  = 7.50–7.40 (m, 10 H, ArH<sup>benzoyl</sup>) 7.18–6.92 (m, 6 H, ArH), 4.72 (s, 4 H, ArCH<sub>2</sub>N), 3.46–3.40 (m, 4 H, NCH<sub>2</sub>CH<sub>3</sub>), 2.37–2.33 (m, 9 H, ArCH<sub>3</sub>), 1.40–1.36 (m, 6 H, NCH<sub>2</sub>CH<sub>3</sub>). – <sup>13</sup>C NMR (CD<sub>3</sub>OD):  $\delta$  = 172.9, 172.3, 167.9, 149.6, 149.3, 148.0, 135.9, 135.2, 131.2–125.6, 123.5, 122.8, 43.2, 42.8, 39.4, 18.8, 12.0, 10.7. – MS (FAB, NBA): *m/z* = 643.3 [M + H]<sup>+</sup>, calcd. for C<sub>41</sub>H<sub>43</sub>N<sub>2</sub>O<sub>5</sub> 643.8. – C<sub>41</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub>

(642.8): calcd. C 76.61, H 6.59, N 4.36, found C 76.38, H 6.54, N 4.60.

**Compound 5:** A mixture of bis(amide) **4** (0.36 g, 0.54 mmol), methyl [D<sub>2</sub>]bromoacetate (0.16 mL, 1.7 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.3 g, 2.2 mmol) in 50 mL of acetonitrile was refluxed for 3 h. After the mixture had cooled down, the salts were removed by filtration and the acetonitrile was removed under vacuum. After addition of 100 mL of dichloromethane, the mixture was washed twice with 1 N HCl, followed by washing with water. The organic layer was dried with MgSO<sub>4</sub>, filtered to remove the salts, and concentrated to dryness. The crude product was purified by column chromatography using ethyl acetate/hexane (1:1) as the eluent. Yield: 0.37 g, 78%, m.p. 58–61 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.20–7.15 (m, 2 H, ArH), 7.15–7.10 (m, 4 H, ArH), 3.70–3.65 (m, 3 H, OMe), 3.63–3.58 (m, 3 H, OMe), 3.42–3.38 (m, 3 H, OMe), 2.39 (s, 9 H, ArCH<sub>3</sub>). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 171.8, 169.0, 168.6, 152.2, 151.3, 136.5–125.5, 68.5 (m), 51.5, 51.1, 42.3–39.0 (m), 20.8, 20.5. – MS (FAB, NBA): *m/z* = 889.3 [M + H]<sup>+</sup>, calcd. for C<sub>50</sub>H<sub>25</sub>D<sub>30</sub>N<sub>2</sub>O<sub>11</sub>: 889.6. – IR (KBr):  $\tilde{\nu}$  = 2270, 2226, 2149, 2116, 2100, 2072 (C–D), 1761 (C=O<sub>ester</sub>), 1630 (C=O<sub>amide</sub>) cm<sup>-1</sup>.

**Compound 5a:** This product was synthesized analogously to **5**, with the exception that undeuterated methyl bromoacetate was used. Yield: 0.22 g, 81%, m.p. 57–59 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.56–7.40 (m, 8 H, ArH<sup>benzoyl</sup>), 7.40–7.35 (m, 2 H, ArH<sup>benzoyl</sup>), 7.20–7.15 (m, 2 H, ArH<sup>o</sup>), 7.14–7.04 (m, 4 H, ArH<sup>o</sup>), 4.98 (s, 2 H, ArCH<sub>2</sub>N), 4.84 (s, 2 H, ArCH<sub>2</sub>N), 4.28 (s, 2 H, OCH<sub>2</sub>CO<sub>2</sub>), 4.18 (s, 2 H, OCH<sub>2</sub>CO<sub>2</sub>), 4.03 (s, 2 H, OCH<sub>2</sub>CO<sub>2</sub>), 3.67 (s, 3 H, OCH<sub>3</sub>), 3.56 (s, 3 H, OCH<sub>3</sub>), 3.48 (s, 3 H, OCH<sub>3</sub>), 3.42–3.38 (m, 2 H, NCH<sub>2</sub>CH<sub>3</sub>), 3.34–3.30 (m, 2 H, NCH<sub>2</sub>CH<sub>3</sub>), 2.40–2.36 (m, 9 H, ArCH<sub>3</sub>), 1.32–1.30 (m, 3 H, NCH<sub>2</sub>CH<sub>3</sub>), 1.20–1.16 (m, 3 H, NCH<sub>2</sub>CH<sub>3</sub>). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 171.8, 169.0, 168.6, 152.2, 151.3, 136.5–125.5, 69.5, 68.5, 68.0, 51.5, 51.1, 46.8, 42.5, 41.7, 40.0, 20.8, 20.5, 13.8, 12.0. – MS (FAB, NBA): *m/z* = 859.3 [M + H]<sup>+</sup>, calcd. for C<sub>50</sub>H<sub>55</sub>N<sub>2</sub>O<sub>11</sub>: 859.4. – IR (KBr):  $\tilde{\nu}$  = 1762 (C=O<sub>ester</sub>), 1632 (C=O<sub>amide</sub>) cm<sup>-1</sup>. – C<sub>50</sub>H<sub>55</sub>N<sub>2</sub>O<sub>11</sub> (860.0): calcd. C 69.91, H 6.34, N 3.26, found C 69.52, H 6.14, N 3.12.

**Compound 1·H<sub>3</sub>:** Trimethyl ester **5** (0.20 g, 0.23 mmol) was refluxed for 1 h with K<sub>2</sub>CO<sub>3</sub> (0.12 g, 0.90 mmol) in 50 mL of a mixture of D<sub>2</sub>O and MeOD. After this had cooled to room temperature, 100 mL of dichloromethane and 100 mL of 1 N HCl solution were added. The organic layer was separated and washed twice with 100 mL of 1 N HCl and once with 100 mL of water, and dried with MgSO<sub>4</sub>, filtered, and concentrated to dryness. Yield: 0.18 g, 96%, m.p. 121–123 °C. – <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ = 7.18–7.09 (m, 2 H, ArH), 7.08–7.02 (m, 2 H, ArH), 6.98–6.92 (m, 2 H, ArH), 2.22 (s, 9 H, ArCH<sub>3</sub>). – <sup>13</sup>C NMR (CD<sub>3</sub>OD): δ = 174.3, 172.8, 153.5, 152.0, 137.5–127.1, 69.8 (m), 30.7, 30.4, 28.4, 23.7, 20.9, 20.8, 14.4. – MS (FAB, NBA): *m/z* = 869.9 [M + Na]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>18</sub>D<sub>30</sub>N<sub>2</sub>NaO<sub>11</sub> 869.5]. – IR (KBr):  $\tilde{\nu}$  = 2228, 2149, 2098 (C–D), 1749 (C=O<sub>acid</sub>), 1627 (C=O<sub>amide</sub>) cm<sup>-1</sup>.

**Compound 1a·H<sub>3</sub>:** The hydrolysis was carried out in the same way as for 1·H<sub>3</sub>, with the exception that undeuterated solvents were used. Yield: 0.15 g, 97%, m.p. 120–123 °C. <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ = 7.43 (s, 6 H, ArH), 7.40 (s, 4 H, ArH), 7.20 (s, 2 H, ArH), 7.17 (s, 2 H, ArH), 7.05 (s, 2 H, ArH), 4.95 (s, 2 H, ArH<sub>2</sub>N), 4.68 (s, 2 H, ArCH<sub>2</sub>N), 4.22 (s, 2 H, OCH<sub>2</sub>CO<sub>2</sub>), 4.10 (s, 2 H, OCH<sub>2</sub>CO<sub>2</sub>), 3.93 (s, 2 H, OCH<sub>2</sub>CO<sub>2</sub>), 3.62–3.57 (m, 2 H, NCH<sub>2</sub>CH<sub>3</sub>), 3.25–3.20 (m, 2 H, NCH<sub>2</sub>CH<sub>3</sub>), 2.38 (s, 9 H, ArCH<sub>3</sub>), 1.25–1.20 (m, 3 H, NCH<sub>2</sub>CH<sub>3</sub>), 1.06–1.02 (m, 3 H, NCH<sub>2</sub>CH<sub>3</sub>). – <sup>13</sup>C NMR (CD<sub>3</sub>OD): δ = 172.4, 170.4, 151.7, 137.8–125.4, 68.8, 68.5, 68.4, 42.8, 41.0, 39.8, 19.0, 12.1, 10.7. – MS (FAB, NBA): *m/z* = 839.4

[M + Na]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>48</sub>N<sub>2</sub>NaO<sub>11</sub> 839.3. – IR (KBr):  $\tilde{\nu}$  = 1756 (C=O<sub>acid</sub>), 1633 (C=O<sub>amide</sub>) cm<sup>-1</sup>. – C<sub>47</sub>H<sub>48</sub>N<sub>2</sub>O<sub>11</sub>·H<sub>2</sub>O (834.9): calcd. C 67.61, H 6.04, N 3.36, found C 67.74, H 5.97, N 3.40.

**Procedure for the Preparation of the Lanthanide Complexes (1·Ln<sup>3+</sup> and 1a·Ln<sup>3+</sup>):** A solution of Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (1.3 equiv.), where x = 5 or 6 depending on the lanthanide ion, was added to a solution (0.02 M) of ligand (1·H<sub>3</sub> and 1a·H<sub>3</sub>) in methanol with 4 equiv. of Et<sub>3</sub>N. After 1 h, the methanol was removed under vacuum and the residue was dissolved in chloroform and washed three times with water. The organic solutions were dried with MgSO<sub>4</sub> and filtered, and the solvents were removed.<sup>[25]</sup>

**1·Nd<sup>3+</sup>:** M.p. > 300 °C (decomp.). – MS (FAB, MB): *m/z* = 988.3 [M + H]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>15</sub>D<sub>30</sub>N<sub>2</sub>NdO<sub>11</sub> 988.3. – IR (KBr):  $\tilde{\nu}$  = 2270, 2227, 2118, 2072 (C–D), 1622 (C=O<sub>amide</sub>), 1599 (C=O<sub>carboxylate</sub>) cm<sup>-1</sup>.

**1·Er<sup>3+</sup>:** M.p. > 300 °C (decomp.). – MS (FAB, MB): *m/z* = 1012.5 [M + H]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>15</sub>D<sub>30</sub>ErN<sub>2</sub>O<sub>11</sub>: 1011.3. – IR (KBr):  $\tilde{\nu}$  = 2270, 2228, 2104, 2072 (C–D), 1634 (C=O<sub>amide</sub>), 1594 (C=O<sub>carboxylate</sub>) cm<sup>-1</sup>.

**1·Yb<sup>3+</sup>:** M.p. > 300 °C (decomp.). – MS (FAB, MB): *m/z* = 1018.5 [M + H]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>15</sub>D<sub>30</sub>N<sub>2</sub>O<sub>11</sub>Yb: 1017.4. – IR (KBr):  $\tilde{\nu}$  = 2229, 2155, 2109 (C–D), 1635 (C=O<sub>amide</sub>), 1600 (C=O<sub>carboxylate</sub>) cm<sup>-1</sup>.

**1a·Nd<sup>3+</sup>:** M.p. > 300 °C (decomp.). – MS (FAB, MB): *m/z* = 958.2 [M + H]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>45</sub>N<sub>2</sub>NdO<sub>11</sub>: 958.1. – IR (KBr):  $\tilde{\nu}$  = 1628 (C=O<sub>amide</sub>), 1598 (C=O<sub>carboxylate</sub>) cm<sup>-1</sup>.

**1a·Er<sup>3+</sup>:** M.p. > 300 °C (decomp.). – MS (FAB, MB): *m/z* = 981.2 [M + H]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>45</sub>ErN<sub>2</sub>O<sub>11</sub>: 981.1. – IR (KBr):  $\tilde{\nu}$  = 1630 (C=O<sub>amide</sub>), 1600 (C=O<sub>carboxylate</sub>) cm<sup>-1</sup>.

**1a·Yb<sup>3+</sup>:** M.p. > 300 °C (decomp.). – MS (FAB, MB): *m/z* = 987.5 [M + H]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>45</sub>N<sub>2</sub>O<sub>11</sub>Yb: 986.9. – IR (KBr):  $\tilde{\nu}$  = 1629 (C=O<sub>amide</sub>), 1601 (C=O<sub>carboxylate</sub>) cm<sup>-1</sup>.

**Photophysics :** NIR emission and excitation spectra were recorded with a Photon Technology International (PTI) Alphascan spectrofluorimeter. Emitted light was collected by a North Coast liquid nitrogen cooled germanium detector under an angle of 90° with optically chopped (40 Hz) excitation light. Lifetime measurements in the NIR were performed with an Edinburgh Analytical Instruments LP900 system, by excitation of the samples with a pulsed nitrogen laser operating at 337 nm. Decay curves were measured by collecting the emitted light with a liquid nitrogen cooled Ge detector by a single-photon counting technique. Deconvolution of the curves was performed using the response of the instrument to a fast dye (IR 140 in methanol, fluorescence lifetime below 1 ns, much shorter than the instrument response). Deconvolution and fitting was performed with commercial software, installed on the instrument computer system (Edinburgh Instruments).

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- [25] No reliable elemental analyses could be obtained from the lanthanide ion complexes. This was already mentioned in ref.<sup>[7b]</sup>

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