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Article

Eu(III) and Tb(III) Luminescence Sensitized by Thiophenyl-Derivatized Nitrobenzoato Antennas

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Thiophenyl-derivatized nitrobenzoic acid ligands have been evaluated as possible sensitizers of Eu(III) and Tb(III) luminescence. The resulting solution and solid-state species were isolated and characterized by luminescence spectroscopy and X-ray crystallography. The Eu(III) complex with 2-nitro-3-thiophen-3-yl-benzoic acid, **1**, crystallizes in the monoclinic space group $C2/c$ with $a = 28.569(3)$ Å, $b = 17.7726(18)$ Å, $c = 17.7073(18)$ Å, $\beta = 126.849(2)°$, and $V = 7194.6(13)$ Å^3. The Tb(III) complex with this ligand, **2**, is isostructural, and its cell parameters are $a = 29.755(6)$ Å, $b = 18.123(4)$ Å, $c = 19.519(4)$ Å, $\beta = 130.35(3)°$, and $V = 8021(3)$ Å^3. Eu(III) crystallizes with 3-nitro-2-thiophen-3-yl-benzoic acid as a triclinic complex, **3**, in the space group $P\bar{1}$ with $a = 11.045(2)$ Å, $b = 12.547(3)$ Å, $c = 15.500(3)$ Å, $\alpha = 109.06(3)°$, $\beta = 94.79(3)°$, $\gamma = 107.72(3)°$. and $V = 1893.5(7)$ Å^3. With the ligand 5-nitro-2-thiophen-3-yl-benzoic acid, Eu(III) yields another molecular compound, **4**, triclinic $P\bar{1}$, with $a = 10.649(2)$ Å, $b = 14.009(3)$ Å, $c = 15.205(3)$ Å, $\alpha = 112.15(3)°$, $\beta = 100.25(3)°$, $\gamma = 106.96(3)°$, and $V = 1900.5(7)$ Å^3. All compounds dissolve in water and methanol, and the methanolic solutions are luminescent. The solution species have a metal ion-to-ligand ratio of 1:1. The quantum yields have been determined to be in the range of 0.9–3.1% for Eu(III) and 4.7–9.8% for Tb(III). The highest values of these correspond to the most intense luminescence reported for Ln(III) solutions with this type of sensitizer. The lifetimes of luminescence are in the range of 248.3–338.9 μs for Eu(III) and 208.6–724.9 μs for Tb(III). The stability constants are in the range of log $\beta_{11} = 2.73$–4.30 for Eu(III) and 3.34–4.18 for Tb(III) and, along with the energy migration pathways, are responsible for the reported efficiency of sensitization.

Introduction

The f−f transitions in lanthanide, Ln, ions lead to interesting light-emission properties. These ions have therefore been widely studied for applications such as biomedical imaging, fluoroimmunoassays, and liquid-crystalline displays.[1] However, since the f−f transitions are forbidden by spin and parity selection rules, the emission occurs through sensitization with coordinated ligands, which function as antennas.[1] The variety of ligands developed for this purpose ranges from simple aromatic acids (e.g. dipicolinic acid, recently suggested as a ligand of choice for Ln complex emission standards)[2] to more complicated multidentate ligand architectures capable of selectively binding different Ln ions.[3] Recently we developed an interest in synthesizing complexes of Ln ions as potential precursors for emitting layers in polymer-based light-emitting diodes.[4,5] While we are focusing on small aromatic acids as coordinating groups, the presence of thiophene in the ligands enables their electrodeposition and subsequent Ln complexation into the polymer film or incorporation of the metal complexes into polymer substrates.[6] Complexes of 2-nitro-4-thiophen-3-yl-benzoic acid with Eu(III) and Tb(III) were recently reported as part of this group of ligands.[5] They are luminescent both in the solid state and in ethanol solution, and therefore, they are the first examples of nitrobenzoic acid derivatives being utilized as antennas,[5] since *o*- and *m*-nitrobenzoic acids had been previously reported to quench Tb(III) luminescence.[7] Choppin

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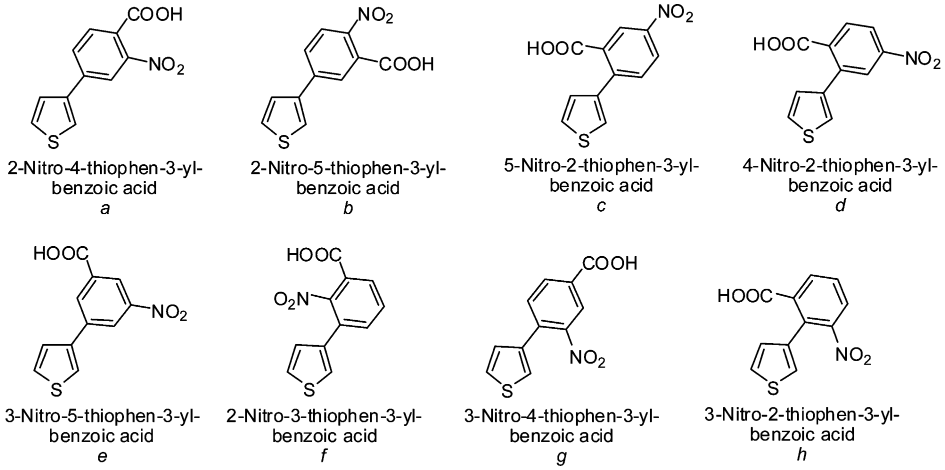

Figure 1. Ligands studied as sensitizers in this work.

and co-workers, who extensively studied the complexation of Ln(III) by small aromatic acids, including nitrobenzoic acid, reported only stability constants obtained through potentiometry and calorimetry, but no solid-state structural characterization and no luminescence.[8] Similarly, Ferenc and co-workers characterized complexes of lanthanides with nitrobenzoic acid derivatives by TGA and IR spectroscopy, but no X-ray single-crystal diffraction and no emission behavior were reported.[9−12] In fact, compared to other ligand systems, fewer carboxylato complexes have been characterized by single-crystal X-ray diffraction and solution speciation and spectroscopy, mostly because of the low inherent solubility of this type of complex and the difficulty in isolating good quality crystals.[13−20] However, because of the potential fields of application of these complexes, such studies are of interest.

Previous results suggest that derivatizing benzoic acid analogues with thiophene has a beneficial tuning effect on the triplet state of the antenna leading to a higher emission quantum yield resulting from a better match between the ligand and lanthanide ion excited states, as derivatization of isophthalic acid with thiophene leads to an average lowering of the triplet state energy by 5000 cm^{-1}.[4] The photophysical characterization of the solutions shows the effect of the presence of the thiophene-derivatization in the antenna on the emission behavior of the coordinated lanthanides. We report here complete solid-state characterization and solution photophysics of several new complexes of lanthanide ions with thiophene-derivatized nitrobenzoic acids.

Results and Discussion

Synthesis. The sensitizers used in this work are displayed in Figure 1. The syntheses of some of these ligands were recently reported.[6] The new ligands studied here, 5-nitro-2-thiophen-3-yl-benzoic acid *c*, 4-nitro-2-thiophen-3-yl-benzoic acid *d*, 3-nitro-5-thiophen-3-yl-benzoic acid *e*, and 2-nitro-3-thiophen-3-yl-benzoic acid *f*, were synthesized by a similar procedure, described in the Experimental Section.

All metal complexes were isolated through solvent evaporation from solutions containing the metal ion as the chloride salt and ligand as the free acid, after adjustment of the pH in the range of 5−6 to ensure complete deprotonation of the carboxylate moiety. X-ray quality crystals usually formed within a week to one month. Details of the syntheses and isolation of the products are given in the Experimental Section.

Crystallographic Characterization. Compounds **1** and **2**, the Eu(III) and Tb(III) complexes with *f*, respectively, are isostructural and crystallize in the monoclinic space group $C2/c$. The coordination environment of Eu(III) in **1** with atom labeling scheme is shown in Figure 2, while a complete molecule of isostructural **2** is shown in Figure 3a. The coordination environment of the Tb(III) atoms and the bridging carboxylates are shown in Figure 3b, along with the atom labeling scheme. Compounds **3** (Figure S1 in Supporting Information) and **4** (Figure S2 in Supporting Information) correspond to Eu(III) complexes with *h* and *c*, respectively, and crystallize in the triclinic $P\bar{1}$ space group. Complete bond lengths and angles for all four complexes can be found in the Supporting Information.

All four compounds in this paper have the same basic building block, which is analogous to the previously

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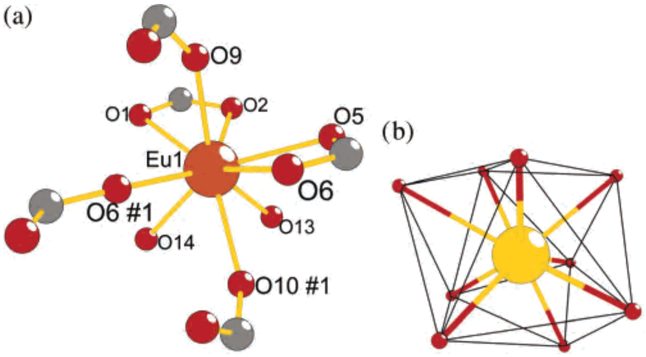

Figure 2. (a) Coordination environment around Eu(III) in **1** with atom-labeling scheme and (b) coordination polyhedron. O9 and O10#1 are oxygen atoms the of bridging moiety and O5 and O6 are the oxygen atoms of the triply coordinated carboxylate moiety, with O6 connecting to two Eu(III) ions. O13 and O14 are water molecules.

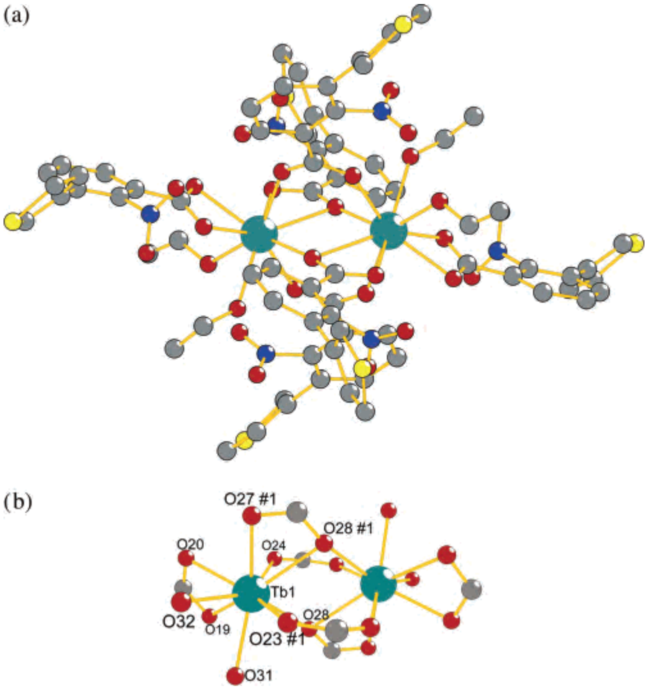

Figure 3. (a) Ball and stick representation of **2** and (b) coordination environment of the Tb(III) ions in this complex with partial atom-labeling scheme. All hydrogen atoms and disordered thiophene moieties were omitted for clarity. O31 and O32 are methanol molecules.

described complexes of Eu(III) and Tb(III) with ligand *a*.[5] The common structure is homobimetallic with six ligands in the molecule. Four of these ligands connect the two metal ions. Two of the ligands have a μ-COO$^-$-bridging moiety, and the other two are triply coordinate. The triply coordinated fashion corresponds to a carboxylato moiety showing bidentate coordination to one metal ion. The fourth ligand coordinates only to one metal ion in a bidentate fashion. The coordination number of nine around each metal ion is completed by two solvent molecules in the coordination sphere. The main differences between the complexes are in the form of different torsion angles, Ln−O bond lengths, metal ion−metal ion distances, and coordination polyhedra around the metal ion. Just as Ferenc had previously deduced on the basis of IR spectra[10] and our group confirmed by X-ray single-crystal diffraction for other nitrobenzoic acid analogues,[5,21,22] coordination of the nitro group to the Ln(III) ions is not observed, although it has been reported in the case of nitrophenolate[23,24] and picrate[25−28] complexes of Ln(III).

The torsion angles (Table 1) range from almost flat, such as 1° for the angle between COO$^-$ and the phenyl ring for a bidentate carboxylate in the complex of Eu(III) and Tb(III) with *a*,[5] to angles as large as 110°, again for COO$^-$ in triply coordinated ligands in the same complexes and in complex **3**. These data indicate that sterics more than electronics dictate the torsion angles of functional groups on the phenyl ring. A functional group in the para position is almost coplanar with the phenyl ring, as shown by torsion angles between 7 and 10° for the thiophenyl moiety in the complexes with ligand *a*. Those in ortho and meta positions will adopt a torsion angle that is roughly dictated by the magnitude of the torsion angle shown between the coordinating carboxylato moiety and the phenyl ring. For example in compounds **1** and **2**, the carboxylate moiety is relatively flat with the phenyl ring, regardless of the type of coordination to the metal ion. The ortho moiety, NO$_2$, on the other hand, is forced to display larger torsion angles.

Metal ion−oxygen bond distances and metal ion−metal ion nonbonding distances show interesting similarities within the compound series described here and when compared to related compounds.[4,5,21,22] These bond lengths are compared in Table 2 as a function of the type of coordination between the metal ions. The types of coordination are shown in Figure 4 for clarity. The Eu−O bond lengths are in the range of 2.330−2.660 Å and the Tb−O bond lengths are in the range of 2.320−2.658 Å, within the expected range for this type of complex.[29] In molecules with the B and D coordination mode, the shortest and longest Ln−O distances correspond to the oxygen atoms which are coordinated in a bridging-bidentate or bridging fashion between the two metal ions. Exceptions are entries e and f, for which the shortest distances are seen for the solvent molecules. Compounds with the coordination modes A and C have the longest Ln−O bonds to the bidentate ligands, while the shortest involve again the bridging ligands.

Molecules with the coordination modes B and D have the shortest metal−metal distances in this family of compounds, in the range of 3.98−5.05 Å for Eu(III) complexes and 3.95−4.23 Å for Tb(III) (Table 2). The longest distances

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Table 1. Coordination Polyhedra and Torsion Angles (deg) of Functional Groups on Phenyl Ring Depending on Position Relative to COO^- and Type of Coordination for Compounds **1**−**4**

functional group	coordination	complexes			complexes with *a*[5]
		1/2	**3**	**4**	
COO^-		irregular	monocapped square antiprism	distorted tricapped trigonal prism	irregular
	bridging	19	34	30	62
	triply coordinated	26	110	54	110
	bidentate	16	25	39	1
thiophenyl		meta	ortho (to NO_2 also)	ortho	para
	bridging	46	90	40	10
	triply coordinated	49	61	41	7
	bidentate	57	75	37	10
NO_2		ortho	meta (ortho to thiophenyl)	meta	ortho
	bridging	71	73	24	21
	triply coordinated	65	109	22	17
	bidentate	79	41	9	100

Table 2. Shortest and Longest Ln−O Bond Lengths and Types and Ln−Ln Distances

			Eu−O (Å)		Tb−O (Å)		oxygen atom involved/ type of bonding		Ln−Ln (Å)	
entry	complex	bridging	short	long	short	long	short	long	Eu−Eu	Tb−Tb
a	**1**	D	2.330	2.660			bridging	triple	3.9808	
b	**2**	D			2.320	2.658	triple	triple		3.9537
c	**3**	D	2.352	2.604			bridging	triple	4.0677	
d	**4**	D	2.359	2.655			triple	triple	4.023	
e	*d*[5]	D	2.363	2.568			solvent	triple	4.0059	
f					2.339	2.540	solvent	triple		3.9655
g	2-chloro-5-nitrobenzoate[22]	A	2.317	2.524			bridging	bidentate	4.6167	
h	2-nitrobenzoate[21]	C	2.282	2.524			bridging	bidentate	4.3507	
h		D	2.377	2.573			bridging	triple	3.9428	
j	3-nitrobenzoate[21]	A	2.307	2.541			bridging	bidentate	5.0468	
k	4-nitrobenzoate[21]	B	2.317	2.719			bridging	triple	4.1756	
l		B			2.283	2.893	bridging	triple		4.2334

are seen in coordination polymers with coordination mode A, entries g and j. Comparison of the Ln−Ln distances with similar structures found in the CSD[29] shows that, while short, they are within the expected ranges of 3.65−5.14 Å for Eu and 3.78−4.53 Å for Tb-containing molecules.

Similar trends in bond lengths and intermetallic distances were observed by Urland and Rohde, who isolated dimeric Gd(III) complexes of trichloroacetic acid displaying antiferromagnetic interactions. The authors observed that the type of coordination mode has a strong influence on the magnetic behavior of this type of compounds.[30]

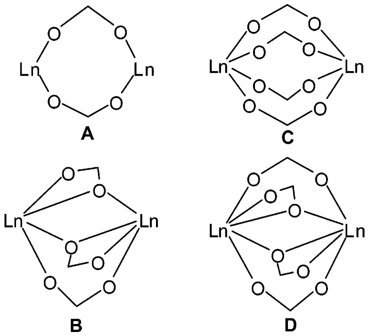

Figure 4. Different types of metallic bridging observed in carboxylato-based complexes of Ln(III). A has two bridging carboxylates between metal ions; B has one bridging and two bridging-bidentate carboxylates between metal ions. C has four bridging carboxylates per metal ion, and D has two bridging and two bridging-bidentate carboxylates between metal ions. Each metal ion has one additional bidentate carboxylate ligand coordinated along with solvent molecules and, in the case of coordination polymers A and B, ligands bridging the adjacent metal ions.

pK_a of Ligands and Stability Constants. Since sensitized red or green luminescence is observed in methanol, the photophysical characterization was undertaken in this solvent. However, given that the determination of the pK_a and stability constants by potentiometry is not possible in methanol, because of the nonlinearity of the pH electrode, 90% methanol/10% water (v/v) at constant ionic strength $I = 0.1$ M (KCl) was utilized for the determination of these data, even though the Ln-containing solutions are only mildly luminescent in this solvent. Potentiometric measurements are possible in this solvent mixture and have been demonstrated for pharmaceutically relevant molecules.[31−35] Details of the experimental procedures are described in the Experimental Section, and the data collected are summarized in Table 3.

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Table 3. pK_a Values of Ligands and Stability Constants for 1:1 Metal Ion-to-Ligand Solutions

ligands	log β Eu[a]	log β Eu[b]	log β Eu[c]	log β Tb[c]	pK_a[c]	av log β Eu[e]
2-nitrobenzoate[21]	2.80	3.29	3.14	3.21	4.82	3.22
a	2.10 ± 0.09	3.51 ± 0.16	3.81 ± 0.02	4.18 ± 0.09	5.35 ± 0.04	3.66 ± 0.15
b	2.25 ± 0.01	3.12 ± 0.03	3.73 ± 0.02	3.55 ± 0.02	5.04 ± 0.01	3.43 ± 0.31
f	2.43 ± 0.03	2.57 ± 0.09	3.19 ± 0.10	3.07 ± 0.03	5.00 ± 0.01	2.88 ± 0.31
3-nitrobenzoate[21]	2.00	4.55	4.19	4.30	5.66	4.37
c	2.71 ± 0.04	3.75 ± 0.07	3.75 ± 0.04	3.81 ± 0.02	5.48 ± 0.05	3.75 ± 0.00
e	n.d.[d]	n.d.[d]	4.30 ± 0.06	4.02 ± 0.02	4.57 ± 0.02	4.30 ± 0.06
g	2.13 ± 0.09	3.45 ± 0.08	3.95 ± 0.01	3.84 ± 0.01	5.78 ± 0.01	3.70 ± 0.25
d	2.29 ± 0.09	3.23 ± 0.10	3.59 ± 0.08	3.34 ± 0.02	4.09 ± 0.01	3.41 ± 0.18
4-nitrobenzoate[21]	2.36	precipitate	3.71	4.10	5.77	3.71
h	2.51 ± 0.11	3.44 ± 0.09	3.48 ± 0.03	3.37 ± 0.02	5.34 ± 0.02	3.46 ± 0.02

[a] Measured by NMR in 99.5% CD_3OD. [b] Measured by NMR in 90% CD_3OD/10% D_2O. [c] Measured by potentiometry in 90% MeOH/10% H_2O. [d] Not determined. [e] Average of columns 2 and 3.

Job plots (Figure S4 in the Supporting Information) for all compounds indicated that the main species in solution correspond to a 1:1 metal-to-ligand stoichiometry. Potentiometric titration was also consistent with the 1:1 species and allowed determination of the stability constant, log β, defined by the equation

$$p\mathrm{Ln}^{3+} + q\mathrm{H}^{+} + r\mathrm{L}^{-} \leftrightarrow [\mathrm{Ln}_p\mathrm{H}_q\mathrm{L}_r]^{(3p+q-r)+}$$

$$\beta_{101} = \frac{[\mathrm{LnL}^{2+}]}{[\mathrm{Ln}^{3+}][\mathrm{L}^{-}]}$$

The 1:1 stoichiometry is in agreement with the previously reported speciation for thiophenyl-derivatized 2-nitrobenzoic acid, *o*-, *m*-, and *p*-nitrobenzoic acid, and 2-chloro-5-nitrobenzoic acid with Eu(III) and Tb(III).[5,8,21,22] The remaining coordination sites of the lanthanide ion are therefore filled by solvent molecules, as discussed below.

We successfully confirmed the data obtained by potentiometry with NMR spectroscopy in 90% MeOD/10% D_2O (v/v) as a second technique. We then used NMR spectroscopy to determine stability constants for Eu(III)-containing solutions in 99.5% MeOD because methanol is the solvent used in the photophysical characterization. Sample spectra of an NMR titration are shown in Figure S3; the stability constants are summarized in Table 3, and titration data are summarized in Tables 5−17 in the Supporting Information.

The stability constants for the Eu(III) species were determined to be in the range of 3.19−4.30 by potentiometry and 2.57−3.75 by NMR. For Tb(III), the stability constants determined by potentiometry range from 3.07−4.18. While log β values are often expected to vary linearly with the pK_a, this is not always true in the presence of steric effects,[8] and such a trend is not observed here for many of the thiophene-derivatized ligands. However, when the values for the derivatized ligand are compared with those for the parent nitrobenzoic acid,[21] some trends in ligand pK_a and stability constants are observed. Derivatizing *o*-, *m*-, and *p*-nitrobenzoic acid with thiophene leads to the expected linear variation of the averaged log β with the pK_a, with the exception of the sterically encumbered ligand *f* and of ligand *g*. While not attempted here, but surely worthy of further investigation, the observed discrepancies in the expected trend might be explained with steric[8] or solvent-related effects.[36] It is also noteworthy that the stability constants obtained by NMR are smaller than the values obtained by potentiometry by about 10%. Bünzli and co-workers observed a similar discrepancy while studying the speciation of triple helical complexes of Ln ions. Their spectrophotometric titration allowed explanation of this difference with the existence of outer-sphere complexes.[37] However, we cannot use UV−vis spectroscopy, because of solubility issues, and our data can neither confirm nor deny the existence of such species. We have also observed that the stability constants in methanol are smaller by about 30% than the ones in 90% methanol/10% water both for these systems, as well as those for the not-derivatized *o*-, *m*-, and *p*-benzoic acids.[21] While further studies have not been performed, this is an indication that methanol competes more successfully than the ligands for coordination with the metal ion.

Table 4. Absorption, Excitation, and Emission Maxima for 1:1 Ligand-to-Metal Solutions

		Eu(III)		Tb(III)	
ligands	λ_{max} (nm)	λ_{exc} (nm)	λ_{em} (nm)	λ_{exc} (nm)	λ_{em} (nm)
f	207	268	619.5	218	547
a	269	320	619.5	222	547
b	333	265	619	235	545
h	245	270	619	240	548
g	254	305	618	220	547
e	262	288	617.5	247	547.5
c	323	274	619	217	547
d	332	286	619	232	547

[L]=[Ln(III)]=1.2×10^{-4} M ($I = 0.1$ M Et_4NCl).

Photophysical Characterization of the 1:1 Metal Ion/Ligand Solutions. All eight ligands sensitize the emission of Eu(III) and Tb(III) in the solid state, as evidenced by the emission from the crystals isolated for X-ray diffraction. However, because of the difficulty in isolating large amounts of these complexes in high purity for photophysical characterization in the solid state, only solution characterization in methanol with 1:1 ligand-to-metal ion ratios was undertaken. Experimental details of the photophysical characterization are summarized in the Experimental Section. The ligands' absorption maxima, excitation wavelengths, and emission maxima in solution (Table 4) are within the

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Table 5. Photophysical Data of 1:1 Metal Ion-to-ligand Solutions

	Φ (%)[b]		τ_{MeOH} (μs)		τ_{MeOD} (ms)		n[d]			
ligands (% complex)[a]	Eu[c]	Tb	Eu	Tb	Eu	Tb	Eu	Tb	$E(^1S)$ (cm^{-1})[e]	$E(^3T)$ (cm^{-1})[e,f]
a (37.5 ± 1.5)	1.4 (3.6)	8.2	328.2	208.6	1.558	0.251	4.6	6.8	31 820	21 680
f (43.4 ± 2.9)	1.7 (3.9)	7.9	300.1	344.9	1.197	0.445	5.2	5.5	33 130	22 600
b (40.4 ± 2.1)	1.4 (3.6)	9.8	338.9	610.2	1.904	1.027	5.1	5.6	32 570	20 110
g (41.5 ± 2.7)	2.3 (5.6)	weak	283.6	weak	1.119	weak	5.5		32 910	25 760
e	weak	weak	308.3	weak	1.591	weak	5.5		32 930	26 080
h (62.9 ± 1.9)	3.1 (5.0)	weak	248.3	weak	0.855	weak	6.0		33 450	23 600
d (52.3 ± 2.5)	1.6 (2.6)	4.7	267.2	724.9	1.486	1.584	6.5	6.3	32 220	not observed
c (77.2 ± 1.1)	0.9 (1.2)	weak	335.4	weak	1.475	weak	4.8		33 090	19 770

[a] Determined from NMR titration data. [b] Measured according to Bünzli.[40] [c] Quantum yield in parentheses corrected for percentage of complex in solution.[39] [d] Measured according to Horrocks.[38] [e] The 0−0 transitions were obtained through vibrational deconvolution of the emission bands. [f] Determined by phosphorescence at 77 K.[41]

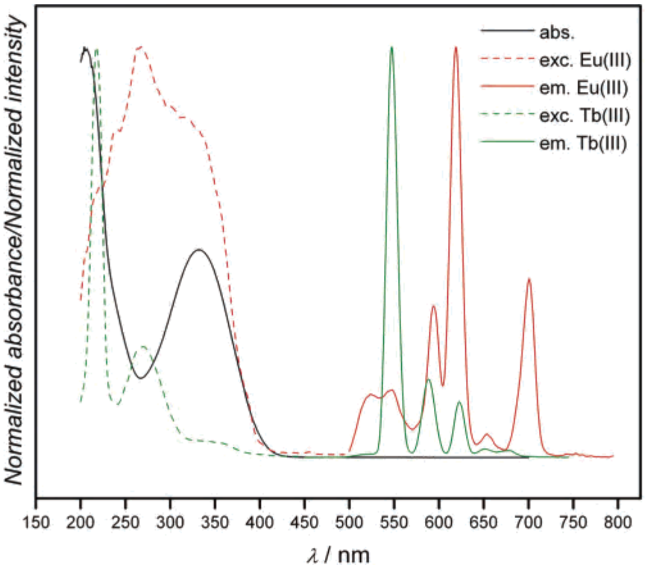

Figure 5. Absorption (black solid line), excitation (dotted lines) and emission spectra (solid lines) of Eu(III) (red) and Tb(III) (green) solutions with *b*. Cutoff filters were set at 430 nm for Tb(III) and 515 nm for Eu(III), to partially remove the ligand fluorescence from the displayed spectra. Peak assignments for Eu(III) at 594, 619, 654, and 701 nm are $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$, respectively, and for Tb(III), at 548, 589, and 623 nm, they are $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$, respectively.

Table 6. Determination of Intrinsic Quantum Yield of Luminescence of Eu^{3+}

ligand	Φ (%)	τ (μs)	τ_0 (ms)	$I_{\mathrm{tot}}/I_{\mathrm{MD}}$	$\Phi_{\mathrm{Eu3+}}$ (%)	Φ_{sens}
a	1.4	328.2	1.7474	15.4951	57.3	0.0
f	1.7	300.1	1.4939	18.1246	44.8	0.0
b	1.4	338.9	2.3536	11.5090	79.7	0.0
g	2.3	283.6	2.2325	12.1281	63.3	0.0
e	weak	308.3	weak	weak	weak	weak
h	3.1	248.3	1.4993	18.0595	37.3	0.1
d	1.4	267.2	2.8222	9.5944	75.4	0.0
c	0.9	335.4	2.9186	9.2773	97.9	0.0

expected ranges for complexes of this type. Results of the photophysical characterization are summarized in Table 5.

Typical absorption, excitation and emission spectra are shown in Figure 5 for Eu(III) and Tb(III) with *b*. The absorption and excitation spectra in both cases are similar and closely follow the absorption spectra of the ligands as potassium salts, confirming the sensitized emission.

The lifetimes of luminescence for all Eu(III)-containing solutions are between 248 and 338 μs, whereas with Tb(III) solutions, a broader range is seen, between 208 and 725 μs. In deuterated methanol, as expected, the lifetimes of the excited states of Eu(III) and Tb(III) increase up to a 3-fold. By utilizing the equation formalized by Horrocks and coworkers,[38] we can estimate the approximate number of methanol molecules coordinated to the metal ion in solution. We find that the slightly larger Eu(III) accommodates between 4.6 and 6.5 methanol molecules in its coordination sphere, while the slightly smaller Tb(III), depending on the ligand, has 5.5−6.8 methanol molecules coordinated, depending on the ligand.

The quantum yields of luminescence for the red-emitting solutions are in the range of 0.9−3.1%, while the green-emitting solutions have an emission process with efficiencies of 4.7 and 9.8%. These sensitization efficiencies are higher than what was found for previously reported nitrobenzoato ligands such as 2-chloro-5-nitrobenzoic acid[22] and non-derivatized nitrobenzoic acids,[21] and thus, the anion of *h* is the best sensitizer reported to date for Eu(III) and *b* is the best sensitizer for Tb(III) within the nitro-derivatized benzoic acid family of ligands. When the percentage of non-dissociated species in solution is accounted for in the calculation of the quantum yields of luminescence in the case of Eu(III),[39] the quantum yields are even higher, as shown in Table 5.

The triplet-state energies of the ligands, determined in Gd(III) solutions at 77 K,[41] were found to be in the range of 19 770−26 080 cm^{-1}. The singlet-state energies are in the range of 31 820−33 450 cm^{-1}. The singlet−triplet gaps are thus too large for an efficient intersystem crossing process, even for ligand *e*, which shows the smallest gap.[39,42] The triplet to excited-state gaps are in some cases conducive to a good energy transfer, as they lie within the range of 2000−5000 cm^{-1}; in some cases they are too large, decreasing thus the efficiency of the energy transfer, and in the remaining

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cases, they are too small, leading to some back transfer, which was not further quantified.[39,42]

The determination of the excited-state lifetimes, τ, of Eu(III) sensitized with each individual ligand and of the radiative lifetime, τ_0, as derived by van Veggel and co-workers,[39] allowed us to calculate the intrinsic quantum yield of emission of Eu(III), Φ_{Eu}, summarized in Table 6, using the equation

$$\Phi_{\mathrm{Eu}} = \tau/\tau_0$$

The Φ_{Eu} values are on the order of 37−98% and demonstrate that the presence of the ligands in the coordination sphere of Eu(III) increases the radiative rate with a consequent decrease of nonradiative deactivation through, for example, O−H vibrations of the coordinated methanol molecules. For the *o*-, *m*-, and *p*-nitrobenzoic acids, values between 65 and 74% were reported,[21] showing that thiophene-derivatization leads to a substantial improvement of Φ_{Eu} for ligands *b* and *c*, while *h* and *f* show a deterioration. Nonetheless, these data are comparable to the values in the range of 20−70% described by van Veggel and co-workers.[39]

The quantum yield of emission, Φ, determined experimentally, reflects the efficiency of all energy-transfer steps and, as demonstrated by the equation

$$\Phi = \Phi_{\mathrm{ISC}} \times \Phi_{\mathrm{ET}} \times \Phi_{\mathrm{Ln}} = \Phi_{\mathrm{sens}} \times \Phi_{\mathrm{Eu}}$$

is a product of Φ_{ISC}, the efficiency of the intersystem-crossing process from ligand singlet to triplet state, Φ_{ET}, the efficiency of the energy transfer from triplet state to Ln(III)-excited state, and Φ_{Eu}. We can thus define a sensitization efficiency, Φ_{sens}, as the combined efficiency of intersystem crossing and energy transfer. As seen in Table 6, the values of Φ_{sens} are zero or close to zero, reflecting the large energy gaps within the emitting species.

Conclusions

Several complexes of Eu(III) and Tb(III) with thiophene-derivatized *o*-, *m*-, and *p*-nitrobenzoic acid anions as ligands were isolated. All of the isolated compounds are molecular, in contrast with previously isolated nitrobenzoic acid complexes,[21] which are coordination polymers. Relatively short Ln−Ln distances are seen in the complexes which display a triply coordinated carboxylate as bridging-bidentate ligand. The complexes are weakly luminescent in the solid state with a metal-to-ligand ratio of 1:3. In solution, only 1:1 species form. Solution quantum yields between 0.9 and 3.1% for Eu(III)-containing and 4.7 and 9.8% for Tb(III)-containing solutions were obtained. Although moderate, they are the highest reported so far for nitrobenzoato-type ligands. Their magnitude can be explained by the small stability constants of the species in solution, as well as the unfavorable energy gaps between singlet and triplet levels of the ligand and the triplet level of the ligand and emissive excited state of the lanthanide ion. The strong electron-withdrawing effect of the nitro group and its position relative to the coordinating carboxylate moiety do not seem to influence strongly the photophysical properties of the sensitizer, as its effect is counterbalanced by the moderate electron-donating thiophene. It is interesting to note that while $-\mathrm{COO}^-$ derivatization of benzene leads to a lowering of the triplet state by approximately 2600 cm^{-1}, $-\mathrm{NO}_2$ derivatization leads to a lowering of approximately 8700 cm^{-1},[43] and thiophene derivatization leads to a lowering of approximately 5000 cm^{-1},[4] the presence of the three functional groups on benzene leads to complicated effects and lack of a good match between energy states for efficient energy transfer. However, the presence of these ligands in the coordination sphere of the Eu(III) leads to an increase of the radiative rate and thus high intrinsic quantum yields of luminescence are seen.

Experimental Section

General Information. NMR spectra were recorded on a Bruker Avance DPX 300 or a Bruker DRX-500 spectrometer. UV spectra were obtained on a Perkin-Elmer Lambda 35 spectrometer, and fluorescence spectra on a Perkin-Elmer LS-55 spectrometer. All commercially available chemicals, including the ligands (Acros), were used as received. However, the $\mathrm{LnCl_3}$ salts were dried under reduced pressure and heat and were kept in a glovebox under a controlled atmosphere ($\mathrm{O_2}$ < 2 ppm, $\mathrm{H_2O}$ < 5 ppm). Solvents were dried by standard methods. All data were collected at a constant temperature of 25.0 ± 0.1 °C.

General Procedure for the Synthesis of Thiophene-Derivatized Nitrobenzoato Ligands. Stoichiometric quantities of 3-(tributyltin)-thiophene and the halide of the ester-protected aromatic acid of choice were mixed with 1 mol % of $\mathrm{Pd(PPh_3)_4}$, and DMF was added under an inert atmosphere. The mixture was heated to 110 °C overnight. The DMF was removed under reduced pressure, and the reaction mixture was eluted with petroleum ether/ethyl acetate over silica to give the products.

3-Nitro-5-thiophen-3-yl-benzoic Acid Ethyl Ester (Ester of *b*). Yield: 75.8%. $\lambda_{\max} = 262$ nm. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS internal standard): δ 1.43 (t, 3H, $^3J = 7.2$ Hz), 4.34 (q, 2H, $^3J = 7.2$ Hz), 7.48 (dd, 2H, $^3J = 1.8$ Hz), 7.67 (dd, 1H, $^3J = 2.1$, 1.8 Hz), 8.55 (d, 1H, $^3J = 1.5$ Hz), 8.58 (dd, 1H, $^3J = 2.4$, 1.5 Hz), 8.73 (dd, 1H, $^3J = 1.5$, 2.1 Hz). ^{13}C NMR: δ 14.13, 62.07, 122.50, 122.94, 124.60, 125.86, 127.55, 132.65, 132.71, 137.79, 138.90, 148.78, 164.50.

4-Nitro-2-thiophen-3-yl-benzoic Acid Ethyl Ester (Ester of *d*). Yield: 25.6%. $\lambda_{\max} = 332$ nm.^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS internal standard): δ 1.14 (t, 3H, $^3J = 7.2$ Hz), 4.18 (q, 2H, $^3J = 7.2$ Hz), 7.12 (dd, 1H, $^3J = 1.5$, 5.1 Hz), 7.35 (dd, 1H, $^3J = 1.5$, 3.0 Hz), 7.39 (dd, 1H, $^3J = 3.0$, 5.1 Hz), 7.86 (d, 1H, $^3J = 8.4$ Hz), 8.20 (dd, 1H, $^3J = 2.1$, 8.4 Hz), 8.28 (d, 1H, $^3J = 2.4$ Hz). ^{13}C NMR: δ 14.17, 62.33, 122.29, 124.15, 125.55, 126.47, 128.33, 130.81, 137.55, 138.44, 167.78, 207.32.

5-Nitro-2-thiophen-3-yl-benzoic Acid Ethyl Ester (Ester of *c*). Yield: 46.3%. $\lambda_{\max} = 318$ nm.^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS internal standard): δ 1.16 (t, 3H, $^3J = 7.2$ Hz), 4.21 (q, 2H, $^3J = 7.2$ Hz), 7.11 (dd, 1H, $^3J = 0.9$, 1.5 Hz), 7.37 (m, 2H, $^3J = 0.9$, 2.4, 1.5, 3.6 Hz), 7.59 (d, 1H, 8.4 Hz), 8.31 (dd, 1H, $^3J = 2.1$, 8.7 Hz), 8.61 (d, 1H, $^3J = 2.4$ Hz). ^{13}C NMR: δ 14.02, 62.36, 124.50, 125.30, 125.93, 126.39, 126.91, 128.39, 131.99, 132.68, 139.67, 143.25, 169.55.

2-Nitro-3-thiophen-3-yl-benzoic Acid Ethyl Ester (Ester of *f*). Yield: 29.4%. $\lambda_{\max} = 221$ nm. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS internal standard): δ 1.31 (t, 3H, $^3J = 7.2$ Hz), 4.36 (q, 2H,

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Table 7. Crystallographic Details for Compounds **1** through **4**

	1	**2**	**3**	**4**
CCDC no.	614084	614085	614086	614087
formula	$C_{66}H_{46}Eu_2N_6O_{29}S_6$	$C_{74}H_{62.8}N_6O_{29.4}S_6Tb_2$	$C_{72}H_{54}Eu_2N_6O_{30}S_6$	$C_{72}H_{60}Eu_2N_6O_{30}S_6$
M (g/mol)	1883.36	2016.70	1979.5	1985.54
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	28.569(3)	29.755(6)	11.045(2)	10.649(2)
b (Å)	17.7726(18)	18.123(4)	12.547(3)	14.009(3)
c (Å)	17.7073(18)	19.519(4)	15.500(3)	15.205(3)
α (deg)	90	90	109.06(3)	112.15(3)
β (deg)	126.849(2)	130.35(3)	94.79(3)	100.25(3)
γ (deg)	90	90	107.72(3)	106.96(3)
V (Å^3)	7194.6(13)	8021(3)	1893.5(7)	1900.5(7)
T (K)	98(2)	97(2)	95(2)	95(2)
Z	4	4	1	1
D_c (g/cm^3)	1.739	1.670	1.736	1.735
μ(Mo Kα) (mm^{-1})	1.993	1.992	1.898	1.892
independent reflns	9590	9993	6665	7034
R_{int} [$F_o \geq 4\sigma(F_o)$]	0.00	0.0773	0.0293	0.0482
reflns collected	54 889	43 018	20 088	16 068
R_1, R_2 [$I > 2\sigma(I)$]	0.0716, 0.1248	0.0524, 0.1196	0.0403, 0.1073	0.0487, 0.1037
data/restraints/params	9590/48/481	7056/22/513	6665/12/518	7034/20/527
GOF on F^2	0.869	1.057	1.072	1.084
largest diff peak and hole (e/Å^3)	1.518 −0.841	1.918 −1.100	3.522 −1.196	1.611 −1.909

$^3J = 7.2$ Hz), 7.14 (m, 1H, $^3J = 2.4, 3.9, 6.3$ Hz), 7.40 (m, 2H, $^3J = 0.9, 3.3, 2.7$ Hz), 7.56 (dd, 1H, $^3J = 7.8$ Hz), 7.67 (dd, 1H, $^3J = 1.2, 7.8$ Hz), 8.01 ppm (d, 1H, $^3J = 7.8$ Hz). ^{13}C NMR: δ 14.20, 63.18, 123.82, 124.97, 127.05, 127.85, 130.07, 130.23, 130.46, 130.98, 134.96, 135.42, 163.57.

Synthesis of Lanthanide Ion Complexes. Europium Complex of *h* (1). A concentrated solution of 3-thiophenyl-2-nitrobenzoic acid dipotassium salt (pH adjusted to ~5−6) was added to a 90% methanol/10% water solution of $EuCl_3 \cdot 6H_2O$, keeping the metal-to-ligand ratio of 1:1. After a week, dark-brown blocks of the Eu(III) complex formed.

Terbium Complex of *h* (2). $TbCl_3 \cdot 6\,H_2O$ in ethanol was added to an ethanolic solution of the ligand adjusted to a pH of 5−6 using aqueous NaOH, keeping the metal-to-ligand ratio of 1:3. After a month, dark-brown needles grew out the concentrated solution.

Europium complex of *f* (3) and Europium complex of *b* (4). A concentrated solution of the ligand in methanol (pH adjusted to ~5−6) was added to a methanolic solution of $EuCl_3 \cdot 6H_2O$, keeping a metal-to-ligand ratio of 1:2. After approximately a week, pale-yellow blocks of the Eu(III) complexes formed.

X-ray Crystallography. Crystal data, data collection, and refinement details for all the compounds are given in Table 7. Full bond lengths and angles are given in Tables 1−4 in the Supporting Information. Suitable crystals were mounted on a glass fiber and placed into the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area-detector diffractometer equipped with a low-temperature device,[44] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were measured using ω scans of 0.3° per frame, and a full sphere of data was collected for a total of 1850 frames. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[45] software and refined using SAINTPlus[46] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus[46] software. Multiscan absorption corrections were applied using SADABS,[47] unless otherwise indicated. The structures were solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL[48] program package. All non-hydrogen atoms were refined anisotropically, with exception of the disordered water molecules of crystallization in compounds **1** and **2**, for which the oxygen atoms were left isotropic. The majority of the hydrogen atoms were added geometrically, and their parameters constrained to the parent site. For all complexes the ethanol, methanol, or water hydrogen atoms of the coordinated or disordered noncoordinated solvent molecules could not be located on the difference map and have been omitted, although the correct formulas are indicated. **1** was refined as a nonmerohedrally twinned crystal with Cell−Now and TwinAbs.[49] This resulted in more than one entry in the reflection file for a given set of *h*,*k*,*l* indices. Therefore, more reflections were used in the refinement than the apparent number of unique reflections, leading to an abnormally large completion rate and a low GOF. Large residual electron density is found close to the metal ion (~0.8−0.9 Å) and is most noticeable for structure **3**. This is an absorption artifact and could not be modeled. Disorder is seen in all structures for the thiophene rings. It could be modeled by assuming two different positions rotated by 180° along the C−C bond between phenyl and thiophene. This type of disorder is common for thiophene-bearing compounds and has been previously observed.[4−6,50] For compound **1**, three disordered thiophene rings were modeled, with partial occupancies of 79, 86, and 82% for the major components. Compound **2** was modeled with two disordered thiophene rings with partial occupancies of 54% for the major component and 46% for the minor component in both cases. Compound **3** could be modeled with only one disordered thiophene ring, with an occupancy refinement of 54% for the major component and 46% for the minor component. In compound **4**, two disordered

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(47) *SADABS: An Empirical Absorption Correction Program*, version 2.01; Bruker AXS: Madison, WI, 2001.
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thiophene rings refined to 75/25 and 86/14% occupancies for the major and minor components of each ring, respectively.

UV−vis and Luminescence Measurements. Solutions for spectroscopic studies were prepared by mixing the ligands as the potassium salt with the lanthanide chloride in methanol at constant ionic strength (0.1 M Et_4NCl) and were used directly in a glovebox with controlled atmosphere ($O_2 < 2$ ppm and $H_2O < 5$ ppm). The formed solutions were diluted to an approximate final concentration of 10^{-4} M, and the final metal-ion concentration was determined by titration with EDTA and xylenol orange as the indicator.[51] The triplet-state energies were determined as described by Crosby.[41] Absorption spectra were measured on a Perkin-Elmer Lambda 35. For the emission spectroscopy, slit widths of 5 and 10 nm and scan rates of 125 and 250 nm/s were used. The quantum yields of emission were determined as described by Bünzli, using Eu(terpy)$_3$(ClO$_4$)$_3$[52] ($\Phi = 1.3\%$)[40] and Tb(terpy)$_3$(ClO$_4$)$_3$[52] ($\Phi = 4.7\%$)[53] as 1×10^{-3} M degassed and dry acetonitrile solutions as reference standards.[40] The concentrations of the solutions were chosen to avoid precipitation but prevent dissociation of the 1:1 species. For the determination of the quantum yield, the excitation wavelength was chosen so that $A < 0.05$.

pK_a Determinations and Speciation by Potentiometry and NMR. The solutions for the pK_a determinations were prepared as described above for the spectroscopic measurements in 90% methanol/10% water (v/v). A minimum of three runs were performed for each solution. Potentiometry was performed using a Mettler DL21 autotitrator with a glass (combination) electrode at a constant temperature of 25.0 ± 0.1 °C. The potentiometer allowed pH readings with up to ±0.001 unit accuracy. The solutions were adjusted to a constant ionic strength of $I = 0.1$ M using KCl. The ligand buffer solutions were prepared using known quantities of NaOH in the range of 0.001−0.01 M. Standardized HCl in the range of 0.01−0.03 M, prepared in 90% methanol/10% water, was used as the titrant. During a typical potentiometric experiment, 10 mL of the ligand buffer solution was titrated with standardized HCl being added in predetermined aliquots. For the stability constant measurements, solutions with ligand-to-metal ratios between 0.5 and 3 were titrated against standardized HCl. After each addition of the acid, the solutions were stirred until a stable pH value was measured. At least 200 data points were collected in each run to allow for a good fitting. Three repeat measurements were performed for each ligand for consistency and accuracy. Fitting and factor analysis were performed using the HYPERQUAD2000 software package.[54] An ionic product of methanol p$K_m = 16.7$[55,56] is assumed for the calculations, substituting for the p$K_w = 13.78$ value used for aqueous solutions. The pH electrode was calibrated before each titration run through a titration of NaOH in 90% methanol/10% water to determine E^0 and s. The software program VLpH was used to convert experimental emf data into apparent pH.[57] NMR titrations were recorded on a Bruker DRX-500 spectrometer at 25 °C. For the purpose of comparison with stability constants measured using potentiometry, the NMR spectra were all measured in 90% methanol-d_4/10% water-d_2 mixtures. The ionic strength of the solutions are adjusted using KCl ($\mu = 0.1$M). The ligand buffer solutions were prepared using known amounts of NaOH, also prepared in the same solvent system. The pD values[58] of the ligand solutions were measured before the measurements using a Symphony SP301 electrode and adjusted to a 6−7 range to ensure complete deprotonation. All spectra are referenced to TMS. Fitting and factor analysis were performed with the HypNMR2000 software package.[59] It was assumed that the equilibrium is attained rapidly on the NMR time scale such that the chemical shift for a given nucleus is a mole fraction − weighted average over all the chemical species in which the nucleus is present. Data input is composed of the chemical shifts of the NMR peaks in relation to the analytical concentrations of reagents in the solutions and optionally its pH (or pD). A typical experiment consisted of titrating 2 mL of a known concentration of Eu(III) with predetermined aliquots of a known concentration of a ligand. In other words, the NMR spectra recorded at any point had excess Eu(III) with increasing concentration of ligand. The titration spanned ligand/metal ratios between 0.1 and 2. Because of the low solubility, we were never able to record more than a 2-fold excess of ligand in the presence of Eu(III). Nonetheless, all spectra recorded showed only the presence of the 1:1 species in solution. The pH was measured before and after the titration experiment and found to be constant throughout the measurements. Each titration experiment consisted of 10−15 measurements allowing for a good fitting.

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Supporting Information Available: Figures showing ball-and-stick respresentations of **3** and **4**, the coordination polyhedra around Eu(III), NMR titrations, and a Job plot of *a* and tables listing the bond lengths and angles for **1**, **2**, **3**, and **4** and NMR titration data. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic information files can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk). CCDC 614084 contains the supplementary crystallographic data for **1**, CCDC 614085 for **2**, CCDC 614086 for **3**, and CCDC 614087 for **4**.

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