

Nitro-functionalization and luminescence quantum yield of Eu(III) and Tb(III) benzoic acid complexes†‡

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In our pursuit of luminescent lanthanide ion-based coordination polymers, we have isolated several complexes with nitrobenzoic acid ligands and characterized these by X-ray crystallography and luminescence spectroscopy. 2-Nitrobenzoic acid reacts with Eu(III) to form **1**, which crystallizes in the *P*-1 space group, with $a = 12.385(3)$, $b = 12.912(3)$, $c = 17.889(4)$ Å, $\alpha = 97.49(3)$, $\beta = 109.64(3)$ and $\gamma = 101.99(3)^\circ$. 3-Nitrobenzoic acid forms a one-dimensional coordination polymer with Eu(III), **2**, which crystallizes in the triclinic space group *P*-1 with $a = 9.7100(19)$, $b = 10.579(2)$, $c = 13.361(3)$ Å, $\alpha = 77.41(3)$, $\beta = 88.78(3)$ and $\gamma = 88.16(3)^\circ$. Structures **3** and **4** correspond to the isostructural one-dimensional coordination polymers of Eu(III) and Tb(III), respectively, with the 4-nitrobenzoate anion. These crystallize in the triclinic space group *P*-1 with $a = 9.2242(18)$, $b = 15.102(3)$, $c = 18.587(4)$ Å, $\alpha = 75.93(3)$, $\beta = 82.88(3)$ and $\gamma = 79.00(3)^\circ$ for **3** and $a = 9.2692(19)$, $b = 15.369(3)$, $c = 18.353(4)$ Å, $\alpha = 75.37(3)$, $\beta = 81.32(3)$ and $\gamma = 78.15(3)^\circ$ for **4**. Potentiometry, absorption and NMR spectroscopy indicate that in solution only 1 : 1 species are present. All compounds are weakly luminescent as solids and the photophysics of solutions of ligands with Ln(III) in 1 : 1 stoichiometry were studied. Quantum yields around 1 and 3% for Eu(III)- and Tb(III)-containing methanolic solutions were measured.

Introduction

Lanthanide ions, Ln(III), have been the target of considerable interest due to the nature of the f-f transitions, which occur through light emission. These ions are therefore interesting for applications which require light-emitting materials. As f-f transitions are electric-dipole forbidden, population of the f excited states is routinely achieved through coordinated ligands, which serve as sensitizers or antennas.¹

Several ligands have been tailored to yield Ln(III) ion complexes with high luminescence quantum yield for applications ranging from biomedical imaging to fluoroimmunoassays and liquid crystal displays.¹ The ligands range from simple aromatic acids, such as the widely utilized dipicolinic acid, to more sophisticated multi-dentate architectures capable of selectively binding different lanthanide ions.^{2,3} Our group has recently become interested in exploiting the light-emitting properties of the lanthanide ions to develop complexes as potential precursors of emitting layers in polymer-based light emitting diodes.^{4,5} We have synthesized aromatic acid molecules that are potentially polymerizable, due to the presence of thiophene, for the electrodeposition of films with cation complexation properties and Ln(III) luminescence sensitization capabilities.⁶ While screening small molecules as potential monomers and sensitizers, it came to our attention that nitrobenzoic acid had not been reported as an antenna.

On the contrary, both *o*- and *m*-nitrobenzoic acids had been previously reported by Panigrahi to quench the luminescence of Tb(III).⁷ Nonetheless, nitrobenzoic acid had been studied by Choppin and Lajunen as a potential complexing agent.⁸ Our observations indicated that derivatization of benzoic acid analogs with thiophene leads to an average lowering of the triplet state energy by 5 000 cm⁻¹.⁴ Lewis and Kasha reported that while carboxylate derivatization of benzene lead to a decrease in the triplet state energy from 29 800 to 27 200 cm⁻¹, nitrobenzene has a triplet excited state at 21 100 cm⁻¹, which corresponds to a decrease of almost 9 000 cm⁻¹.⁹ Beer and co-workers utilized nitro-derivatization of a calixarene to increase the p*K*_a of the hydroxyl groups present and thus facilitate the coordination of uranyl cations for extraction purposes.¹⁰ They also observed a change in the phosphorescence properties of their nitro vs. a similar non-nitro substituted calixarene, but few details are given.¹¹ Based on our own observations and the data reported by Lewis and Kasha, the nitro moiety is thus a stronger auxochrome than thiophene, and we are interested in observing its effect on the triplet state of the ligands and thus on the overall sensitization and complexation ability.

We have recently isolated and characterized Eu(III) and Tb(III) complexes with 2-nitro-4-thiophen-3-yl-benzoic acid, which were the first examples of red and green luminescent complexes involving nitrobenzoate as the sensitizer.⁵ We have also reported the formation of a one-dimensional coordination polymer with 2-chloro-5-nitrobenzoic acid with Eu(III), which yields luminescent solutions with Eu(III).¹² The same ligand sensitizes green luminescence in solutions with Tb(III).¹² In this paper we extend the family of nitrobenzoic acid containing complexes with the isolation of several Eu(III) and Tb(III) complexes. The work presented here serves the purpose of systematizing the effect of

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‡ Electronic supplementary information (ESI) available: Full bond lengths and angles in Tables S1–S4 for compounds **1**–**4**. See DOI: 10.1039/b606970c

the nitro moiety in the antenna on the emission behavior of the coordinated lanthanides ions and thus the sensitizing ability of the nitrobenzoic acid ligands. We report the characterization by X-ray crystallography and solution luminescence spectroscopy and rationalize the effect of functional group positioning on the emission properties of the solutions studied.

Results and discussion

We chose *o*-, *m*- and *p*-nitrobenzoic acid ligands as the sensitizers of lanthanide ion luminescence to investigate the influence of the nitro-group position on the solid state structure of the complexes and on the solution luminescence properties. The stability constants of *m*-nitrobenzoic acid with all lanthanide ions have been previously reported in aqueous media by Choppin and Lajunen, but luminescence properties were not described.⁸

Syntheses of the metal complexes

The metal complexes described in this paper were isolated either by slow solvent evaporation of ethanol/water or methanol solutions of ligand and metal chloride with the pH adjusted with NaOH to allow for complete deprotonation of the ligand or by slow interdiffusion of solutions of metal ion in ethanol and ligand in water again with pH adjusted to ensure complete deprotonation. The synthesis of compound **1** required a stoichiometry that was less than 2 : 1 ligand-to-metal ion in the growth solution, and compounds **2**, **3** and **4** were grown in solutions with either a stoichiometric ratio of the two components or an excess of the anion. X-Ray quality crystals formed within one to two weeks at room temperature. The procedure is described in detail in the experimental section.

Crystallographic characterization

2-Nitrobenzoato derivative 1. 2-Nitrobenzoic acid forms homobimetallic molecules with Eu(III), with structures similar to the 2-nitro-4-thiophen-3-yl-benzoic acid previously described by our group.⁵ Interestingly, two distinct molecules, shown in Fig. 1 in the orientations which best display the coordination environments around metal ions Eu1 and Eu2, are present in this compound. Se-

Table 1 Selected bond lengths (Å) for **1**

Eu(1)–O(11)	2.282(5)	Eu(2)–O(19)	2.377(4)
Eu(1)–O(14)	2.354(5)	Eu(2)–O(22)#2	2.388(4)
Eu(1)–O(1)	2.382(5)	Eu(2)–O(15)	2.408(5)
Eu(1)–O(4)	2.433(5)	Eu(2)–O(26)	2.410(5)
Eu(1)–O(8)	2.435(5)	Eu(2)–O(28)	2.410(5)
Eu(1)–O(12)	2.443(6)	Eu(2)–O(27)	2.453(5)
Eu(1)–O(13)	2.461(4)	Eu(2)–O(16)	2.494(5)
Eu(1)–O(5)	2.524(5)	Eu(2)–O(23)	2.542(5)
Eu(1)–Eu(1)#1	4.3507(13)	Eu(2)–O(22)	2.573(5)
		Eu(2)–Eu(2)#2	3.9428(11)

lected bond distances are summarized in Table 1. Both molecules are homobimetallic and contain three ligands and two methanol molecules per metal ion. However, the coordination numbers are different. The molecule containing Eu1 in Fig. 1a has two eight-coordinate metal ions bridged by four μ -OCO[−] nitrobenzoato anions. Further, each Eu1 has a bidentate nitrobenzoato in addition to the two coordinated methanol molecules. The Eu1–O distances are in the range 2.282–2.524 Å with the shortest bond corresponding to the coordination to an oxygen atom O11 of a bridging ligand and the longest to an oxygen atom O5 from a bidentate ligand. The second molecule in Fig. 1b has two bridging μ -OCO[−] nitrobenzoato anions between the two Eu2 ions. Two more nitrobenzoato anions are coordinated in a bridging-bidentate fashion. This mode of coordination is common for lanthanide ions and was previously seen in our group for 2-nitro-4-thiophen-3-yl-benzoato complexes of Eu(III) and Tb(III).⁵ Another 76 structures for Eu(III) and 36 for Tb(III) found in the Cambridge Crystallographic Structural Database (CSD, v. 5.27) also show this type of coordination.¹³ While the Eu1–Eu1 distance in the first molecule is 4.3507 Å, the Eu2–Eu2 distance is shortened by approximately 0.4 to 3.9428 Å as a consequence of this triply coordinating mode of two bridging-bidentate nitrobenzoato anions. The ninefold coordination around the Eu2 ions is completed by a bidentate nitrobenzoato as well as two methanol molecules. While the intermetallic distance is shorter in this molecule, the Eu2–O bonds are longer *ca.* 2.377–2.573 Å. The shortest Eu–O bond is also to an oxygen atom (O19) of a bridging ligand and the two longest bonds to oxygen atoms (O22 and O23) of a bridging-bidentate ligand. In the Eu2 molecule,

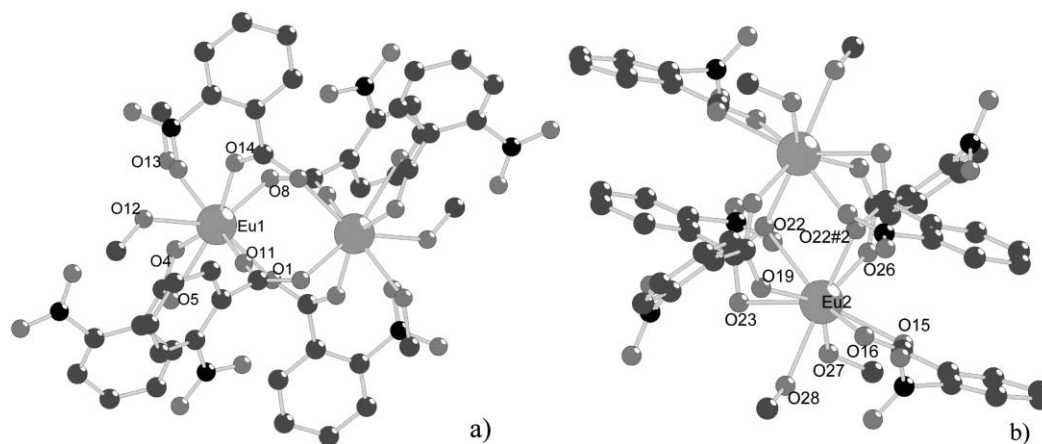


Fig. 1 Ball-and-stick representation of **1** with atom labelling of selected atoms. The two different molecules in the unit cell are shown with different relative orientations in (a) and (b). Hydrogen atoms are omitted for clarity (#2 $-x + 2, -y + 1, -z$).

weak π - π stacking of the triply coordinated and the bidentate coordinated edge phenyl rings, is also seen. The π - π distance is short, 2.792 Å. However, the rings are not parallel as the planes that they span intersect with an angle of 7.08°. The coordination polyhedra around Eu1 and Eu2 are shown in Fig. 2a and 2b, respectively. Eu1 is surrounded by eight oxygen atoms forming a distorted square antiprism and Eu2 with its coordinated oxygen atoms forms an irregular coordination polyhedron which can be either regarded as monocapped square antiprismatic or tricapped trigonal prismatic.

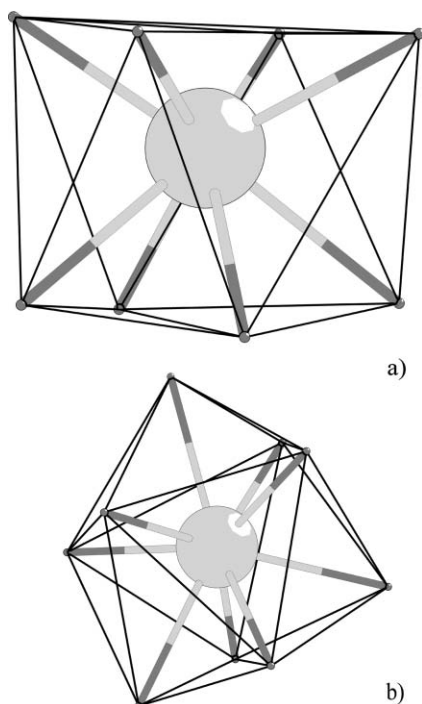


Fig. 2 Coordination polyhedra of the two Eu(III) ions in **1**: (a) Eu1, distorted square antiprism, (b) Eu2, monocapped square antiprism or tricapped trigonal prism.

3-Nitrobenzoato derivative 2. 3-Nitrobenzoic acid forms a one-dimensional coordination polymer with Eu(III), compound **2**. The asymmetric unit of this complex is shown in Fig. 3 and selected bond distances are summarized in Table 2. The metal

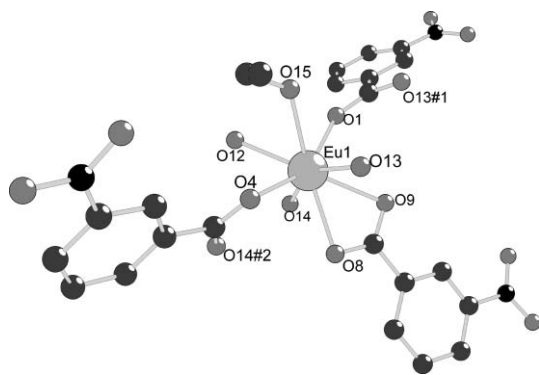


Fig. 3 Ball and stick representation of Eu(III) in **2** with a full coordination environment and atom labelling of selected atoms. Hydrogen atoms and solvent molecules of crystallization are omitted for clarity (#1 $-x, -y + 2, -z + 1$, #2 $-x + 1, -y + 2, -z + 1$).

Table 2 Selected bond lengths (Å) for **2**

Eu(1)–O(13)	2.307(2)	Eu(1)–O(12)	2.412(2)
Eu(1)–O(1)	2.329(2)	Eu(1)–O(8)	2.468(2)
Eu(1)–O(14)	2.355(2)	Eu(1)–O(15)	2.509(2)
Eu(1)–O(4)	2.372(2)	Eu(1)–O(9)	2.541(2)

ion is coordinated to eight oxygen atoms, which correspond to a carboxylate bound in a bidentate coordination mode and four other carboxylate groups coordinated only through one oxygen atom. The coordination sphere is completed by one ethanol and one water molecule. Furthermore, a non-coordinated methanol solvent molecule, not shown in Fig. 3, is present in the structure. The Eu–O distances range from 2.307–2.541 Å. The shortest of these corresponds to the bonds between the metal ion and the oxygen atoms of the bridging carboxylate anions, O13 and O1, while the longest involve the coordinated ethanol molecule, O15, and one oxygen atom of the bidentate carboxylate, O9. The eight-fold coordination around the Eu(III) is irregular, as shown in Fig. 4a, and cannot be assigned to a particular geometry. Neighboring metal ions are connected through two bridging carboxylate ions and the intermetallic distance is long, 5.0468 Å. The bridging arrangement leads to the packing structure shown in Fig. 4b. The Eu(III) ions bridged by the 3-nitrobenzoato anions form a one-dimensional chain along the crystallographic *a* axis. Two chains interact with each other through π - π stacking of adjacent nitrobenzoato rings. The distance between the planes spanned by these rings is 3.253 Å.

4-Nitrobenzoato derivatives of Eu(III) and Tb(III) **3** and **4**.

Compounds **3** and **4** are isostructural and crystallize in the triclinic *P*-1 space group. The asymmetric unit of **4** is shown in Fig. 5 and is representative for both compounds. Two non-equivalent Tb(III) ions are present, each with a coordination number of 9. A total of six ligands surround the two ions. In compound **3** the Eu–O distances range from 2.317–2.719 Å, while the Tb–O distances in compound **4** are between 2.283 and 2.893 Å (Tables 3 and 4). Each Tb(III) ion is connected to its neighbor by two bridging and through two bridging-bidentate coordinated carboxylate moieties. Similar to the structures previously described in our group,⁵ the longest Ln–O bonds in structures **3** and **4** are between the metal and the triply coordinated carboxylate anions. The bond lengths are Eu(1)–O(18) at 2.709 Å and Eu(2)–O(5) at 2.719 Å for **3** and O(6)–Tb(1) at 2.893 Å and O(17)–Tb(2) at 2.778 Å for **4**. Compared to structures **1** and **2** and within **3** and **4** these bonds are longer by ~0.15 to 0.3 Å with respect to the longest bonds in other coordination modes. This bridging-bidentate bonding mode is absent in a nitrobenzoato ligand structure recently reported by our group, in which the bond distances are from 2.317–2.524 Å.¹² Despite being longer, these bonds are still within the range expected for Ln–O distances, as a search in the CSD¹³ yields distances between 2.247–3.276 Å for Ln=Eu and 2.026–3.044 Å for Ln=Tb. The coordination environment around the metal ions is shown in more detail for **3** in Fig. 6. The coordination polyhedron can be described as a distorted capped square antiprism. The Eu–Eu distance between the two Eu(III) ions in the asymmetric unit is relatively short at 4.1756 Å, while the intermetallic distance to the neighboring pair of Eu(III) is 5.1418 Å, longer by approximately 1 Å. The shorter distance is consistent with the presence of the triply coordinated

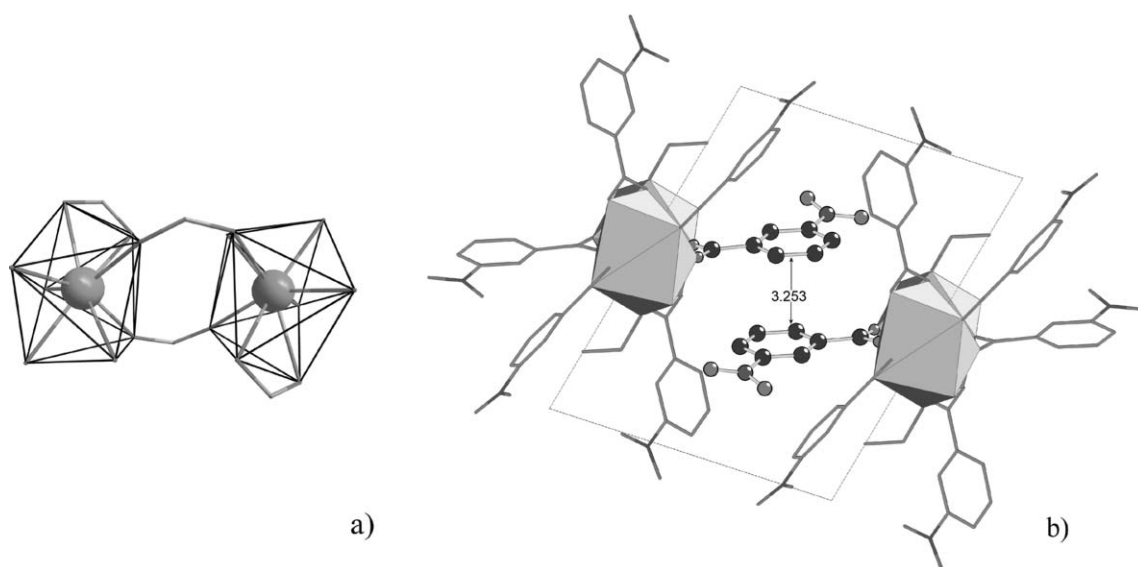


Fig. 4 (a) Two coordination polyhedra of the Eu(III) ion in **2** showing the bridging and the bidentate carboxylate moieties; (b) ball and stick and wire representation of the packing structure of **2**. The π - π distance of 3.253 Å is shown. The polyhedra correspond to the europium ions surrounded by the coordinated oxygen atoms. Hydrogen atoms and solvent molecules of crystallization are omitted for clarity.

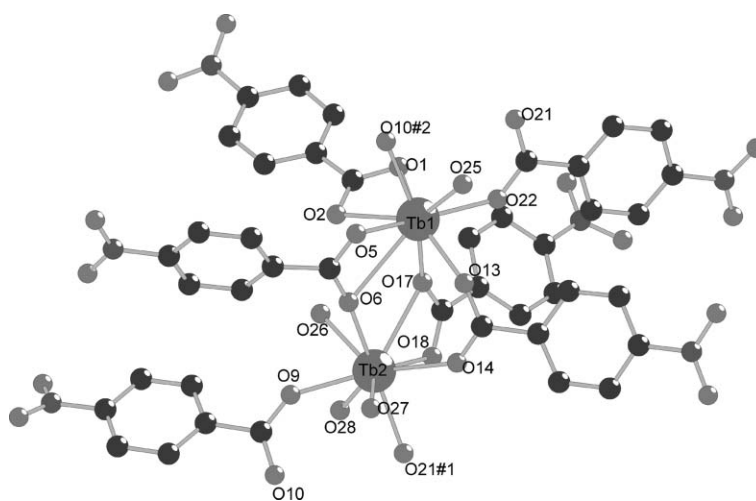


Fig. 5 Ball and stick representation of the Tb(III) ions in **4** with complete coordination environment and atom labelling of selected atoms. Hydrogen atoms and solvent molecules of crystallization are omitted for clarity (#1 $x + 1, y, z$, #2 $x - 1, y, z$).

carboxylato bridging the ions in the asymmetric unit and the longer with μ -OCO⁻ in between pairs of Eu(III). The intermetallic distances for the Tb(III) analog are similarly 4.2334 and 5.1086 Å, a lengthening of approximately 0.9 Å. Again, by comparison with the structures in the CSD,¹³ these distances are within the observed range of 3.659–5.141 Å for Eu and 3.785–4.532 Å for Tb, for

complexes in which the bridging bidentate coordination mode is seen. The packing diagrams for the isostructural compounds **3** and **4** are shown in Fig. 7. These structures form one-dimensional coordination polymers which interact with each other through π - π stacking of the phenyl rings of the nitrobenzoato moieties.

Table 3 Selected bond lengths (Å) for **3**

Eu(1)–O(14)#1	2.327(3)	Eu(2)–O(22)	2.317(3)
Eu(1)–O(2)	2.353(3)	Eu(2)–O(13)	2.357(3)
Eu(1)–O(5)	2.402(3)	Eu(2)–O(1)#2	2.362(3)
Eu(1)–O(21)	2.428(3)	Eu(2)–O(18)	2.391(3)
Eu(1)–O(17)	2.452(3)	Eu(2)–O(6)	2.494(3)
Eu(1)–O(27)	2.465(3)	Eu(2)–O(28)	2.509(3)
Eu(1)–O(26)	2.490(3)	Eu(2)–O(9)	2.535(3)
Eu(1)–O(25)	2.506(3)	Eu(2)–O(10)	2.548(3)
Eu(1)–O(18)	2.709(3)	Eu(2)–O(5)	2.719(3)

Table 4 Selected bond lengths (Å) for **4**

O(1)–Tb(1)	2.523(2)	O(6)–Tb(2)	2.349(2)
O(2)–Tb(1)	2.507(2)	O(9)–Tb(2)	2.318(2)
O(5)–Tb(1)	2.428(2)	O(14)–Tb(2)	2.403(2)
O(6)–Tb(1)	2.893(3)	O(17)–Tb(2)	2.778(2)
O(10)–Tb(1)#1	2.323(2)	O(18)–Tb(2)	2.405(2)
O(13)–Tb(1)	2.283(2)	O(21)–Tb(2)#2	2.299(2)
O(17)–Tb(1)	2.352(2)	O(26)–Tb(2)	2.432(2)
O(22)–Tb(1)	2.319(2)	O(27)–Tb(2)	2.482(2)
O(25)–Tb(1)	2.464(2)	O(28)–Tb(2)	2.472(2)
Tb(1)–O(10)#2	2.323(2)	Tb(2)–O(21)#1	2.299(2)

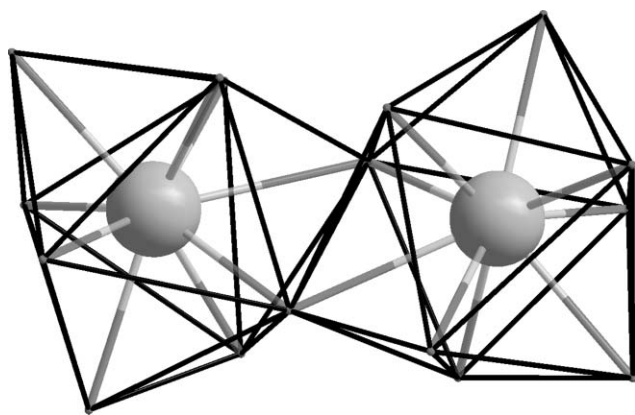


Fig. 6 Coordination polyhedra around the non-equivalent Eu(III) ions in **3**.

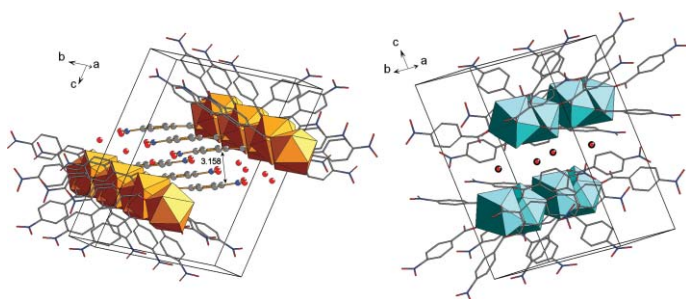


Fig. 7 Packing structures of **3** and **4**. The Eu(III) ions are represented by the orange and the Tb(III) ions by the blue polyhedra. π - π stacking interactions are shown in the Eu(III) structure with the corresponding distance of 3.158 Å. Hydrogen atoms are omitted for clarity.

The π - π distances between the planes spanned by the rings are 3.158 Å for **3** and 2.970 Å for **4**. Water molecules of crystallization are also present in the structures and are localized between the columns made up by the metal ions, most likely interacting through hydrogen bonding with the water molecules coordinated to the metal ions.

pK_a of ligands and stability constants

Aqueous solutions of our complexes are not appreciably luminescent and all photophysical data were collected in methanol. This solvent precludes the determination of stability constants and ligand pK_a values by potentiometry, while the use of water would not correctly mimic the luminescence conditions. We have therefore determined pK_a of ligands and stability constants for the

species in solution in 90% methanol/10% water (v/v) at constant ionic strength $I = 0.1$ M (KCl). In this solvent mixture only weak luminescence is observed but potentiometric determinations are possible as the pH electrode shows linear behavior. Potentiometry in methanol–water mixtures has been demonstrated for a myriad of pharmaceutically important molecules.^{14–18} Details of the experimental procedure and of the data fitting utilizing Hyperquad2000¹⁹ are described in the experimental section and the data collected are summarized in Table 5.

The pK_a of the ligands under these conditions are 4.81, 5.66 and 5.77 for *o*-, *m*- and *p*-nitrobenzoic acids, respectively. These values, not previously reported, agree well with the values of 4.95 for *m*-nitrobenzoic acid reported by Sarmini and Kenndler²⁰ determined in a solution containing 78.25% methanol and 7.556, 8.344 and 8.326 reported by Grunwald and Meiboom for three acids in pure methanol,²¹ as well as the tabulated data in water.²² The various data points do not give rise to a linear relationship of pK_a with the methanol percentage in solution. However, Grunwald's data was obtained not by potentiometry but by NMR at 24.8 °C, Kenndler's at 25 °C at $I = 0.05$ M (unknown electrolyte), while our data was collected at 25 °C at $I = 0.1$ M (KCl). In addition to possible errors due to the different experimental conditions, the pK_a of these acids is expected to increase with the methanol content in solution in a non-linear fashion, as pointed out by Sarmini and Kenndler, due to electrostatic interactions, the formation of solvent clusters, or the medium effect.²⁰

The stability constants, summarized in Table 5, and the nature of the species in the luminescent solutions were determined by two different methods. Potentiometry was first utilized in 90% methanol–10% water (v/v) solutions for both Eu(III) and Tb(III). To rule out method errors, NMR spectroscopy was utilized for the determination of the stability constants of the Eu(III) species in the same solvent and sample spectra of an NMR titration are shown in Fig. 8. Titration data are summarized in Tables S5–S10 in the ESI.† The bottom spectrum in Fig. 8 corresponds to the deprotonated free ligand, with the peaks in the aromatic region corresponding to the four protons in 2-nitrobenzoic acid. During the titration of Eu(III) with this ligand, three of the four peaks are shifted upfield by about 1 ppm. The signal corresponding to the α -proton to the carboxylate group is the most affected by the paramagnetic Eu(III) ion and can now be seen considerably broadened in the 5.5 ppm region.

The close agreement between the $\log \beta$ data obtained through these two methods along with the fact that the solutions were prepared independently and at different points in time rules out systematic errors. As we were able to determine $\log \beta$ in 90%

Table 5 The pK_a values of ligands and stability constants for 1 : 1 metal ion-to-ligand solutions

Ligand	$\log \beta$ Eu-NMR 99.5% CD ₃ OD ^a	$\log \beta$ Eu-NMR 90% CD ₃ OD/10% D ₂ O ^b	$\log \beta$ -potentiometry 90%MeOH/10%H ₂ O ^c			
			Eu	Tb	pK_a ^c	pK_a ^d
2-Nitrobenzoato	2.80 ± 0.07	3.30 ± 0.04	3.14 ± 0.02	3.21 ± 0.02	4.81 ± 0.03	2.18
3-Nitrobenzoato	2.00 ± 0.34	4.55 ± 0.04	4.19 ± 0.03	4.30 ± 0.02	5.66 ± 0.01	3.446(3.28 ± 0.02 ^e)
4-Nitrobenzoato	2.36 ± 0.21	precipitates	3.71 ± 0.04	4.06 ± 0.02	5.77 ± 0.01	3.41

^a Measured by NMR in 99.5% CD₃OD. ^b Measured by NMR in 90% CD₃OD–10% D₂O. ^c Measured by potentiometry in 90% MeOH–10% H₂O.

^d Tabulated data in water.²² ^e Data acquired in water at constant ionic strength $I = 0.1$ M (NaClO₄).⁸

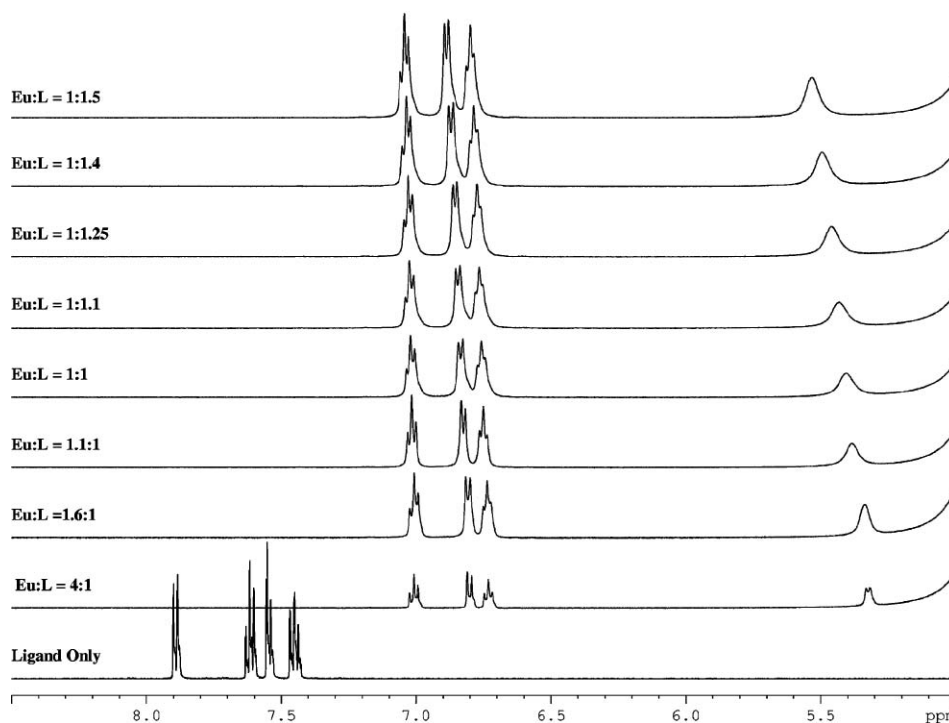
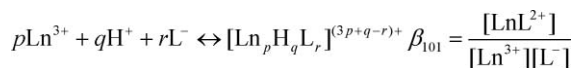


Fig. 8 NMR titration of Eu(III) with L = 2-nitrobenzoic acid in 90% methanol–10% water (v/v). Bottom spectrum corresponds to the deprotonated ligand.

methanol–10% water (v/v) by NMR, the technique was also utilized to determine stability constants for Eu(III)-containing solutions in pure deuterated methanol. These data are also summarized in Table 5.

The stability constants determined through potentiometry and NMR spectroscopy could be fitted by assuming the presence of only one complex species in solution, as represented in the equation below.



This species corresponds to a 1 : 1 metal-to-ligand ratio and is in agreement with what we had previously observed through absorption spectroscopy for the closely related thiophenyl-derivatized 2-nitrobenzoic acid and for 2-chloro-5-nitrobenzoic acid,^{5,12} as well as through Job plots, such as the one shown in Fig. 9 for a solution of 3-nitrobenzoic acid and Eu(III). Choppin and Lajunen also observed the presence of almost exclusively 1 : 1 species in aqueous solutions of *m*-nitrobenzoic acid and Ln(III).⁸ The remaining coordination sites of the lanthanide ion are therefore filled by solvent molecules, as is further discussed below.

The stability constants for Eu(III) in the mixed solvent system were determined to be in the range 3.14–4.19 by potentiometry and 3.30–4.55 by NMR. The most acidic ligand, 2-nitrobenzoic acid, is also the one ligand showing the most unstable coordination behavior. The two other ligands, less acidic, show a slightly increased stability, but the trend is not linear. While the stability constants are indeed expected to vary linearly with the pK_a , this is only true in the absence of steric effects.⁸ The stability constants for Eu(III) and Tb(III) in aqueous solution with *m*-nitrobenzoic acid are 1.76 and 1.61, respectively, as determined by Choppin and

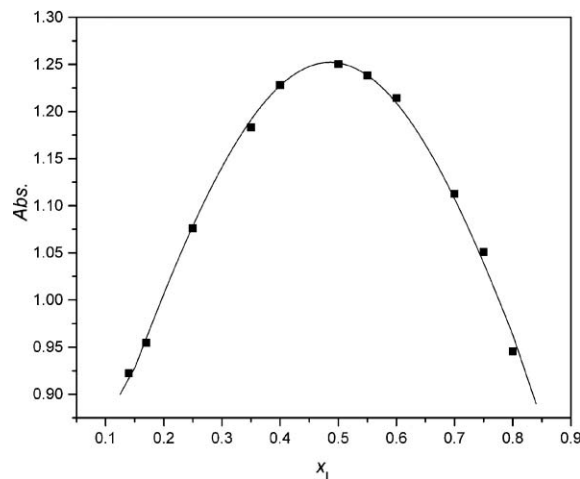


Fig. 9 Job plot of 3-nitrobenzoic acid (5×10^{-5} M) in the presence of Eu(III) at 25 °C in methanol ($I = 0.1$ M Et_4NCl) at $\lambda_{\text{abs}} = 219$ nm.

Lajunen.⁸ These values are smaller than the ones for the solvent mixture, but also smaller than the stability constants determined in pure methanol for Eu(III), which are in the range 2.00–2.80. While not attempted here and surely worthy of further investigation, a reason for this seeming discrepancy might be explained with steric effects or solvent related effects put forward by Sarmini and Kenndler (*vide supra*).²⁰

Photophysical characterization of the 1 : 1 metal ion : ligand solutions

All three ligands sensitize the emission of Eu(III) and Tb(III) in the solid state, as evidenced by the emission from the crystals isolated

Table 6 Photophysical data of 1 : 1 metal ion-to-ligand solutions

Ligands	Φ (%) ^a		$\tau_{\text{MeOH}}/\mu\text{s}$		$\tau_{\text{MeOD}}/\text{ms}$		n^b		$E(^1\text{S})/\text{cm}^{-1}$	$E(^3\text{T})/\text{cm}^{-1c}$
	Eu	Tb	Eu	Tb	Eu	Tb	Eu	Tb		
2-Nitrobenzoato	0.97	3.00	305.4 \pm 13.7	557.8 \pm 4.0	0.916 \pm 0.010	0.962 \pm 0.007	4.6	6.3	32 760	25 620
3-Nitrobenzoato	1.09	3.14	331.4 \pm 10.7	666.7 \pm 28.5	1.084 \pm 0.014	1.013 \pm 0.352	4.4	4.3	32 720	25 590
4-Nitrobenzoato	0.99	2.91	307.2 \pm 9.2	789.0 \pm 3.2	0.845 \pm 0.008	1.556 \pm 0.148	4.4	5.2	32 590	25 020

^a Measured according to Bünzli *et al.*³³ ^b Measured according to Horrocks *et al.*²³ ^c Determined by phosphorescence at 77 K,²⁴ the 0–0 transitions were obtained through vibrational deconvolution of the emission bands.

for X-ray diffraction. Extensive photophysical characterization of these ligands as sensitizers was performed in solution and the data is summarized in Table 6. The evidence collected by potentiometry along with absorption and emission spectroscopy, in which the maxima of absorption and emission are seen for metal ion to ligand ratios of 1 : 1 in solution prompted us to do the photophysical characterization of the species in methanol with the same stoichiometry. Experimental details of the photophysical characterization are summarized in the experimental section.

Typical absorption, excitation and emission spectra are shown in Fig. 10a for Eu(III) and Fig. 10b for Tb(III) with *o*-nitrobenzoic acid. The absorption and excitation spectra in both cases are similar and closely follow the absorption spectra of the ligands as free acids. For the Eu(III) solution a feature in the excitation spectrum at 386 nm can be seen, which corresponds to an intra-4f transition. Such a feature is absent in the Tb(III) excitation spectrum. The emission spectra display the characteristic peaks for Eu(III) (595, 619, 656 and 699 nm for $^3\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$, respectively) and Tb(III) (492, 547, 589 and 623 nm for $^3\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^3\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$, respectively).

The lifetimes of luminescence for all Eu(III)-containing solutions are between 305 and 331 μs , whereas with Tb(III) solutions, a broader range is seen, between 558 and 789 μs . In deuterated methanol the lifetimes triple for the Eu(III) and double for the Tb(III)-containing solutions. From this data we can estimate the approximate number of methanol molecules coordinated to the

metal ion in solution, utilizing the following equation, which was derived by Horrocks and co-workers.²³

$$n = A(\tau_{\text{MeOH}}^{-1} - \tau_{\text{MeOD}}^{-1})/A = 2.1 \text{ for Eu(III), } 8.4 \text{ for Tb(III)}$$

n is the number of methanol molecules in the first coordination sphere and τ the lifetime of the excited state in deuterated and non-deuterated methanol. We find that the slightly larger Eu(III) accommodates approximately 4.5 methanol molecules in its coordination sphere, while Tb(III), depending on the ligand, has 4 to 6 methanol molecules coordinated.

The quantum yields of luminescence for the red-emitting solutions are consistently around 1%, while the green-emitting solutions have an emission process with efficiencies of the order of 3%. As the triplet state energies, determined through phosphorescence of Gd(III)-containing solutions at 77 K,²⁴ are very close in the range 25 020–25 620 cm^{-1} , as are the singlet state energies (32 590–32 760 cm^{-1}), it is not surprising that their sensitization efficiency is similar. These energies correspond to singlet–triplet gaps of approximately 7 000 cm^{-1} , too large for an efficient intersystem crossing process (*vide infra*). Further, the energy differences between triplet state and Ln(III) excited state are on the order of approximately 8 000 cm^{-1} for Ln=Eu (energy of $^5\text{D}_0$ at 17 277 cm^{-1}) and 5 000 cm^{-1} for Ln=Tb (energy of $^5\text{D}_4$ at 20 500 cm^{-1}), which are also large for an efficient sensitization process (*vide infra*).

The determination of the excited state lifetimes τ of Eu(III) sensitized with each individual ligand allowed us to further

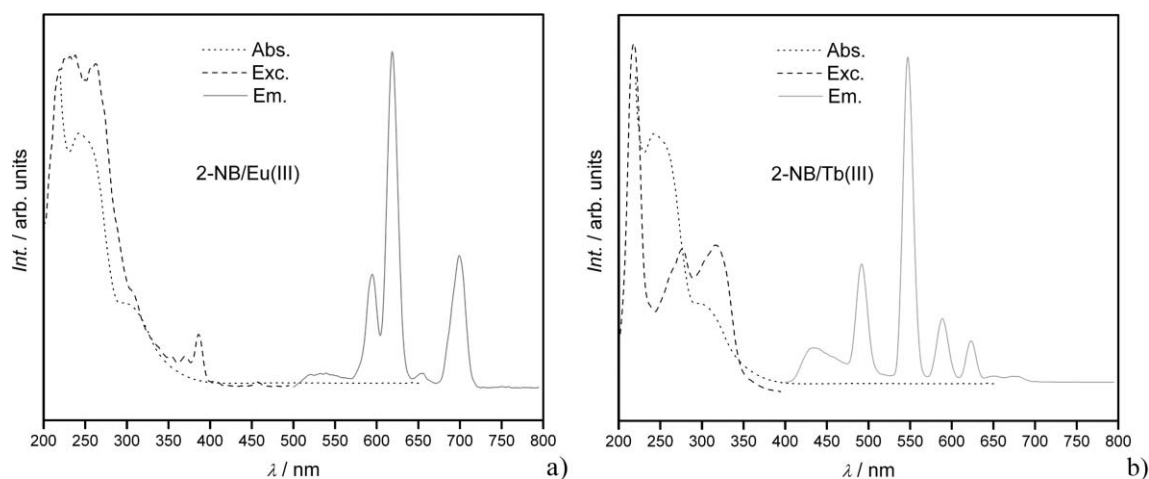


Fig. 10 Absorption (dotted), excitation (dashed) and emission (solid) spectra of (a) Eu(III) and (b) Tb(III) solutions with 2-nitrobenzoic acid anion as the sensitizer in methanol ($[\text{Eu}^{3+}] = [\text{Tb}^{3+}] = [\text{L}] = 1 \times 10^{-4} \text{ M}$, $I = 0.1 \text{ M Et}_4\text{NCl}$). Slit widths were 10 nm and scan rate 250 nm s^{-1} . Filters were set at 515 nm (a) and 430 nm (b) to cut off not completely quenched ligand emission, which is seen as a broad pre-peak in both cases.

Table 7 Determination of intrinsic quantum yield of luminescence of Eu³⁺

Ligand	Φ (%)	$\tau/\mu\text{s}$	τ_0/ms	$\Phi_{\text{Eu}^{3+}}$ (%)	Φ_{sens}
2-Nitrobenzoato	0.97	305.4	2.4254	74.1	0.01
3-Nitrobenzoato	1.09	331.4	1.9806	65.6	0.02
4-Nitrobenzoato	0.99	307.2	2.1212	65.2	0.02

calculate the intrinsic quantum yield of emission of Eu(III) Φ_{Eu} , since

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

and the radiative lifetime τ_0 can be obtained through the equation below, derived by van Veggel and co-workers,²⁵

$$1/\tau_0 = 14.65 \times n^3 (E_{\text{TOT}}/E_{5D_0 \rightarrow 7F_1})$$

where n is the refractive index of the solution, E the integrated corrected emission spectrum for all emission bands TOT and for the magnetic dipole transition $5D_0 \rightarrow 7F_1$. These values, which are in the order of 65–74% and are summarized in Table 7, demonstrate that the presence of the ligands in the coordination sphere of the Eu(III) increases its radiative rate with a consequent decrease of non-radiative deactivation through, for example, O–H vibrations of the coordinated methanol molecules and thus improve the intrinsic luminescence quantum yield of the metal ion. These values of Φ_{Eu} are comparable to values of 0.6–0.7 observed by van Veggel and co-workers for a terphenyl-based complex in the presence of hexafluoroacetylacetonate or benzoyltrifluoroacetate and higher than values of 0.2 and 0.3 for the same complex in the presence of phenanthroline or dibenzoylmethane.²⁵ However, despite the high values of intrinsic quantum yield determined here, due to the less favorable match between singlet and triplet energies, triplet level and $5D_0$ or $5D_4$ levels of Eu(III) and Tb(III) respectively, and the low stability constants of the species in solution, only very moderate quantum yields are observed with these ligands as sensitizers.

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

$$\Phi = \Phi_{\text{ISC}}\Phi_{\text{ET}}\Phi_{\text{Ln}} = \Phi_{\text{sens}}\Phi_{\text{Ln}}$$

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_{Ln} the intrinsic quantum yield of emission (*vide supra*). We can thus define a sensitization efficiency Φ_{sens} and the calculated values are summarized in Table 7. These values are very small, on the order of 0.01–0.02 and reflect the low efficiency of energy transfer within the ligand and from ligand to Ln(III) excited state due to the large energy gaps.

While it could be demonstrated that nitrobenzoato ligands are weak sensitizers in solution, little information was gathered about the photophysical behaviour of the complexes characterized crystallographically, due to difficulties in isolating enough bulk material. It could, however, be expected that the solid state materials should display longer lifetimes of luminescence, as previously observed for isophthalato derivatives isolated in our group,⁴ due to fewer solvent molecules coordinated to the metal

ion. Little can be inferred regarding the emission efficiency of the solids from the solution measurements, but visual observation of the crystals isolated for X-ray diffraction shows that the luminescence process is weak.

Conclusions

Several complexes of Eu(III) and Tb(III) with *o*-, *m*- and *p*-nitrobenzoic acid anions as ligands were isolated. While three of the solids isolated are coordination polymers, the complex involving *o*-nitrobenzoic acid is molecular, with two homobimetallic molecules in the unit cell. Relatively short Ln–Ln distances are seen in the complexes which display a triply coordinated carboxylate as a bridging-bidentate ligand. These complexes are luminescent in the solid state, showing a metal-to-ligand ratio of 1 : 3. In solution, experimental evidence points to the formation of only a 1 : 1 species. These are also luminescent in the characteristic wavelengths of the metal ions, with quantum yields of approximately 1% for Eu(III)-containing and 3% for Tb(III)-containing solutions. The moderate quantum yields can be explained by the small stability constants of the species in solution, as well as the large energy gaps between singlet and triplet levels of the ligand and triplet level of the ligand and emissive excited state of the lanthanide ion. Despite the strong electron-withdrawing effects of the –NO₂ group, for spectroscopic purposes its effect is not strongly dependent on the relative position of this functional group in the benzoic acid, as triplet and singlet states of the ligand in solution with Ln(III) are relatively close. It is also interesting to note that while –COO[–]-derivatization of benzene leads to a lowering of the triplet state by approximately 2 600 cm^{–1}, and –NO₂-derivatization to a lowering of approximately 8 700 cm^{–1} as described by Lewis and Kasha,⁹ the presence of both functional groups on benzene leads to a decrease of only approximately 4 500 cm^{–1}. The triplet energy is thus too high for an efficient energy transfer. However, the presence of these ligands in the coordination sphere of the Eu(III) leads to an increase in the radiative rate and thus high intrinsic quantum yields of luminescence are seen.

Experimental

General information

NMR spectra were recorded on a Bruker DRX-500 spectrometer. UV spectra were obtained on a Perkin Elmer Lambda 35 and fluorescence spectra on a Perkin Elmer LS-55 spectrometer. All commercially available chemicals, including the ligands (Acros), were used as received. However, the LnCl₃ salts were dried under reduced pressure and heating and kept in a glove box under controlled atmosphere (O₂ < 2 ppm, H₂O < 5 ppm). Solvents were dried by standard methods. All data were collected at a constant temperature of 25.0 ± 0.1 °C.

Synthesis of the metal complexes

Europium 2-nitrobenzoato complex 1. To 2 ml of 0.027 M EuCl₃·6H₂O in methanol 0.6 ml of a concentrated solution of 2-nitrobenzoate (0.17 M, pH adjusted to ~5) is added, for a final metal-to-ligand ratio of 1 : 2. After two weeks, colorless blocks of **1** formed.

Europium 3-nitrobenzoato complex 2. *m*-Nitrobenzoic acid (0.5013 g, 3 mmol) is dissolved in 20 ml ethanol. The pH of the solution is adjusted to ~6.5 using 1 M NaOH (aq). To this, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) in 5 ml water is added dropwise. The reaction mixture is left to reflux overnight, after which any precipitate formed is filtered off and the filtrate is left sitting at room temperature. After two weeks, long yellow needles of **2** formed.

Europium 4-nitrobenzoato complex 3 (similar to the terbium 4-nitrobenzoato complex 4). A solution of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (1 eq.) in ethanol is allowed to diffuse slowly into a concentrated solution of 4-nitrobenzoate in water, with pH adjusted to ~5. Within a week, colorless needle-like crystals of **3** and **4** formed.

X-Ray crystallography

Crystal data, data collection and refinement details for all the compounds are given in Table 8. Full bond lengths and angles are given in Tables S1–S4 in the ESI.† Suitable crystals were mounted on a glass fiber and placed in the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with a low-temperature device,²⁶ using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were measured using omega 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 SMART²⁷ software and refined using SAINTPlus²⁸ on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus²⁸ software. Multi-scan absorption corrections were applied using SADABS,²⁹ unless otherwise indicated. The structures were solved by direct methods and refined by least square methods on F^2 using the SHELXTL³⁰ program package. All non-hydrogen atoms were refined anisotropically. 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 non-coordinated solvent molecules could not be located on the difference map and have been omitted, although the correct formulae are indicated. CCDC reference numbers 606245 and 603285–603287 for **1** and **2–4**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606970c.

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 used directly in a glove box with a controlled atmosphere ($\text{O}_2 < 2 \text{ ppm}$ and $\text{H}_2\text{O} < 5 \text{ ppm}$). 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.³¹ The triplet state energies were determined as described by Crosby *et al.*²⁴ Absorption spectra were measured on a Perkin Elmer. For the emission spectroscopy slit widths of 5 and/or 10 nm and scan rates of 125 and 250 nm s^{-1} were used. The quantum yields of emission were determined as described by Bünzli *et al.* utilizing $\text{Eu}(\text{terpy})_3(\text{ClO}_4)_3$ ³² ($\Phi = 1.3\%$)³³ and $\text{Tb}(\text{terpy})_3(\text{ClO}_4)_3$ ³² ($\Phi = 4.7\%$)³⁴ as $1 \times 10^{-3} \text{ M}$ degassed and dry acetonitrile solutions as reference standards.³³ Eqn 1 was utilized for the calculations of the quantum yield.³³

$$\Phi_x = \left(\frac{n_x^2 A_{\text{ref}} I_{\text{ref}} E_x}{n_{\text{ref}}^2 A_x I_x E_{\text{ref}}} \right) \Phi_{\text{ref}} \quad (1)$$

Φ is the quantum yield of sample x and reference ref, n is the refractive index, A the absorbance at the excitation wavelength, I the intensity of the corrected excitation spectrum at the excitation wavelength and E the integrated corrected emission spectrum. The concentrations of the solutions were chosen to avoid precipitation but prevent dissociation of the 1 : 1 species. For the determination

Table 8 Crystallographic details for compounds **1–4**

Complex	1	2	3	4
CCDC number	606245	603285	603286	603287
Formula	$\text{C}_{46}\text{H}_{36}\text{Eu}_2\text{N}_6\text{O}_{28}$	$\text{C}_{24}\text{H}_{23}\text{EuN}_3\text{O}_{15}$	$\text{C}_{42}\text{H}_{34}\text{Eu}_2\text{N}_6\text{O}_{29}$	$\text{C}_{42}\text{H}_{34}\text{N}_6\text{O}_{29}\text{Tb}_2$
$M/\text{g mol}^{-1}$	1424.73	739.37	1390.67	1404.59
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P-1$	$P-1$	$P-1$	$P-1$
$a/\text{\AA}$	12.385(3)	9.7100(19)	9.2242(18)	9.2692(16)
$b/\text{\AA}$	12.912(3)	10.579(2)	15.102(3)	15.369(3)
$c/\text{\AA}$	17.889(4)	13.361(3)	18.587(4)	18.353(4)
$\alpha/^\circ$	97.49(3)	77.41(3)	75.93(3)	75.37(3)
$\beta/^\circ$	109.64(3)	88.78(3)	82.88(3)	81.32(3)
$\gamma/^\circ$	101.99(3)	88.16(3)	79.00(3)	78.15(3)
$V/\text{\AA}^3$	2572.9(9)	1338.7(5)	2457.2(8)	2462.2(9)
T/K	95(2)	99(2)	97(2)	96(2)
Z	2	2	2	2
$D_c/\text{g cm}^{-3}$	1.839	1.834	1.880	1.895
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	2.517	2.425	2.634	2.954
Independent reflections, $R_{\text{int}} [F_o \geq 4\sigma(F_o)]$	11779, 0.0639	6584, 0.0254	11169, 0.0351	11802, 0.0272
Reflections collected	27369	14194	24013	25707
Data/restraints/parameters	11779/0/743	6584/0/389	11169/0/712	11802/0/712
Goodness-of-fit on F^2	1.017	1.043	1.059	1.041
R_1, wR_2 (all data)	0.0859, 0.1342	0.0311, 0.0743	0.0500, 0.0855	0.0360, 0.0748
Largest diff. peak and hole/ e \AA^{-3}	4.003, -1.731	1.109, -1.198	1.597, -1.675	1.785, -1.579

of the quantum yield the excitation wavelength was chosen so that $A < 0.05$.

pK_a determinations and speciation by potentiometry and NMR

Solutions for 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 auto-titrator with a glass (combination) electrode, at 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 0.001–0.01 M. Standardized HCl in the range 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 pre-determined aliquots. For the stability constant measurements, solutions with ligand-to-metal ratios between 3–0.5 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.¹⁹ An ionic product of methanol $pK_m = 16.7^{35,36}$ is assumed for the calculations, substituting for the $pK_w = 13.78$ used for aqueous solutions.

The pH electrode was calibrated before each titration run through titration of NaOH in 90% methanol–10% water to determine E° and s . The software program VLpH was utilized to convert experimental *emf* data into apparent pH.³⁷

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% d^4 -methanol–10% d^2 -water 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 values³⁸ 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 referred to TMS. Fitting and factor analysis were performed with the HypNMR2000 software package.³⁹ 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 comprised 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 pre-determined 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 0.1–2. Due to low solubility we were never able to record more than a two-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 fit.

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References

- 1 *Lanthanide Probes in Life, Chemical and Earth Sciences-Theory and Practice*, ed. J.-C. G. Bünzli and G. R. Choppin, Elsevier, Amsterdam, 1989.
- 2 A.-S. Chauvin, F. Gumy, D. Imbert and J.-C. G. Bünzli, *Spectrosc. Lett.*, 2004, **37**, 517–532.
- 3 C. Piguet and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 1999, **28**, 347–358.
- 4 A. de Bettencourt-Dias, *Inorg. Chem.*, 2005, **44**, 2734–2741.
- 5 A. de Bettencourt-Dias and S. Viswanathan, *Chem. Commun.*, 2004, 1024–1025.
- 6 A. de Bettencourt-Dias, S. Viswanathan and K. Ruddy, *Cryst. Growth Des.*, 2005, **5**, 1477–1484.
- 7 B. S. Panigrahi, *Spectrochim. Acta, Part A*, 2000, **56**, 1337–1344.
- 8 G. R. Choppin and L. H. J. Lajunen, *Inorg. Chem.*, 1986, **25**, 3512–3514.
- 9 G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, 1944, **66**, 2100–2116.
- 10 P. D. Beer, G. D. Brindley, O. D. Fox, A. Grieve, M. I. Ogden, F. Szemes and M. G. B. Drew, *Dalton Trans.*, 2002, 4525.
- 11 P. D. Beer, F. Szemes, P. Passaniti and M. Maestri, *Inorg. Chem.*, 2004, **43**, 3965–3975.
- 12 S. Viswanathan and A. de Bettencourt-Dias, *Inorg. Chem. Commun.*, 2006, **9**, 444–448.
- 13 *Cambridge Structural Database V. 5.27*, (Nov. 2005).
- 14 A. Avdeef, K. J. Box, J. E. A. Comer, M. Gilges, M. Hadley, C. Hibbert, W. Patterson and K. Y. Tam, *J. Pharm. Biomed. Anal.*, 1999, **20**, 631–641.
- 15 A. Avdeef, J. E. A. Comer and S. J. Thomson, *Anal. Chem.*, 1993, **65**, 42–49.
- 16 K. Takacs-Novak, K. J. Box and A. Avdeef, *Int. J. Pharm.*, 1997, **151**, 235–248.
- 17 K. C. Ong, R. A. Robinson and R. G. Bates, *Anal. Chem.*, 1964, **36**, 1971–1972.
- 18 A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, 1955, **20**, 747–762.
- 19 P. Gans, A. Sabatini and A. Vacca, *Talanta*, 1996, **43**, 1739–1753.
- 20 K. Sarmini and E. Kenndler, *J. Chromatogr. A*, 1998, **806**, 325–335.
- 21 E. Grunwald and S. Meiboom, *J. Am. Chem. Soc.*, 1963, **85**, 2047–2050.
- 22 *Lange's Handbook of Chemistry*, McGraw-Hill, Boston, 15th edn, 1999.
- 23 R. C. Holz, C. A. Chang and W. D. Horrocks, Jr., *Inorg. Chem.*, 1991, **30**, 3270–3275.
- 24 G. A. Crosby, R. E. Whan and R. M. Alire, *J. Chem. Phys.*, 1961, **34**, 743–748.
- 25 S. I. Klink, G. A. Hebbink, L. Grave, P. G. B. Oude Alink, F. C. J. M. van Veggel and M. H. V. Werts, *J. Phys. Chem. A*, 2002, **106**, 3681–3689.
- 26 H. Hope, *Prog. Inorg. Chem.*, 1994, **41**, 1–19.
- 27 *SMART: v.5.626, Bruker Molecular Analysis Research Tool*, Bruker AXS, Madison, WI, 2000.
- 28 *SAINTPlus: v.6.36a, Data Reduction and Correction Program*, Bruker AXS, Madison, WI, 2001.
- 29 *SADABS: v.2.01, an empirical absorption correction program*, Bruker AXS, Madison, WI, 2001.
- 30 G. M. Sheldrick, *SHELXTL: v.6.10, Structure Determination Software Suite*, Bruker AXS, Madison, WI, 2001.
- 31 J. Bassett, R. C. Denney, G. H. Jeffery and J. Mendham, *Vogel-Análise Inorgânica Quantitativa*, Editora Guanabara, Rio de Janeiro, 4th edn, 1978.
- 32 D. A. Durham, G. H. Frost and F. A. Hart, *J. Inorg. Nucl. Chem.*, 1969, **31**, 833–838.

-
- 33 S. Petoud, J.-C. G. Bünzli, K. J. Schenk and C. Piguet, *Inorg. Chem.*, 1997, **36**, 1345–1353.
- 34 L. J. Charbonnière, C. Balsiger, K. J. Schenk and J.-C. G. Bünzli, *J. Chem. Soc., Dalton Trans.*, 1998, 505–510.
- 35 H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, 3 edn, 1958.
- 36 J. S. Fritz, *Acid–Base Titrations in Nonaqueous Solvents*, G. Frederick Smith Chem. Co., Columbus, OH, 1952.
- 37 VLpH, <http://www.hyperquad.co.uk/vlph.htm>.
- 38 P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, 1960, **64**, 188–190.
- 39 C. Frassinetti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi and A. Vacca, *Anal. Biochem.*, 1995, **231**, 374–382.