Lanthanide Macrocyclic Quinolyl Conjugates as Luminescent Molecular-Level Devices

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Abstract: The Eu(III) tetraazamacrocyclic complexes **[Eu·1]** and **[Eu·2]**, and the Tb(III) and Yb(III) complexes [**Tb·1]** and **[Yb·2]**, have been synthesized as luminescent molecular-level devices. The Eu complexes exhibit unique dual pH switching behavior in water under ambient conditions. The delayed Eu emission is reversibly switched on in acid, with an enhancement factor of several hundred for **[Eu·1]**. These observations are consistent with the protonation of the quinoline aryl nitrogen moiety ($pK_a \approx 5.9$ for **[Eu·1]**). The fluorescence emission spectra of these complexes are unaffected by acid, but pronounced changes occur in alkaline solution due to the deprotonation of the aryl amide nitrogen ($pK_a \approx 9.4$ for **[Eu·1]**). **[Tb·1]** shows a more intriguing pH dependence; Tb emission is switched "on" *only* in the presence of H^+ and in the absence of molecular oxygen, whereas the fluorescence emission properties are similar to those observed with **[Eu·1]**. This behavior can be conveniently described as a molecular-level logic gate, corresponding to a two-input INHIBIT function, $A \wedge B'$. The analogous **[Yb·2]** complex shows no such pH or O_2 dependence.

Introduction

Over the past decade advances in supramolecular chemistry[1] have led to the development of miniaturized devices based on assemblies of single molecules that can execute functions on a "molecular level", driven by photon, magnetic, or electronic stimuli.[2,3] Based principally upon molecular recognition and concomitant modulation of physical properties such as the redox potential, magnetism, photochemical, and photophysical properties, these molecular-level devices can mimic some of the basic functions of macroscopic electronic and mechanical machinery.[2,4] Examples of such supramolecular-level devices include shuttles,[5] wires,[6] gears,[7] ratchets,[8] molecular pistons, machines, and motors,[9] giving rise to the fast growing field of nanotechnology.[10] Of particular interest to us are those devices exhibiting switching between two states, off−on switching, through host−guest interactions, observable as changes in luminescent properties such as lifetime, quantum yield, and wavelength.[11] Such

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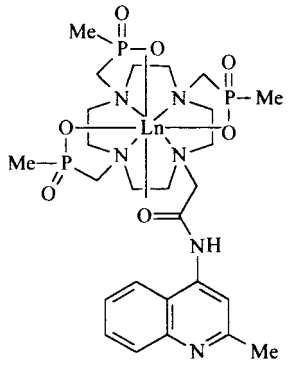
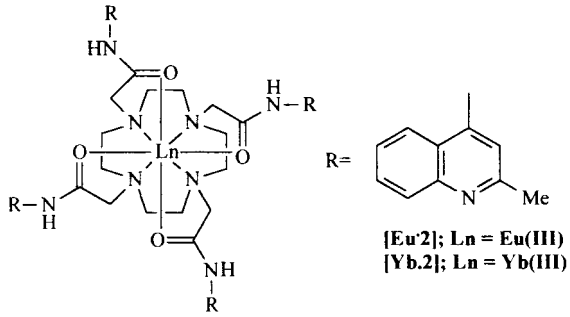
simple devices can be employed as chemosensors for the detection of ions and molecules in physiological systems[12] and can conveniently be described as logic operations.[13]

Mimicking logic functions, the basis of modern computing, is of particular interest; the relationship between the input and the output may be described by truth tables, where 1 represents an active input/output and 0 an inactive one.[14] Molecular logic devices have recently been demonstrated, in each case using fluorescence or phosphorescence as an output, triggered by ionic (H^+, Na^+, etc.)[13,15] or molecular inputs[16] (O_2 and β-CD). Being able to modulate the nature of these devices in a controllable way could, in principle, lead to the construction of arrays of molecular-level systems which may be important in the development of molecular information processing. The potential of such a supramolecular system has recently been illustrated by de Silva and McClenaghan, who demonstrated a molecular-level arithmetic addition operation on 2-bit integers.[17]

We set out to develop luminescent molecular-level devices, based on modulating the photophysical properties of metal complexes, using lanthanide ions as emitting moieties (output signal).[18] The quinoline amide-derived macrocyclic Eu(III) complexes [**Eu·1**][19] and **[Eu·2]**, the Tb(III) complex **[Tb·1]**,[20] and the Yb(III) complex **[Yb·2]** can be considered as such devices. In these complexes the metal center can govern the response of the device to some external perturbations such as those arising from ion or molecular recognition. Our goal is twofold: First we wish to demonstrate the use of such systems for the signaling of ions and molecules through "off−on" luminescent signaling. The neutral monoamide complex **[Eu·1]** and the cationic tetraamide complex **[Eu·2]** are examples of such systems. These systems can also be considered as lanthanide-based luminescent chemosensors,[18] possessing a long-lived excited state (in the millisecond range), emitting at long wavelengths (500−700 nm), with large Stokes shifts and line-like emission bands (10−30 nm bandwidth) under ambient conditions.[18−21]



[Eu·1]; Ln = Eu(III)
[Tb·1]; Ln = Tb(III)



[Eu·2]; Ln = Eu(III)
[Yb.2]; Ln = Yb(III)

Second, we wish to develop molecular logic gates by exploiting the photophysical switching ability of lanthanide ions, and we have chosen the binary inhibit (INH) logic gate, which has not been previously reported.[20] The neutral Tb(III) complex **[Tb·1]** behaves as such a logic gate, reading ionic and molecular inputs, specifically the presence of H^+ and the absence of oxygen. The output is a delayed lanthanide emission with the advantages of long-lived emission, long wavelengths, and line-like emission bands, leading to a large signal-to-noise ratio and a high signal quality. Tb(III) was chosen since it has previously been shown that Tb(III) complexes with a sensitizing chromophore possessing a triplet energy of ca. 250−260 kJ mol^{-1} are susceptible to quenching by O_2.[22] As such, **[Tb·1]** is in fact a chemosensor for O_2 in an acidic environment, and O_2 may therefore be considered as a (molecular) logic gate input.

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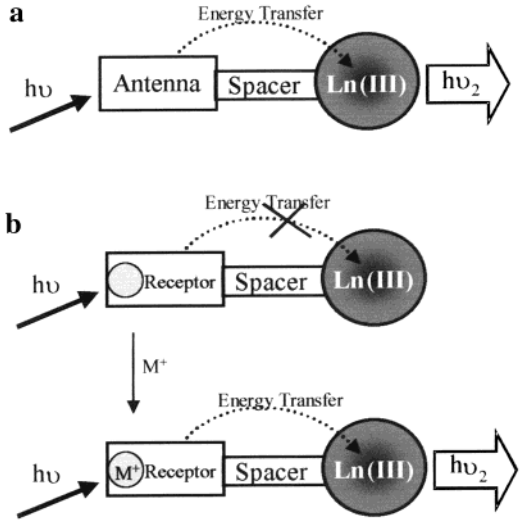
Scheme 1. (a) Schematic Representation of Antenna Connected to a Macrocyclic Lanthanide Emitter, Showing the Sensitization and Emission from the Lanthanide Ion Ln(III) after Excitation of the Antenna, and (b) Excitation of the Lanthanide Ion Now Dependent on the State of the Receptor[a]

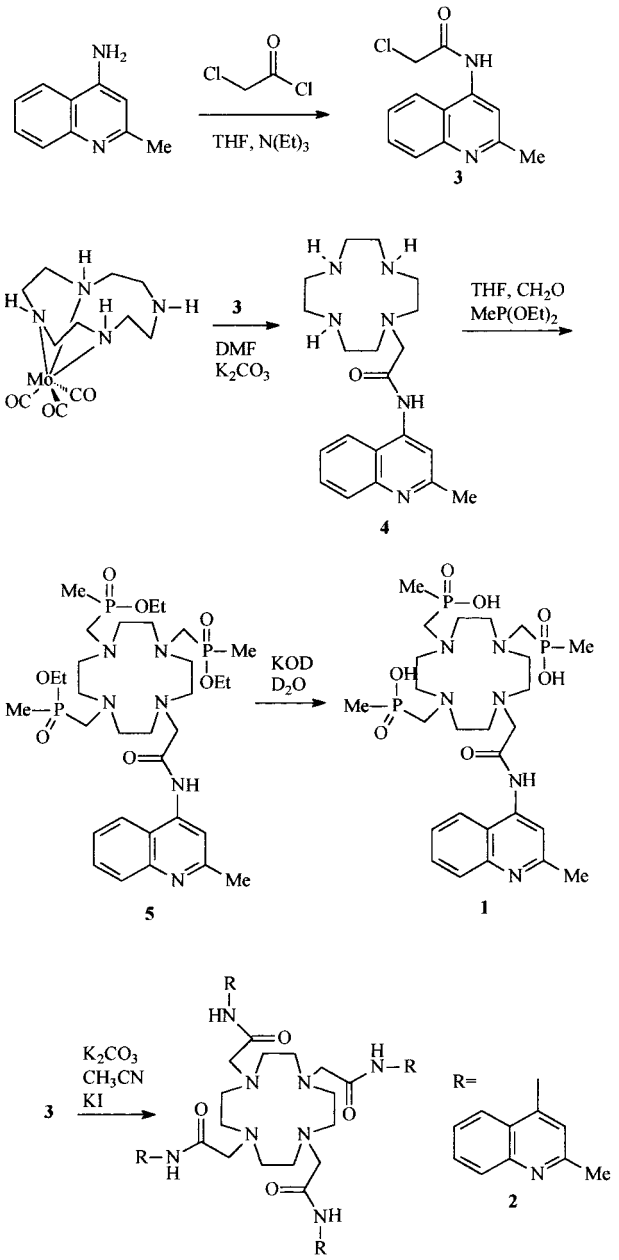


[a] In the example shown, a cation must be complexed to the receptor for an efficient sensitization.

Results and Discussion

Ligands **1** and **2** are derived from 1,4,7,10-tetraazacyclododecane (cyclen), but such eight-coordinated derivatives form kinetically and thermodynamically stable complexes with lanthanide ions, possessing low hydration numbers $q \leq 1$ (the number of coordinated water molecules).[18,23] These complexes also possess adequate water solubility (submillimolar). Lanthanide ions are in general photophysically inert due to their low molar absorptivities[24] and large energy gaps between the emissive and ground states.[25] However, the emissive states, $^5D_0$ and the $^5D_4$ for Eu(III) and Tb(III), respectively, can be populated indirectly by using a sensitizing "antenna", that is, a chromophore connected to cyclen via a covalent spacer which transfers its own excited-state energy to the lanthanide ion, Scheme 1a. Population of these emissive states is accomplished if the triplet excited state of the antenna is sufficiently long-lived, and if the triplet (T_1) energy of the antenna is close to those of $^5D_0$ Eu(III) ($E = 17\,200$ cm^{-1}) and $^5D_4$ Tb(III) ($E = 20\,500$ cm^{-1}).[25,26] By carefully choosing the antenna, it is possible to tune the efficiency of the sensitization by selectively populating S_1 (and subsequently T_1) via external perturbation, for instance by using a recognition moiety, sensitive to the presence or absence of a targeted species in solution. The receptor is an intrinsic part of the antenna, and the sensitization mechanism can be switched on by recognition of the ion or molecular species appropriate for the receptor; see Scheme 1b for the recognition of a cation.[18] The quinoline chromophore in **1**−**3** has a high extinction coefficient, and a T_1 energy ($E = 21\,980$ cm^{-1} measured for the protonated form of **3** in glacial ethanol) that is close to those of the Eu $^5D_0$ and Tb $^5D_4$ emissive states; it is therefore suitable for efficient Eu and Tb sensitization. Importantly, the quinoline possesses a simple recognition element since the aryl nitrogen is also a H^+ acceptor and can be used to tune the energy transfer from the antenna. This is achieved by choosing an excitation wavelength that has a low excitation coefficient in alkaline solution (no or relatively small absorption), whereas in acidic solution the excitation coefficient at this wavelength is greatly enhanced due to spectral shifts and concomitant enhancement in energy transfer to the lanthanide ion excited state.

Scheme 2. Synthesis of the α-Chloroamide **3** and the Ligands **1** and **2**



Ligand and Complex Synthesis. The syntheses of ligands **1** and **2** are shown in Scheme 2. The α-chloroamide **3** was made in one step by reacting chloroacetyl chloride with 2-methyl-4-aminoquinoline at −10 °C in dry THF and 1 equiv of NEt_3, followed by acid−base extraction and single recrystallization, to yield off-white solids. Monoalkylation of **3** with a molyb-

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(24) The extinction coefficient is very small for these ions, $\epsilon \approx 1$ [L/mol cm^{-1}], which is related to Laporte forbidden f−f transitions making direct excitation difficult.

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(26) The sensitization mechanism is via inter-system crossing (ISC) from (singlet) S_1 to T_1 of the excited antenna, followed by an intramolecular energy transfer from T_1 to $^5D_0$ and $^5D_4$.

denum tricarbonyl complex of cyclen[27] at 80 °C in DMF and K_2CO_3 yielded **4** after aqueous basic workup, which was reacted (without further purification) with CH_2O and $MeP(OEt)_2$ (4.5 equiv) in refluxing dry THF and in the presence of 4 Å molecular sieves, to give the phosphinoxymethylated product **5**.[28] This intermediate was purified by column chromatography on alumina (gradient elution from CH_2Cl_2 to 5% MeOH/CH_2Cl_2), followed by basic hydrolysis (D_2O, NaOD) at room temperature to yield the octadentate ligand **1**.

The tetrasubstituted ligand **2** was made by reacting the corresponding α-chloroamides with cyclen in a 4:1 ratio under an inert atmosphere in dry DMF at 80 °C for 12 h in the presence of Cs_2CO_3 and KI (4.1 equiv), followed by acid−base extraction and recrystallization to give off-white powders. All products were analyzed using ^{1}H NMR, ^{13}C NMR, IR, electrospray (ES) MS, and elemental analysis or HRMS (ES) accurate mass determination.

The Eu(III), Tb(III), and the Yb(III) complexes of **1** and **2** were made by reacting, in freshly distilled acetonitrile, equimolar quantities of the appropriate ligand and the dried $Ln(CF_3SO_3)_3$ (Ln = Eu, Tb, Yb) salt (2−3 mL per 10 mg of ligand).[29] The resulting solutions were cooled to room temperature and poured into 150 mL of dry ether under viscous stirring. In each case this gave a fine off-white powder which was collected by centrifugation, followed by purification on alumina (gradient elution from CH_2Cl_2 to 10% MeOH:CH_2Cl_2). The ^{31}P NMR spectrum of the ligand **1** showed two well-defined signals, in a ratio of 2:1, at 42.9 and 33.5 ppm, whereas **[Eu·1]** gave a set of three signals in a ratio of 1:1:1 at 95.4, 85.5, and 83.7 ppm.[30] For **[Tb·1]** only two broad signals were observed at 442 and 428 ppm, also in a 2:1 ratio. The ^{1}H NMR of **[Eu·2]** showed signals at 38.2, −5.7, and −9.9 ppm for the ring axial and equatorial protons, and at −15.8 and −20.0 ppm for the α-protons of the pendant arm, consistent with a complex possessing a square antiprismatic geometry with >90% of a single isomeric species.[30] Similar NMR results were observed for the **[Yb·2]** complex.

Absorption and Fluorescence Investigation of the α-Chloroamide 3. The UV−vis absorption spectrum of the α-chloroamide **3** was recorded in water, in the presence of tetramethylammonium perchlorate (2×10^{-2} M) to maintain a constant ionic strength. The absorption spectrum of **3** was highly pH dependent. In alkaline solution an intense absorption band occurred at 298 nm ($\log \epsilon = 3.80$), which shifted upon acidification to 317 nm ($\log \epsilon = 4.18$), with a new band appearing at 261 nm ($\log \epsilon = 4.00$), and with isosbestic points at 296, 253, and 245 nm, Figure 1a. A pH vs absorption titration profile of **3** gave a sigmoidal curve, consistent with a simple ion-binding equilibrium, with a pK_a of 6.0 ± 0.1. Further changes were observed at higher pH corresponding to a pK_a of approximately 10; these changes were too small for accurate pK_a determination. However, potentiometric measurements of **3** showed two distinct pK_a values of 6.18 ± 0.05 and 9.83 ± 0.05, the latter being associated with the deprotonation of the aryl amide nitrogen.

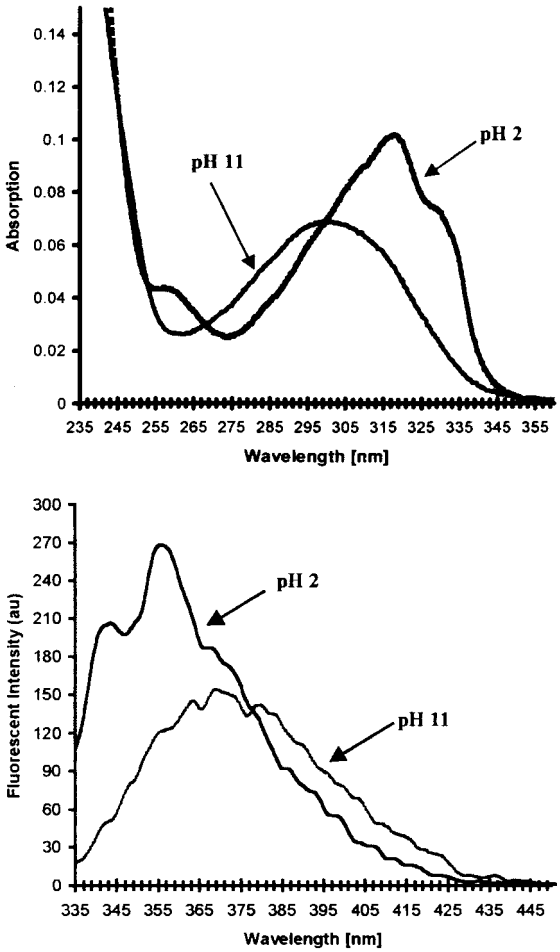


Figure 1. (a) Corrected absorption spectra of **3** at pH 11 and 2.5. (b) The corresponding emission spectra.

The fluorescence spectrum of **3** was also pH dependent, Figure 1b. Upon acidification (from alkaline solution) there was a band shift from 373 to 357 nm, with an isoemissive point at 390 nm, and intensity (hypochromic) changes were observed when the sample was excited at 330 nm. The fluorescence emission was also investigated when the sample was exited at the isosbestic point. The quantum yield of fluorescence (Φ_F)[31] was measured in both acid (pH 2−3) and base (pH 11−12) as 0.064 ± 0.001 and 0.018 ± 0.001, respectively, corresponding with singlet excited-state lifetimes (τ_S) of 0.87 ± 0.01 and 1.12 ± 0.01 ns, respectively.[32] Analysis of the pH vs fluorescence profile
(λ_{ex} = 330 nm, λ_{em} = 357 nm) showed that the major changes in the fluorescence spectra were observed in the alkaline range, Figure 2, corresponding to a process with pK_a = 9.2 ± 0.1. Much smaller changes were seen for the protonation of the quinoline nitrogen moiety (p$K_a \approx 6$).

The fluorescence excitation spectrum of **3** was recorded in various solvents. These showed that the 317 nm band was dependent on solvent polarity, shifting to longer wavelength (H_2O > MeOH > MeCN > Et_2O > CH_2Cl_2) with increasing polarity, an observation consistent with the formation of an internal charge-transfer (ICT) excited state.[33] The effect of pH was also investigated; at pH 10.6 only a small band was

(27) Parker, D. In *Macrocyclic Synthesis, a Practical Approach*; Parker, D., Ed.; Oxford University Press: Oxford, England, 1996.

(28) Pulukkody, K.; Norman, J. T.; Parker, D.; Royle, L.; Broan, C. J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 605.

(29) Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1581.

(30) Aime, S.; Barge, A.; Bruce, J. I.; Botta, M.; Howard, J. A. K.; Moloney, J. M.; Parker, D.; de Sousa, A. S.; Woods, M. *J. Am. Chem. Soc.* **1999**, *121*, 5762. Howard, J. A. K.; Kenwright, A. M.; Moloney, J. M.; Parker, D.; Port, M.; Navet, M.; Rousseau, O.; Woods, M. *Chem. Commun.* **1998**, 1381.

(31) Fluorescence quantum yields were determined using quinine sulfate in aqueous H_2SO_4 as standard (Φ = 0.546): Penedo, J. C.; Mosquera, M.; Rodriguez-Prieto, F. *J. Phys. Chem. A* **2000**, *104*, 7429.

(32) The quantum yields and singlet excited-state lifetimes were measured at $\lambda_{F\,max}$ = 356 and 372 nm for **4**, respectively, using single photon counting, in both aqueous acid and base, by exciting at 330 nm.

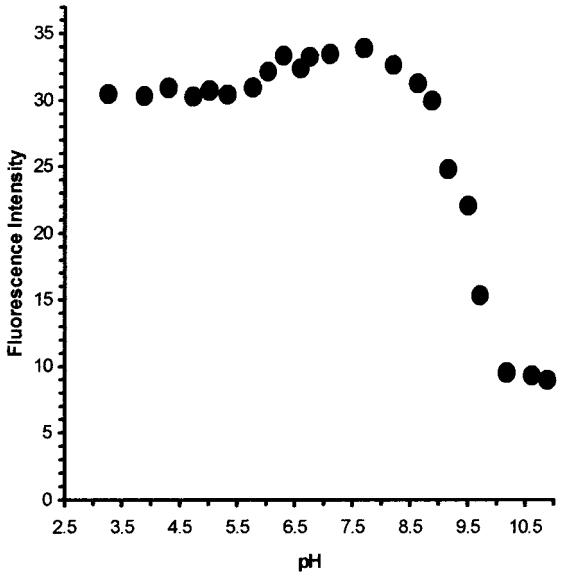
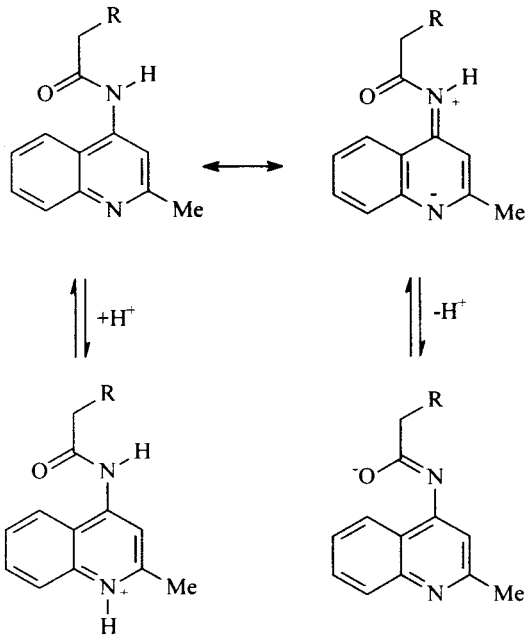


Figure 2. Fluorescence intensity changes for **3** as a function of pH.

Scheme 3. Protonated and Deprotonated Forms of **3**



observed at ~317 nm, but at pH 2.5 this band had increased substantially in intensity and shifted to longer wavelength. The observed sensitivity to pH, in both the absorption and the excitation spectra, is due to the tuning of the ICT excited state, which is modified by protonation or deprotonation of the two nitrogen moieties in **3** as depicted in Scheme 3.

Absorption and Fluorescence Investigation of the Ligands 1 and 2. The ligands **1** and **2** showed pH dependence similar to that seen in the absorption and the fluorescence spectra of **3**. In the absorption spectra of **1**, the major changes were again due to the protonation of the quinoline nitrogen moiety, pK_a = 6.2 ± 0.1, with smaller changes being observed for the deprotonation of the amide. In the fluorescence spectra the opposite effect was observed, with a pK_a = 9.4 ± 0.1 and little change in acidic media. The quantum yield for **2** was somewhat smaller than that seen with **3**. In base it was determined to be 0.0044 ± 0.0005, whereas in acid it was 0.0098 ± 0.0005; the corresponding singlet excited-state lifetimes were too short for accurate determination. The low Φ_F in base can be partly explained by photoinduced electron-transfer (PET) quenching from one of the amine groups of the macrocycle, whereas in acid this quenching pathway is mostly suppressed since the oxidation potential of the amine is increased upon protonation.[2]

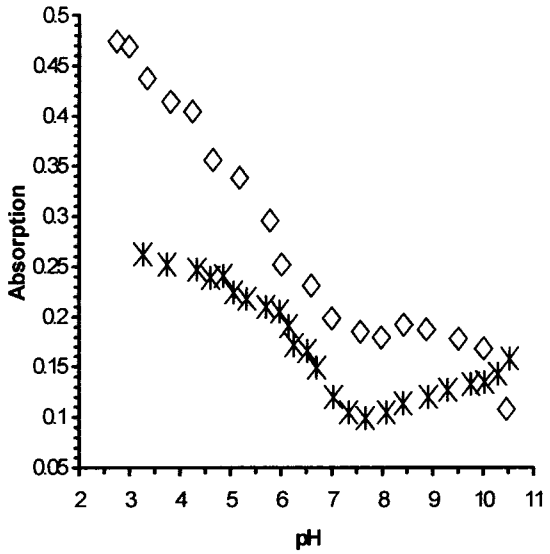


Figure 3. Absorption changes for **[Eu·1]** (∗) and **[Eu·2]** (◇) measured at 318 and 256 nm, respectively, as a function of pH.

Ground and Singlet Excited-State Investigation of [Eu·1] and [Eu·2]. The absorption spectra of the neutral **[Eu·1]** complex and the cationic **[Eu·2]** complex showed λ_{max} at 300 and 299 nm, respectively, and pH-dependent bathochromic shifts upon acidification with λ_{max} = 318 nm (log ϵ = 4.18) and 314 nm for **[Eu·1]** and **[Eu·2]**, respectively, with a new band being formed at 261 (log ϵ = 4.0) and 262 nm. In both cases the protonation of the quinoline nitrogen moiety was the main contributor to the spectral changes. The titration profiles of **[Eu·1]** and **[Eu·2]** measured at 318 and 256 nm, respectively, are shown in Figure 3. From these measurements pK_a values of 6.2 ± 0.1 and 10.3 ± 0.1 were determined for **[Eu·1]**. A single pK_a was difficult to determine for **[Eu·2]** as discussed earlier, but potentiometric titration showed that 4 equiv of base was consumed upon titration of an acidic solution of **[Eu·2]**. These results are summarized in Table 1.

The fluorescence emission spectrum of **[Eu·1]**, Figure 4, revealed a λ_{max} = 375 nm, following excitation at 330 nm in alkaline solution, with Φ_F = 0.026 ± 0.001 and τ_S = 2.16 ± 0.01 ns. Upon acid titration, the intensity of this band dramatically reduced, with the formation of a new band at 357 nm (Φ_F = 0.045 ± 0.001 and τ_S = 0.83 ± 0.01 ns)[32] and an isoemissive point at 375 nm. Similar changes were observed for **[Eu·2]** when excited at 330 nm, with λ_{max} = 377 and an isoemissive point at 375 nm. In each case the fluorescence emission was highly pH dependent in alkaline pH (pH 8−11), while little or no changes were seen in acidic solution, indicating that the protonation of the nitrogen quinoline moiety was not occurring. pK_a values of 9.6 ± 0.1 and 9.4 ± 0.1 were determined for **[Eu·1]** and **[Eu·2]**, respectively, for the changes at 357 nm. The emission properties of **[Eu·1]** were also investigated by exciting the complex at 310 nm and monitoring the intensity at 375 nm. Again the deprotonation of the aryl amide nitrogen was the main contributor to the overall emission changes. However, unlike the case for excitation at 330 nm, the intensity of the 372 nm band

(33) Valeur, B.; Bourson, J.; Pouget, J.; Keschke, M.; Ernsing, N. P. *J. Phys. Chem.* **1992**, *96*, 6545. Valeur, B. In *Fluorescent Biomolecules: Methodologies and Applications*; Jameson, D. M., Reinhart, G. D., Eds.; Plenum: New York, 1989.

Table 1. Various Physical Parameters Measured for the Eu(III) Complexes of **1** and **2**

parameters	**[Eu·1]**[a]	**[Eu·2]**[b]
λ_{abs}/base (nm)	300	299
	261	262
log ϵ/base (L/mol cm)	3.82	
λ_{abs}/acid (nm)	318	319
	261	262
log ϵ/acid	4.2	
	4.0	
λ_{Flu}/base[b] (nm)	375	377
λ_{Flu}/acid[b] (nm)	357	356
$\lambda_{Eu(III)}$ (nm)	581	581
	593	594
	615	617
	624	652
	654	687
	682	701
	702	
Φ_F/base[c]	0.026	
Φ_F/acid[c]	0.045	
τ_S/base (ns)[d]	2.16	
τ_S/acid (ns)[d]	0.83	
$\tau_T(H_2O)$/acid[e] (ms)	0.71	0.55
$\tau_T(D_2O)$/acid[e] (ms)	1.98	1.55
q^{Eu}[f] (q uncorrected)	0.8 (1.07)	0.8 (1.05)
Eu EF[g]	~250	34
pK_a[h]	6.2	~6
	10.3	
pK_a[i]	9.4	9.4
pK_a[j]	5.9	~5.8

[a] Measured in water in the presence of 1×10^{-2} M tetramethylammonium perchlorate to maintain constant ionic strength. [b] Measured at longest wavelength. [c] Measured at λ_F. [d] Excitation at 330 nm and observing the decay at λ_F max. [e] Measured by excitation at 330 nm and observing the single-exponential decay at 594 nm. Calculated from the rate constant of deactivation of the Eu(III)* (±10%), values not shown. [f] Calculated using $q^{Eu} = 1.2(\Delta k_{corr})$, where $\Delta k_{corr} = (k_{H_2O} - K_{D_2O}) - 0.25 - 0.075x$, in which x = number of bound amide NH oscillators.[39] [g] Eu(III) emission enhancement factors ("ON" vs "OFF" state). [h] Measured for the changes in absorption. [i] Measured for changes in fluorescence (see *b*). [j] Measured using changes in Eu(III) emission ($\Delta J = 1$).

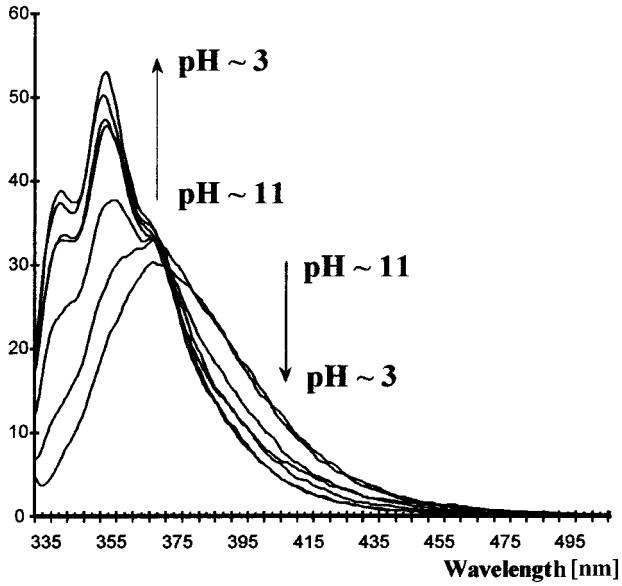


Figure 4. Fluorescence spectra of **[Eu·1]** as a function of pH: 10.7, 10.1, 9.5, 9.1, 8.4, 7.5, 3.8.

increased in alkaline solution rather than decreasing (cf. 357 nm band), Figure 5. From these changes a protonation constant pK_a of 9.4 ± 0.1 was determined. The changes in the pH 3−8 range were too small for accurate pK_a analysis. The fluorescence

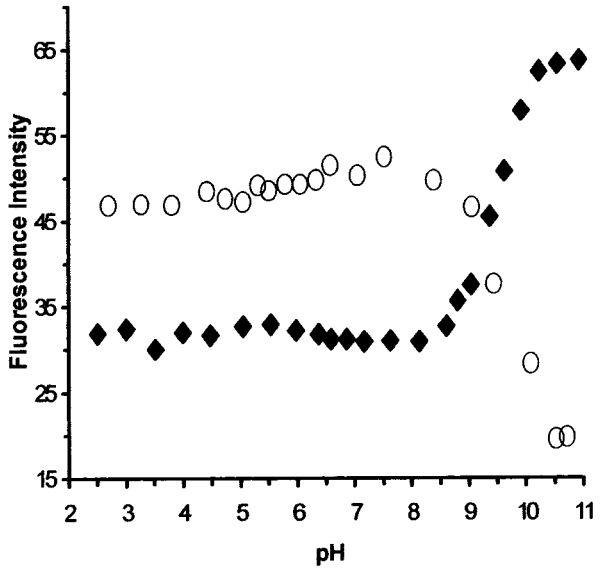


Figure 5. Fluorescence changes as a function of pH when excited at 310 nm and monitoring the intensity at 375 (○), and when excited at 330 nm and monitoring the intensity at 372 nm (◆).

excitation spectrum of **[Eu·1]** was also investigated as a function of solvent polarity and pH. Results were observed similar to those observed previously with **3**; i.e., the excitation spectrum was solvent polarity dependent, while the 314 nm excitation band was "switched on" upon acidification.

Delayed Europium Luminescence Studies of [Eu·1] and [Eu·2] as pH Chemosensors. The most intriguing pH dependence was seen in the delayed Eu(III) luminescence emission spectra of **[Eu·1]** and **[Eu·2]**. The Eu(III) emission of **[Eu·1]**, when excited at 330 nm in alkaline solution (under ambient conditions; room temperature and *aerated* solution) in the range of 550−720 nm, was found to be of low intensity and was independent of pH above pH 10. The emission can thus be said to be "*switched off*" in alkaline solution. However, the Eu(III) emission intensity was gradually enhanced, with increasing acidity, appearing as well-separated emission bands at 581, 593, 615, 624, 654, 686, and 702 nm, representing the deactivation of the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2, 3, and 4) ground states, with at least a 250-fold luminescence enhancement for $\Delta J = 1$ and a Stokes shift of 250−370 nm (for each of the $^5D_0 \rightarrow {}^7F_J$ bands), Figure 6. The relative intensity of each band is determined by the Franck−Condon overlap of the two energy levels $^5D_0 \rightarrow {}^7F_J$.[25] For **[Eu·1]** the $\Delta J = 1$ transition showed the largest intensity changes, but the hypersensitive transitions $\Delta J = 2$ and 4 are also significantly enhanced (switched on), indicating that any of these three bands can be used for observing the pH changes. The lifetime in aqueous (τ_{H_2O}) alkaline solution of the Eu(III) emission of **[Eu·1]** was too short to measure accurately with the available instrumentation, but at pH 1.8 τ_{H_2O} was measured to be 0.71 ms. This significant "off−on" switching was assigned to the protonation of the quinolyl nitrogen moiety, as is evident from the Eu(III) emission vs pH profile shown in Figure 7, which showed a sigmoidal curve in accordance with simple ion-binding equilibria extending over 2 pH units. From these changes a pK_a of 5.8 ± 0.1 was determined, indicating that the Eu(III) emission was signaling the protonation of the remote antenna, a feature not seen in the fluorescence emission spectrum when excited at 330 nm. Thus, the sensitization of the Eu excited state is greatly enhanced by protonation, giving rise to a large increase in the Eu(III) emission.

These measurements were repeated by exciting **[Eu·1]** at the isosbestic point and at 310 nm. In these cases the Eu(III)

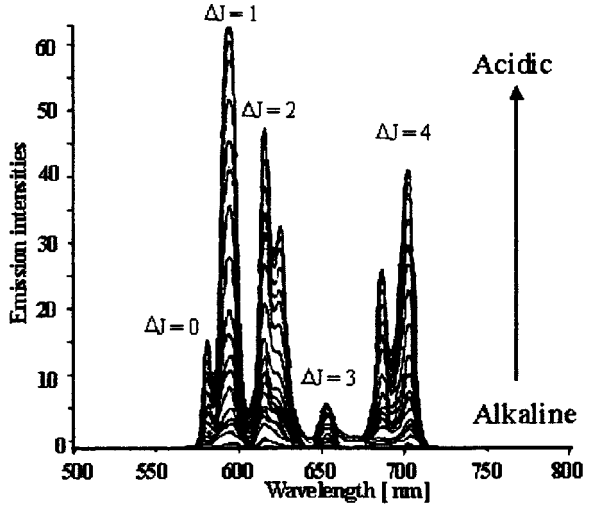


Figure 6. Changes in the Eu(III) luminescence emission of **[Eu·1]** at 593 nm ($\Delta J = 1$) when excited at 330 nm, upon addition of acid, showing the "switching on" of the emission with increasing acidity in the pH range of 11.4−2.7.

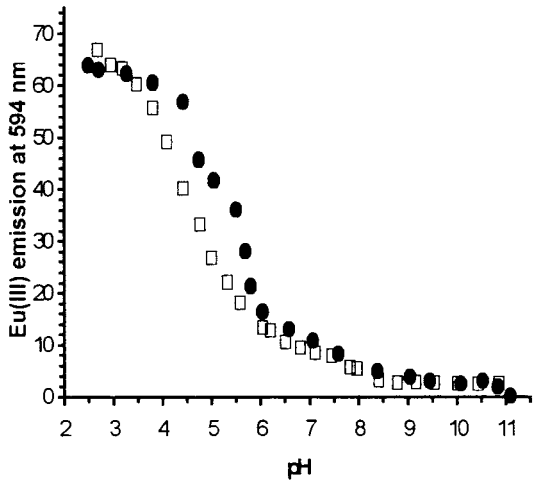


Figure 7. Sigmoidal pH dependence for the lanthanide metal emission of both **[Eu·1]** (●) and **[Eu·2]** (□).

enhancement factor was much smaller than that seen when the sample was excited at 330 nm, indicating that the suppression of any active (and competitive) PET from the singlet excited state of the antenna to the Eu(III) metal ion following protonation was contributing by a factor of 3 to the overall luminescent enhancements.[34] The large emission enhancements are thus more likely due to increased ease of populating the S_1 and subsequently the T_1 excited states of the quinoline chromophore at 330 nm in acidic solution versus that in alkaline solution.[35] The protonation of the quinoline nitrogen moiety, as previously seen in the absorption and the excitation spectra, is thus mirrored in the Eu(III) emission spectrum. Similar changes have been defined for the protonation of a sensitizing phenanthraidine moiety.[36]

The pH dependence of the Eu(III) emission for the cationic complex **[Eu·2]**, Figure 8, was similar to that of **[Eu·1]**. In

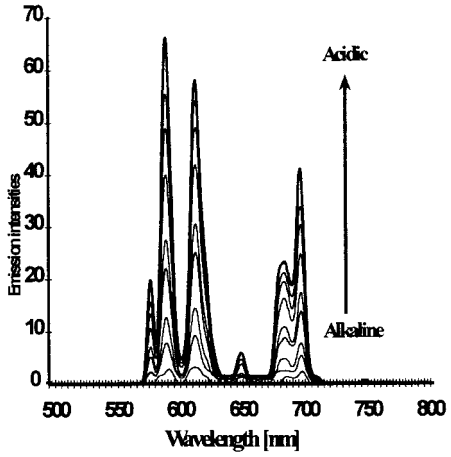


Figure 8. Changes in the Eu(III) luminescence emission of **[Eu·2]** at 593 nm ($\Delta J = 1$) when excited at 330 nm, upon addition of acid, showing the "switching on" of the emission with increasing acidity in the pH range of 10.9−2.7.

alkaline solution the emission was switched off, but it was switched on at low pH. The largest emission enhancements were seen for the $\Delta J = 1$, 2, and 4 transitions with much smaller changes in the $\Delta J = 0$ and 3. The luminescent enhancement factor was also smaller, ca. 30, for $\Delta J = 1$. The pH vs intensity profile of **[Eu·2]**, Figure 7, showed an emission which was "switched on" over a broader pH range (pH 6.5−2.5) than in **[Eu·1]**. It may be noted that switching occurred at ca. 1 pH unit below that of **[Eu·1]**. This may be interpreted as indicating a successive protonation of all the four quinolines (with different pK_a values); these were difficult to determine individually, but a pK_a = 5.8 was estimated as a reasonable average. Multistep protonation was confirmed by potentiometric titration. In addition to the large emission changes, a small inflection in the metal-based emission was apparent at ca. pH 7 (Figure 7). This is possibly not a ligand-based feature and may be due to the deprotonation of a proximate water molecule coordinated to the metal complex, fulfilling its high coordination requirements.[37] Such observations have previously been reported for related cyclen systems.[38] For **[Eu·1]**, a similar inflection was seen around pH 8.5. The emission lifetime for **[Eu·2]** at pH 1.8 was 0.55 ms, somewhat smaller than that seen for **[Eu·1]** (0.71 ms). In D_2O, the lifetimes (τ_{D_2O}) for **[Eu·1]** and **[Eu·2]** were measured to be 1.98 and 1.55 ms, respectively, which are longer than those in water, due to the decreased vibrational deactivation by O−D as compared to O−H oscillators.[39] This behavior is consistent with an overall hydration state $q = 0.8$ for both **[Eu·1]** and **[Eu·2]** (after compensating for vibrational quenching by closely diffusing energy-matched OH oscillators).[21,40]

The pH dependence of the cationic **[Yb·2]** complex was very different from that of the Eu(III) complexes. The absorption and the fluorescence properties of **[Yb·2]**, however, were similar to those observed with Eu(III). Yb(III) complexes are known to emit in the near-infrared following either direct or sensitized

(34) de Silva, A. P.; Gunaratne, H. Q. N.; Rice, T. E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2116.

(35) It is also notable that the Φ_F and τ_S for **[Eu·1]** are smaller than those for **4**, but the Φ_F is much larger than that for **2**. Because of this the population of the T_1 might be more efficient than in the case of **[Eu·1]** than **[Eu·2]**. However, these features were not investigated any further.

(36) Parker, D.; Senanayake, K.; Williams, J. A. G. *Chem. Commun.* **1997**, 1777. Parker, D.; Senanayake K.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2129.

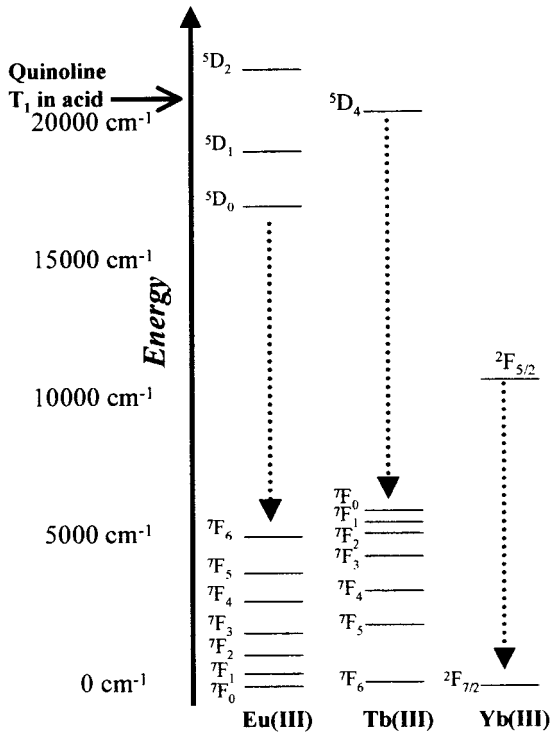
(37) Parker, D. *Coord. Chem. Rev.* **2000**, *205*, 109.

(38) Aime, S.; Barge, A.; Botta, M.; Parker, D.; De Sousa, A. S. *J. Am. Chem Soc.* **1997**, *119*, 4767.

(39) Dickins, R. S.; Parker, D.; de Sousa, A. S.; Williams, J. A. G. *Chem. Commun.* **1996**, 697.

(40) The effect of anion quenching on the Eu(III) emission of **[Eu·1]** was also investigated. At pH 1.85 (fully protonated quinoline) and in the presence of 0.01 M $(CH_3)_4NClO_4$, the Eu(III) emission was unaffected (after dilution correction) upon addition of NaCl or $NaNO_3$ solution (final concentration of 0.2 M and 0.1 M Cl^- and NO_3^- respectively). It may be concluded that Cl^-, which has been shown to quench the singlet excited states of N-alkylated quinolines (via an electron-transfer mechanism), was not observed to affect the protonated form of **[Eu·1]**.

Scheme 4. State Energies for the Protonated Form of the Quinoline **3** and the Eu(III), Tb(III), and Yb(III)



excitation of the $^2F_{5/2}$ state of Yb(III).[41] Luminescence is observed around 980 nm associated with the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition.[41,42] However, emission from **[Yb·2]** showed no pH dependence, unlike that from **[Eu·1]** and **[Eu·2]**. This is most likely due to the fact that the energy of the $^2F_{5/2}$ state (E = 10 300 cm^{-1})[25] is much lower than that of the T_1 (E = 21 980 cm^{-1}) of the antenna; the energy gap between the T_1 and the $^2F_{5/2}$ states is too large for selective tuning of the Yb(III) emitting state; ΔE = 11 680 cm^{-1}.[25] The energy gaps for the deactivation of Eu(III), Tb(III), and Yb(III) emitting states to the relevant ground states are shown in Scheme 4. The above results show that the complexes **[Eu·1]** and **[Eu·2]** display dual luminescent behavior dependent on pH, whereas **[Yb·2]** shows no such dependence. The fluorescence emission spectra of [**Eu·1]** and **[Eu·2]** are independent of pH in the range of 3−7, while showing significant pH dependence in alkaline solution, following excitation at 330 nm. The Eu(III) emission possesses pH sensitivity distinctly different from that of the fluorescence emission, mirroring the pH changes observed in the absorption spectrum in the pH range of 3−7. These Eu(III) complexes are thus interesting candidates for measuring pH in competitive media, since by simply changing the observation wavelength and the time gating, changes spanning 10 pH units can be observed.

[Tb·1] as a Logic Gate: Mimicking the INH Logic Function. The **[Tb·1]** complex also showed a pH dependence similar to that of the **[Eu·1]** complex. Under alkaline and ambient conditions (non-degassed solution), the Tb(III) emission was only weak, observed at 491.5, 547.5, 588.0, and 623 nm,

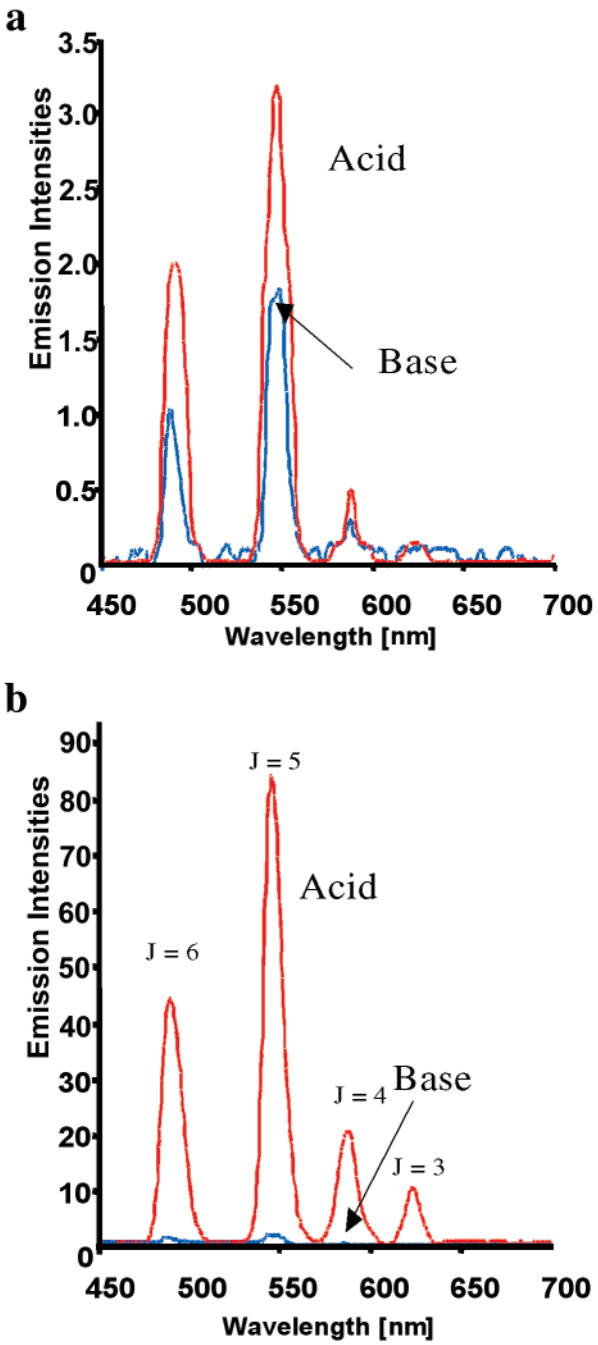


Figure 9. Tb(III) metal emission dependence of **[Tb·1]** when excited at 330 nm, displaying the output of the molecular INH logic gate: (a) in aerated acidic solution (red; pH 2.9), and in aerated alkaline solution (blue; pH 11); (b) in degassed acidic solution (red; pH 2.9), and in degassed alkaline solution (blue; pH 11). High-intensity output is achieved only under the conditions of (i) low pH and (ii) degassed solution (b). Note the difference in the intensity scales for the two graphs; 0−3.5 for (a) vs 0−90 for (b).

and the emission lifetime was 0.39 ms for the deactivation of the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, and 3; Stokes shifts of 160−300 nm for each of the Tb $^5D_4 \rightarrow {}^7F_J$ bands). However, upon addition of an acid (CF_3CO_2H, pH 2.9), the Tb(III) emission intensity was enhanced in an analogous way to the Eu(III) emission, but by a factor of only ca. 1.7 (measured for ΔJ = 5), Figure 9a, much smaller than that seen for the Eu(III) emission in **[Eu·1]** (factor of ca. ∼250). The fluorescent emission changes were more apparent, with both a hypsochromic shift (373−357 nm) and intensity changes (two shoulders at 373 and 357 nm), and

(41) Beeby, A.; Faulkner, S. *Chem. Phys. Lett.* **1997**, *266*, 116. Faulkner, S.; Beeby, A.; Dickins, R. S.; Parker, D.; Williams, J. A. G. *J. Fluorescence* **1999**, *9*, 45.

(42) Steemers, F. J.; Verboom, W.; Hofstraat, J. W.; Geurts, F. A. J.; Reinhoudt, D. N. *Tetrahedron Lett.* **1998**, *39*, 7583. Beeby, A.; Dickins, R. S.; Faulkner, S.; Parker, D.; Williams, J. A. G. *Chem. Commun.* **1997**, 1401. Werts, M. H. V.; Hofstraat, J. W.; Geurts, F. A. J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1997**, *276*, 196.

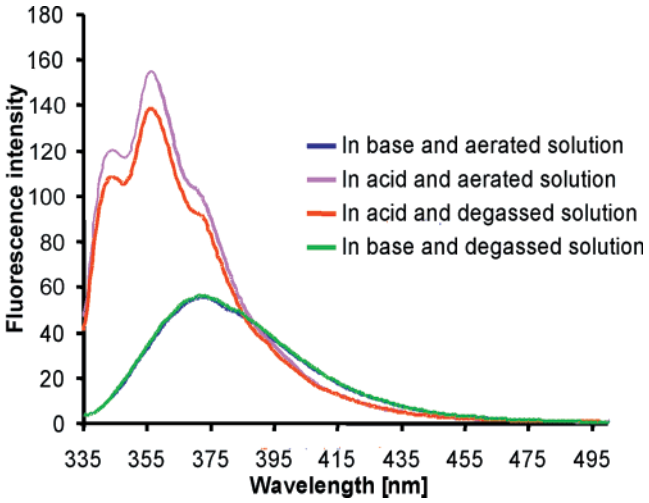


Figure 10. Fluorescence emission changes as a function of pH for **[Tb·1]** when excited at 330 nm, in the four possible combinations of aerated/degassed and acidic/basic solutions. These output pattern does not correspond to the INH function.

Table 2. Emission Intensities for **[Tb·1]** as a Function of Various Combinations of Acid, Base, and O_2

chemical input	Tb(III) intenisty[a,b]	gate output[c]
base + O_2[d]	~1.7	0
acid + O_2[e]	~3.2	0
base − O_2	86	1
acid − O_2	~1.7	0

[a] Measured in water in the presence of 1×10^{-2} M tetramethylammonium perchlorate to maintain constant ionic strength. [b] Measured at ΔJ=5. [c] Representing logic gate output in accordance with Figure 11. [d] Measured at pH 11.5 in aerated solution. [e] Measured at pH 2.9, $[O_2] < 10^{-6}$ M after several cycles of degassing using "freeze−pump−thaw" technique.

an isoemissive point was observed at 387 nm upon acidification, Figure 10. Table 2 summarizes these and related results.

As mentioned earlier, the Tb(III) emissions of complexes with a sensitizing chromophore possessing a triplet energy of ca. 250−260 kJ mol^{-1} are susceptible to quenching by O_2.[22] However, when the above measurements were repeated in degassed solution ("freeze−pump−thaw", $[O_2] < 10^{-6}$ M) at high pH, the Tb emission spectra and lifetime, $\tau_{Tb} = 0.39$ ms, did not change. However, in degassed acidic solution, the Tb(III) emission exhibited a greater than 50-fold luminescent enhancement for the $\Delta J = 5$ transition, Figure 9b. Thus, it may be concluded that the protonation of the quinoline nitrogen was enhancing the population of the $^5D_4$ state in degassed solution. The emission lifetime $\tau_{Tb} = 0.98$ ms was also greatly increased from that seen in the aerated solution. The large differences in enhancement factors are due to competitive quenching of the T_1 state of the antenna by O_2. The energy of the T_1 state is close to that of the $^5D_4$ state ($\Delta E = 1480$ cm^{-1}), so both back and forward energy transfer can take place between the two states (T_1 and $^5D_4$). Quenching of the quinoline T_1 by O_2 reduces the population of the $^5D_4$ state since the intramolecular energy-transfer step has now to compete with collision quenching by O_2, and Tb(III) emission is "switched off". Upon degassing the sample, this quenching process is removed, and the Tb(III) sensitization is "switched on" with concomitant enhancement in the Tb(III) emission. The fluorescence spectra of **2** were also pH dependent, similar to those of **[Tb·1]**, Figure 10, with both a hypsocromic shift from 373 to 357 nm (isoemissive point at 387 nm) and intensity changes observed upon acidification under ambient conditions; fluorescence was only slightly affected by the removal of O_2.

A	B	X
0	0	0
0	1	0
1	0	1
1	1	0

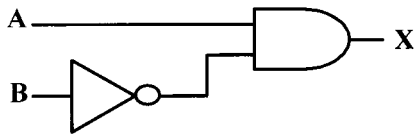


Figure 11. (a) Truth table for the INH logic function; input A corresponds to H^+, while B corresponds to O_2, and X is the output signal (Tb(III) emission). (b) Conventional representation of the INH− logic gate; an active output signal is obtained when A = 1 and B = 0; i.e., the Tb(III) emission is "switched on" only in the absence of O_2 and the presence of H^+.

From these results it is apparent that the Tb(III) emission is governed by two inputs, namely H^+ and O_2. The Tb(III) emission is "switched on" only in the *presence* of H^+ and *absence* of O_2 and no other combinations: (i) in the presence of a base and absence of O_2, (ii) in the presence of base and O_2, and (iii) in the presence of acid and O_2, based upon the difference in luminescent enhancement factors, Table 2 (1.7 vs 50). This behavior can be conveniently described using the two-input logic notation $A \wedge B'$, Figure 11, where A and B represent the two inputs H^+ and O_2, respectively, and X represents the Tb(III) emission. This is the inhibit (INH) logic function, one of 16 (two-input) logic operations which can be described by truth tables, and it is a particular integration of the AND and NOT logic functions. Other logic gate operations have recently been demonstrated, such as the YES (ID), AND, OR, and NOT functions by deSilva, and the XOR by Balzani and Stoddart.[5,13] The remaining logic functions are the (trivial) ONE and ZERO gates, the output being 1 and 0, respectively, regardless of the input, the two-input NAND, NOR, and XNOR gates that satisfy commutation, and the INH and the IMP gates which do not satisfy commutation.[14] A three-input INH function has previously been demonstrated by de Silva et al., but this is the first time that the more fundamental two-input analogue has been demonstrated.[16]

Even though practical integration of such devices to yield computationally useful machines is not imminent,[10] the availability of a full suite of molecular devices corresponding to fundamental logic operations may facilitate such a development.[43] We set out to demonstrate the feasibility of employing the lanthanide ion complexes as such logic gate mimics, and **[Tb·1]** is the first example of such a two-input INH logic gate. Such devices could be of importance in the future once efficient "spatially defined" addressing methods have been devised. Our results constitute a significant development to molecular computation,[17] not least since the current silicon-based computer chips are expected to reach their physical limits soon.[44]

In conclusion, we have made a number of logic devices based upon lanthanide conjugates derived from cyclen. Protonation selectively populates the excited states of both the Eu(III) and

(43) For a discussion of the current state of the art of molecular computing, see: Ball, P. *Nature* **2000**, *406*, 118. Reed, M. A.; Tour, J. M. *Sci. Am.* **2000**, June, 68. Brown, B. *New Scientist* **1999**, 28 Aug, 39.

(44) Muller, D. A.; Sorsch, T.; Moccio, S.; Baumann, F. H.; Evans-Lutterodt K.; Timp, G. *Nature* **1999**, *399*, 759.

Tb(III) complexes. This is reflected in their enhanced emission properties. The Eu(III) complexes **[Eu·1]** and **[Eu·2]** are all highly sensitive to pH, and all display distinct pH switching ranges: the fluorescence emission spectra show a pronounced pH dependence in alkaline solution, whereas the delayed Eu(III) emission is enhanced by several orders of magnitude, i.e., "switched on" in acidic solution. These devices can thus be considered as luminescent chemosensors for H^+ in competitive media.[45] The Tb(III) emission of complex **[Tb·1]** is also pH dependent, but it is different from that of Eu(III), since the emission is dependent on the presence or the absence of O_2: the Tb(III) emission is only switched on in the *presence* of H^+ and the *absence* of O_2, mimicking the function of the 2-bit INH logic gate $A \wedge B'$.

Experimental Section

Reagents and Solvents. Reagents (obtained from Aldrich) and solvents were purified using standard techniques. Solvents were dried over an appropriate drying agent before use: CH_3CN and $N(CH_2CH_3)_3$ over CaH_2, THF over Na with benzophenone as an indicator; DMF was used directly from a "sure-seal" bottle. 1,4,7,11-Tetraazacyclododecane is commercially available from Strem Chemicals and was used as received.

Spectroscopy. ^1H and ^{13}C NMR spectra were recorded using Varian VXR400, Varian Mecury-200, Varity Unity 300, and Varian Unity Inova-500 spectrometers. Mass spectra were recorded using a VG Platform II electrospray mass spectrometer with methanol as a carrier solvent. Elementary analyses were determined using a Carlo ERBA 1106 instrument. Accurate masses were measured by EPSRC National MS Service at the University of Swansea. UV absorption spectra were recorded at 20−25 °C using a UNI-CAM (UV2) spectrometer and on a Shimadzu UV-2401PC. Fluorescence, excitation emission spectra, lanthanide emission spectra, fluorescence quantum yields, and lanthanide excited-state lifetimes were obtained using a Perkin-Elmer LS50B. Singlet excited-state lifetimes were measured using an SPC FL900 Edinburgh Instrument λ_{ext} 337 with a N_2-filled lamp. All spectra were measured by excitation at the given wavelength and were corrected for the wavelength dependence of the photomultiplier tube. Throughout the titration experiments, the ligand and complex solution were in the concentration range of $(5-7) \times 10^{-5}$ M. Aliquots of 3 cm^{-3} were taken for absorption and luminescence measurements in standard quartz cuvetts with a 1 cm path length. Determination of p*K* values was done according to published procedures.[46] Potentiometric measurements were carried out at 298 K using a Molspin 1 mL autotitrator equipped with a calibrated Carmin microelectrode to measure pH. Data were analyzed using Superquad and gave pK_a values within 0.02 pH unit.[47]

Chloro-*N*-(2-methyl-4-quinolyl)ethanamide (3). 4-Amino-2-methylquinoline (3 g, 0.0189 mol) and triethylamine (1.92 g, 0.0190 mol) were dissolved in dry dichloromethane (CH_2Cl_2) (60 mL), and the mixture was cooled to −10 °C in an ice/salt bath. To this mixture, over a period of 20 min, was added chloroacetyl chloride (2.134 g, 0.0190 mol) in 20 mL of dry CH_2Cl_2. The resulting suspension was stirred for a further hour at −10 °C and for 2 h at room temperature under an inert atmosphere. The resulting triethylammonium chloride was filtered off, and the organic layer was washed once with 1.0 M HCl solution (20 mL). The aqueous acid solution was washed with CH_2Cl_2 (25 mL), the pH brought to 7.5 using $NaHCO_3$, and the solution extracted three times with CH_2Cl_2 (30 mL). The combined organic layers were dried over K_2CO_3, and the solvent was removed under reduced pressure to give **3** as a yellow oil in 60% yield which crystallized upon standing. Calculated for $C_{12}H_{11}N_2OCl$ (%): C, 61.41; H, 4.72; N, 11.93. Found for $C_{12}H_{11}N_2OCl$: C, 59.98; H, 4.70; N, 11.69. δ_H ($CDCl_3$, 200 MHz): 9.14 (1H, bs, N−H), 8.19 (1H, s, Ar−H), 8.07 (1H, d, J = 8.5 Hz, Ar−H), 7.75 (2H, dd, J = 8.0 Hz, Ar−H), 7.56 (1H, t, J = 6.9 Hz, Ar−H), 4.36 (2H, s, CH_2), 2.76 (s, 3H, Ar−CH_3). δ_C ($CDCl_3$, 100.58 MHz): 164.1, 160.1, 148.5, 139.9, 129.9, 129.7, 122.1, 118.5, 111.4, 43.4, 25.8. *m*/*z* (% ES^+): 234.8 (100, M^+), 256.9 (20, M + Na^+), 200.8 (5), 178.8 (5), 162.7(3), 158.8 (20), 148.7 (5), 118.7 (5). ν (oil)/cm^{-1}: 3264, 1679, 1618, 1605, 1560, 1534, 1350, 1121, 780, 755, 531.

1-[*N*-(2-Methyl-4-quinolyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane (4). To a solution of freshly made 1,4,7,10-tetraazacyclododecane−molybdenum tricarbonyl complex (0.37 g, 0.00105 mol) in dry DMF (20 mL) was added under an inert atmosphere Cs_2CO_3 (0.37 g, 0.00105 mol), and the reaction was stirred for 10 min at 80 °C, before addition in one portion of chloro-*N*-(2-methyl-4-quinolyl)-ethanamide (**3**) (0.246 g, 0.00105 mol). The resulting mixture was stirred for a further 2.5 h at this temperature before the reaction was allowed to cool to room temperature. The solvent was removed under reduced pressure, and 1 M HCl (20 mL) was added. This solution was stirred in air for 12 h before the pH was adjusted to 14 using KOH pellets. The resulting green solution was filtered and extracted several times with CH_2Cl_2 (30 mL each time). A pale yellow solution was obtained which was dried over K_2CO_3, and the solvent was removed under reduced pressure to give **4** as a pale yellow oil in 75% yield. Calculated for $C_{20}H_{27}N_6O$: 370.2481. Found for $C_{20}H_{27}N_6O$: 370.2456. δ_H ($CDCl_3$, 200 MHz): 8.34 (d, 1H, J = 8.4 Hz, Ar−H), 8.26 (1H, s, Ar−H), 7.99 (1H, d, J = 8.8 Hz, Ar−H), 7.67 (1H, q, J = 8.4 Hz, Ar−H), 7.47 (1H, t, J = 7.2 Hz, Ar−H), 3.42 (2H, s, CH_2), 2.77 (19H, m, Ar−CH_3 and NH−CH_2−CH_2−NH ring-H). δ_C ($CDCl_3$, 100.58 MHz): 170.88, 159.66,149.94, 148.33, 140.45, 124,98, 123.59, 120.74, 120.17, 118.62, 60.52, 53.54, 47.05, 46.96, 45.65, 25.49. *m*/*z* (% ES^+): 371.11 (20, M^+), 285.5 (4), 251 (8), 229.9 (20), 186.01 (100, M^{2+}), 155.9 (65), 113 (14), 86.87 (15). ν (oil)/cm^{-1}: 3210, 2925, 2826, 1686, 1618, 1590, 1560, 1519, 1490, 1457, 1437, 1381, 1366, 1351, 1335, 1270, 1185, 1097, 1061, 985, 751.

1,4,7-Tris-ethyl(2-ethoxymethylphosphinate)-10-[*N*-(2-methyl-4-quinolyl)carbamoyl-methyl]-1,4,7,10-tetraazacyclododecane (5). 1-[*N*-(2-methyl-4-quinolyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane (**4**) (0.59 g, 1.587 mmol) was dissolved in dry THF (30 mL). To this solution was added 4.5 equiv (0.214 g, 7.14 mmol) of paraformaldehyde, and the solution was heated at reflux under an inert atmosphere for 20 min, before addition of 4.5 equiv of methyldiethoxyphosphine (0.972 g, 7.14 mmol). The resulting solution was then stirred and refluxed over 4 Å molecular sieves for a further 12 h. After the solution cooled to room temperature, the excess paraformaldehyde was filtered off and the solvent removed under reduced pressure. The oily residue was dissolved in CH_2Cl_2 (30 mL) and extracted twice with 0.1 M HCl solution (20 mL). The pH of the combined acidic solution was brought up to 13 (using KOH), the solution was extracted three times with CH_2Cl_2 (20 mL) and dried over K_2CO_3, and the solvent was removed under reduced pressure to give **5** as an oil. The product was further purified by column chromatography on alumina (gradient elution from CH_2Cl_2 to 5% MeOH/CH_2Cl_2, R_f = 0.85) to give the product (**5**) as a yellow oil in 66% yield. Calculated for $C_{32}H_{57}N_6O_7P_3$: 730.3501. Found for $C_{32}H_{57}N_6O_7P_3$: 730.3507. δ_H ($CDCl_3$, 200 MHz): 8.18 (2H, m, Ar−H), 7.99 (1H, d, J = 8.4 Hz, Ar−H), 7.66 (1H, t, J = 8.0 Hz, Ar−H), 7.43 (1H, t, J = 8.0 Hz, Ar−H), 3.98 (8H, m, 3 CONCH_2P; CONHCH_2P), 2.68 (25H, m, 16 ring-H, 3 CO−CH_2−CH_3, Ar−CH_3), 1.33 (18H, m, 3 CO−CH_2−CH_3, 3 P−CH_3). δ_C ($CDCl_3$, 50.3 MHz): 170.8, 159.79, 148.38, 140.78, 129.07, 124.84, 124.04, 123.48, 120.49, 120.49, 119.39, 118.89, 118.68, 60.08, 59.96, 59.83, 55.47, 54.74, 54.58, 53.34, 54.26, 54.15, 54.04, 53.39, 53.29,53.01,52.84, 52.68 25.50, 16.51, 14.46, 12.69. δ_P ($CDCl_3$, 101.25 MHz): 51.93, 51.62. *m*/*z* (% ES^+):

(45) Fluorescent chemosensors have been extensively investigated for the detection of physiological species in vitro and in vivo. However, the use of fluorescent chemosensors in vivo has been somewhat restricted by a poor signal-to-noise ratio, due to short-lived (approximately nanoseconds) background emission (autofluorescence) and light scattering from an active biological environment. These problems may be partially overcome by the use of lanthanide-based signal moieties. The advantage of using the Eu(III) emission to report on local pH variations in physiological systems is due to long-lived excited states and long-wavelength emission bands which give rise to high signal quality, since autofluorescence and light scattering are overcome under ambient conditions. Human tissues inefficiently absorb long-wavelength light, and interference from short-lived background emission is minimized, making these systems feasible for ion detection in vivo. Such devices are highly desirable for monitoring, for instance, the changes of pH in the vicinity of cell membranes where pH changes can often be over several pH units: Bissell, R. B.; deSilva, A. P. *J. Chem. Soc., Chem. Commun.* **1991**, 1148.

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371.01 (100, $M^+ + 1$), 753.02 (75, $M + Na^+$), 768.68 (10, $M + K^+$), 690 (4), 675.7 (14), 674.87 (50), 652.91 (70), 638.8 (5), 385.16 (38), 346.12 (50), 312.15 (10), 102.0 (90). ν (oil)/cm^{-1}: 3416, 2979, 2924, 2810, 1697, 1964, 1622, 1603, 1562, 1533, 1444, 1419, 1386, 1333, 1297, 1237, 1187, 1096, 1031, 953, 884, 854, 466, 727, 492.

1,4,7-Tris[ethyl(2-methylphosphinic acid)]-10-[*N*-(2-methyl-4-quinolyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane (1). 1,4,7-Tris[ethyl(2-ethoxymethylphosphinate)]-10-[*N*-(2-methyl-4-quinolyl)-carbamoyl-methyl]-1,4,7,10-tetraazacyclododecane (**5**) (0.20 g, 2.739 mmol) was dissolved in KOD solution (5 mL of 1.37 M) and stirred at room temperature for 12 h. The hydrolysis of the ethyl esters was followed by monitoring the changes in the ^{31}P NMR spectrum. After complete hydrolysis, the pH was adjusted to 5.5 and the solvent removed under reduced pressure. The resulting residue was redissolved in ethanol, and the inorganic salts were removed using a 0.5 μm syringe filter (Milex-LCR 0.5 μm). The solvent of the resulting pale yellow solution was removed under reduced pressure and dried under high vacuum to give **1** as a light yellow oil in 97% yield. Calculated for $C_{26}H_{45}N_6O_7P_3$: 795.1328. Found for $C_{26}H_{45}N_6O_7P_3$: 795.1326. δ_H (CD_3-OD, 300 MHz): 8.17 (1H, d, $J = 8.7$ Hz, Ar−H), 7.81 (1H, t, $J = 8.4$ Hz, Ar−H), 7.80 (1H, d, $J = 8.7$ Hz, Ar−H), 7.54 (1H, t, $J = 8.4$ Hz, Ar−H), 6.55 (1H, s, Ar−H), 3.58 (1H, d, $J = 5.7$ Hz, 1 ring-H), 3.21 (24H, m, 15 ring-H; Ar−CH_3; 3 CONCH_2P; CONHCH_2P; CO*N*HCH$_2$P), 2.53 (3H, s, Ar−CH$_3$), 1.204 (9H, m, PO_2CH_3). δ_C (CD_3OD, 100 MHz): 160.05, 154.59, 140.25, 135.11, 127.40, 124.28, 120.40, 116.66, 103.05, 55, 20, 18, 17, 16. δ_P (CD_3OD, 100 MHz): 42.95, 33.54. *m*/*z* (% ES$^-$): 646.27 (45 M^-), 668.23 (8 Na^+), 684.21 (3 K^+), 647.32 (20), 645.05 (38), 624.6 (12), 576.69 (11), 548.95 (20), 538.85 (22), 474.95 (13), 380.92 (25), 333.15 (5), 333.24 ($M + Na^+/2$), 323.05 (50, $M^-/2$), 322.23 (70, $M^-/2$), 269.00 (100), 222.98 (38), 94.82 (23), 61.87 (28). ν (oil)/cm^{-1}: 3250, 2974, 2935, 2835, 1654, 1603, 1566, 1508, 1451, 1421, 1375, 1295, 1147, 1033, 964, 872, 838, 761, 599.

Europium(III) 1,4,7-Tris[ethyl(2-methylphosphinato acid)]-10-[*N*-(2-methyl-4-quinolyl)-carbamoylmethyl]-1,4,7,10-tetraazacyclododecane ([Eu·1]). 1,4,7-Tris[ethyl(2-methylphosphinic acid)]-10-[*N*-(2-methyl-4-quinolyl)carbamoylethyl]-1,4,7,10-tetraazacyclododecane (**1**) (0.05 g, 0.0775 mmol) was dissolved in dry ethanol (0.1 mL). To this solution was added acetonitrile (8 mL), and the solution was stirred at room temperature for a few minutes before addition of europium triflate [$(CF_3SO_3)_3$Eu] (0.051 g, 0.0852 mmol). The solution was stirred at room temperature for 1 h and then at 50 °C for 1 h. The solvent was then removed under reduced pressure to give an off-white solid. The complexation of the Eu(III) ion was monitored by following the changes both in the electrospray mass spectrum (ES$^-$) and in the ^{31}P NMR spectrum. The product was purified by column chromatography on alumina (gradient elution from CH_2Cl_2 to 10% MeOH/CH_2Cl_2) to give the product **[Eu·1]** as a yellow solid in 50% yield. Calculated for $C_{26}H_{42}N_6O_7P_3Eu$: 795.1328. Found for $C_{26}H_{45}N_6O_7P_3Eu$: 795.1324. δ_H (D_2O, 200 MHz): 26.7, 23.7, 18.7, 13.5 (ring H_{ax}), 10 to −5 (bs, Ar−H; P−CH$_3$, ring H), −6.2, −7.9, −8.6, −9.6, −10.6, −12.8, −13.5, −16.5 (ring H; NCH_2). δ_P (CH_3CN, 101 MHz): 95.4, 85.5, 83.7. *m*/*z* (% ES$^-$): 795.05 (15, M^-), 944.93 (10, CF_3SO_3), 797.25 (3), 796.28 (10), 793.96 (9), 793.03 (5), 472.90 (15), 472.20 (21), 470.64 (100 $CF_3SO_3/2$), 456.79 (40), 399.83 (9), 338.61 (12), 336.69 (55), 320.75 (53), 298.75 (15). ν (solid)/cm^{-1}: 3363.6, 2362, 1651, 1612, 1573, 1522, 1242, 1161, 1054, 1026, 760, 630.

Terbiuim(III) 1,4,7-Tris[ethyl(2-methylphosphinato acid)]-10-[*N*-(2-methyl-4-quinolyl) carbamoylmethyl]-1,4,7,10-tetraazacyclododecane ([Tb·1]). The procedure from **([Eu·1])** was adopted, with the exception that the reaction was boiled under reflux for 12 h, using 7.3 mg (0.0113 mmol) of **1** and terbium triflate [$(CF_3SO_3)_3$Tb] (0.08 g, 0.0113 mmol). The complexation of the Tb(III) ion was monitored by following the changes in the ES$^+$ mass spectrum. The product was further purified by column chromatography on alumina (gradient elution from CH_2Cl_2 to 10% MeOH/CH_2Cl_2) to give the product (**[Tb·1]**) in 55% yield. δ_P (CH_3CN, 101 MHz): 442 (bs), 428 (bs). *m*/*z* (% ES$^-$): 802.94 (15, $M^+ + 1$), 826.30 (13, $M + Na^+$), 802.34 (10, M^+), 677.49 (4), 550.66 (4), 549.22 (18), 508 (8), 466 (32), 413 (56, $M + Na^+/2$), 402.23 ($M^+/2$), 393.15 (18), 261.04 (24), 216.75 (55), 215.0 (100).

1,4,7,10-Tetrakis[*N*-(2-methyl-4-quinolylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (2). 1,4,7,10-Tetracyclododecane (0.1 g, 0.58 mmol) was dissolved in dry DMF (5 mL) and stirred under an inert atmosphere. To this solution were added 4 equiv of Cs_2CO_3 (0.82 g, 2.32 mmol) and KI (0.39 g, 2.32 mmol). After the solution was stirred at room temperature for 10 min, 4 equiv of chloro-*N*-(2-methyl-4-quinolyl)-ethanamide (**3**) was added, and the resulting mixture was heated at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into HCl (20 mL, 0.1 M) and extracted twice with $CHCl_3$, before adjustment of the pH to 7 using K_2CO_3. The aqueous layer was then extracted twice with $CHCl_3$, the combined organic layers were dried over K_2CO_3, and the solvent was removed under a reduced pressure to give **2** as a white solid in 41% yield. Calculated for $C_{56}H_{60}N_{12}O_4$: 964.4860. Found for $C_{56}H_{60}N_{12}O_4$: 964.4856. δ_H (CD_3-OD, 300 MHz): 8.14, (4H, d, $J = 8.1$ Hz, Ar−H), 7.73 (4H, m, Ar−H), (8H, d, $J = 8.3$ Hz, Ar−H), 7.56, (4H, m, Ar−H), 7.30 (4H, t, $J = 7.43$ Hz, Ar−H), 4.1−2 (bs, 16H, ring-H), 3.31, (8H, s, NCH_2CON), 2.10 (12H, s, Ar−CH_3). δ_C (CD_3OD, 100.57 MHz): 172.0.70, 172.00, 159.34, 159.19, 147.96, 147.88, 129.609, 129.40, 127.390, 125.30, 125.88, 125.29, 121.61, 113.50, 112.95 57 (m), 23.46, 23.06. *m*/*z* (% ES$^+$): 965.15 (2 M^+), 987.28 (100, $M + Na^+$), 1003.01 (15, $M + K^+$), 804.79 (3). ν (solid)/cm^{-1}: 3250, 2972, 2825, 1697, 1604, 1623, 1563, 1534, 1498, 1413, 1382, 1305, 1270, 1189, 1105, 999, 948, 870, 761.

Europium(III) 1,4,7,10-Tetrakis[*N*-(2-methyl-4-quinolylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane Tri(trifluoromethylsulfonate) ([Eu·2]($CF_3SO_3^-$)). 1,4,7,10-Tetrakis[*N*-(2-methyl-4-quinolyl-carbamoylmethyl]-1,4,7,10-tetraazacyclododecane (**2**) (30 mg, 0.031 mmol) was dissolved in dry acetonitrile (2 mL), and 1 equiv of europium triflate [$(CF_3SO_3)_3$Eu] (18.6 mg, 0.031 mmol) was added. The mixture was heated at 80 °C for 12 h under an inert atmosphere. After cooling to room temperature, the solution was poured into dry diethyl ether (100 mL) and stirred vigorously. The product precipitated out as an off-white suspension which was collected by centrifugation and dried under high vacuum to give a 46% yield of **3**. Calculated for $C_{56}H_{60}N_{12}O_4Eu$: 1116.3860. Found for $C_{56}H_{60}N_{12}O_4Eu$: 1116.3853. δ_H (CD_3OD, 300 MHz): 38.18 (H_{ax}), 10−0 (m, aromatic and aliphatic H), −5.68 (d, H_{eq}, H'_{ax}), −9.88 (s, H'_{eq}), −15.83 (CHCO), −19.92 (CHCO). *m*/*z* (% ES$^+$): 1115.78 (5, M^+), 1265.77 ($M + CF_3SO_3$), 965.02 (3), 708.57 (5), 708.57 (10), 633.50 ($M + CF_3SO_3/2$), 558.45 ($M^+/2$), 425 (8), 372.59 (37), 322.68 (100). ν (solid)/cm^{-1}: 3396, 3357, 3245, 3171, 3017, 1665, 1644, 1603, 1509, 1479, 1407, 1224, 1158, 1027, 1022, 938, 808, 759, 620.

Ytterbium(III) 1,4,7,10-Tetrakis[*N*-(2-methyl-4-quinolylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane, (Tri(trifluoromethylsulfonate) ([Yb·2]($CF_3SO_3^-$)). The procedure from (**[Eu·2]**) was adopted, using 10 mg of 1,4,7,10-tetrakis[*N*-(2-methyl-4-quinolylcarbamoyl-methyl]-1,4,7,10-tetraazacyclododecane (**2**) (0.010 mmol) and 6.43 mg of ytterbium triflate [$(CF_3SO_3)_3$Yb] (0.010 mmol). Calculated for $C_{56}H_{60}N_{12}O_4Yb$: 1137.4860. Found for $C_{56}H_{60}N_{12}O_4Yb$: 1137.4849. δ_H (CD_3OD, 400 MHz): 37.01 (H_{ax}), 10−0 (m, aromatic and aliphatic H), −6.01 (d, H_{eq}, H'_{ax}), −11.00 (s, H'_{eq}), −16.10 (CHCO), −21.56 (CHCO). *m*/*z* (% ES$^+$): 1138.74 (8, M), 1285.79 (8, $M + CF_3SO_3$), 1436.01 (8, $M + 2CF_3SO_3$), 642.39 (100, $M + CF_3SO_3/2$), 567.54 (70, M/2). ν (solid)/cm^{-1}: 3437, 3061, 1612, 1583, 1487, 1440, 1362, 1231, 1223, 1168, 1082, 1025, 963, 912, 838, 784, 838, 784, 756, 632.

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Supporting Information Available: Absorption pH titration of **[Eu·1]**; fluorescence emission spectra of **[Eu·1]** in various solvents; fluorescence excitation spectra of **[Eu·1]** at pH 2.5, 7.47, and 10.64; fluorescence emission−pH profile for **3**; and [otentiometric pH measurements of **3**, **2**, and **[Eu·2]** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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