Effect of Mixed Pendant Groups on the Solution Properties of 12-Membered Azapyridinomacrocycles: Evaluation of the Protonation Constants and the Stability Constants of the Europium(III) Complexes

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The protonation constants ($\log K_i^H$) of new *N*-acetate or *N*-propionate substituted azamacrocycles derived from 12-membered pyridinoazamacrocycles were determined by potentiometric methods. The number of coordinated water molecules, determined from the luminescence lifetime of the Eu^{III} complexes, indicates a decreasing degree of hydration upon increasing the ring size of the pendant arms. Each ligand forms a 1:1 complex with Eu^{III}, for which the stability constants ($\log K_{therm}$) have been measured by time-resolved laser-induced europium luminescence. The replacement of acetate pendant groups by propionate increases the overall basicity of 12-membered pyridinoazamacrocycles but decreases the stability constant of the Eu^{III} complexes from $\log K = 21.1$ with three *N*-acetate pendant arms to $\log K = 13.7$ with two *N*-propionate and one *N*-acetate pendant arms and to $\log K = 10.7$ with three *N*-propionate pendant arms.

Introduction

Polyazamacrocyclic paramagnetic and radioactive metal ion chelates are of interest in biomedical applications such as Magnetic Resonance Imaging (MRI),[1,2] diagnostic[3] and therapeutic radiopharmaceuticals,[4] and as luminescent probes to investigate biochemical systems.[5]

Numerous 12-membered tetraazamacrocycles derived from "cyclen" with acetate, substituted acetate or propionate side chains have been studied.[2,6] The selectivity of complexation of such ligands towards various metal ions (i.e. the relative stability of the resulting complexes) can be tuned by adjusting the ring size, the number and the nature of coordinating atoms in the ring, and the type of side chains. Introduction of a pyridine in the 12-membered tetraazamacrocycles "cyclen" is expected to increase the conformational rigidity of the resulting macrocycle, and changing chelate ring size from five- to six-membered may influence the ion selectivity and properties of the macrocyclic compounds. Therefore, we studied the effect of the pendant arms (acetate versus propionate side chains) on protonation constants and Eu^{III} stability constants in a series of 12-membered pyridinoazamacrocycles L^1, L^2, and L^3 (Figure 1).

Potentiometric titrations have been used to determine the stability constants of L^1 ligands with alkaline-earth metal and first-row transition-metal ions[7] but this could not be applied to lanthanide ions due to both their extremely high constants ($\log K_{ML} > 20$) and their slow kinetics of formation. The "out-of-cell" potentiometric and competition titrations performed on cyclen derivatives are, necessarily, indirect, and the results depend on the validity of the assumptions made concerning the species present in the solution and the attainment of equilibrium at the time of the measurement. Gd^{III} complexes formed with L^1 ligand have been characterized by relaxometric experiments.[8,9]

The low extinction coefficients of Laporte-forbidden lanthanide f−f transitions mean that lanthanide ions have very small absorption coefficients, resulting in inefficient direct excitation.[10] This problem can be solved by using heterocycles as sensitizers or laser beams.[11] Tunable dye lasers excite the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{III} ion in the range 577−581 nm, while the $^5D_0 \rightarrow {}^7F_2$ emission is monitored at 614 nm.[11] This provides an original method to directly monitor the binding of Eu^{III} to ligands in solution and has been used to determine the stability constants of lanthanides with polyaminocarboxylates.[12] However, complex and expensive tunable dye laser apparatus are required.

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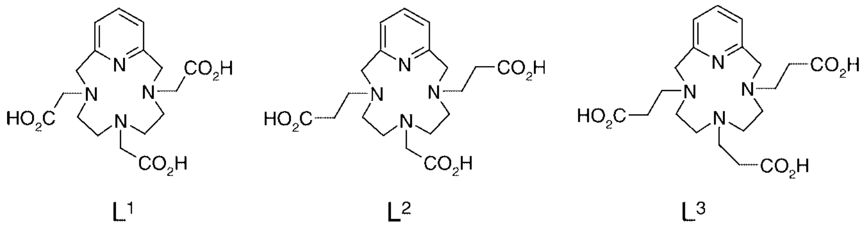

Figure 1. Structure of the ligands

Time-Resolved Laser-Induced Fluorescence (TRLIF) is widely used as a very sensitive and selective method for several luminescent actinides (U, Cm, Am) and lanthanides (Eu, Tb, Dy, Sm) in nuclear, environment, and medicinal chemistry, and is of growing interest in inorganic and organic speciation.[13,14] It is, therefore, an attractive analytical technique to apply to stability constant measurements.

Here we report, the protonation constants, the stoichiometries and the stability constants of the Eu^{III} complexes of ligands L^1, L^2, and L^3 bearing three carboxylic acid functions as well as seven potential donor atoms of various hardness.

Results and Discussion

Acidity Constants of L^1, L^2, and L^3

The ligands L^1, L^2, and L^3 each have seven basic centers, but only four constants could be determined by the potentiometric technique used. The protonation constants were found by potentiometric titrations of the fully protonated ligands. Figure 2 shows the potentiometric titration curve of macrocyclic ligands L^1, L^2, and L^3 with KOH. Analysis of the potentiometric titration curves with the Hyperquad program[15] yielded the protonation constants (Table 1).

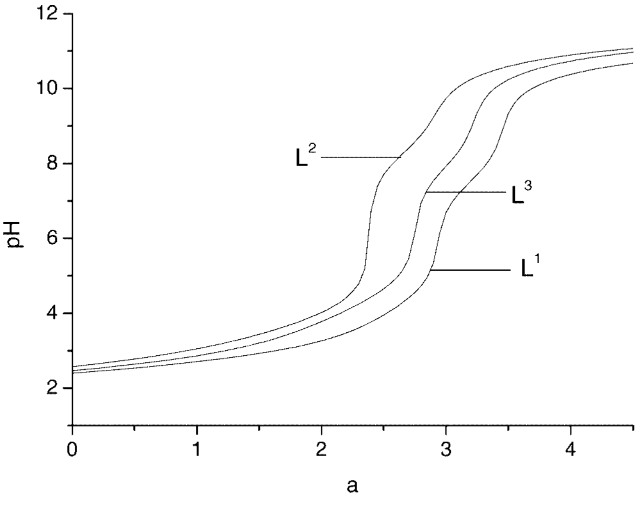

Figure 2. Potentiometric titration curve for 0.005 mM ligand: *a* = mol of base added per mol of ligand; solution temperature $T = 25$ °C, ionic strength $I = 0.1$ M (KCl)

Table 1. Comparison of the protonation constants of L^1, L^2, and $L^3$with the constants of an analogue (DOTA); the values in parentheses are standard deviations for the last figure given by the program[15]

Equilibrium quotient	L^1 [a]	L^2 [a]	L^3 [a]	L^1 [b]	L^1 [c]	DOTA[d]
[HL]/[H] [L]	10.73(5)	10.74(2)	10.72(3)	10.90	10.6	12.09
$[H_2L]$/[HL] [H]	7.52(9)	8.27(6)	7.89(9)	7.11	7.6	9.76
$[H_3L]$/$[H_2L]$ [H]	4.2(1)	3.97(7)	4.5(1)	3.88	4.4	4.56
$[H_4L]$/$[H_3L]$ [H]	2.4(1)	3.26(7)	3.7(1)	2.27	–	4.09
$[H_4L]$/[L] $[H]^4$	24.86	26.24	26.85	24.16	–	30.50

[a] 0.1 M KCl. [b] Ref.[7] 0.1 M NMe_4NO_3. [c] Ref.[16] 0.1 M KCl. [d] Ref.[17] 0.1 M NMe_4NO_3.

Ligands L^2 and L^3 differ from L^1 in their carboxylic acid side chains and, consequently, have significantly different protonation constants. All ligands have two high (or fairly high) and two low protonation constants. The first two are due to the protonation of two nitrogen atoms of the ring and the last two correspond to the protonation of carboxylate groups.[7,8] The separation of the pK_a values for a given ligand is greater than 0.7, which is consistent with non-interacting pendant arms.[18] For ligand L^3, the pK_a values are higher than those for L^1 owing to the presence of a second methylene group, which acts as an electron donor.[19]

Stoichiometry of the Complexes

The stoichiometry of the Eu^{III} complexes formed with L^1, L^2, or L^3 were determined by a mol ratio method. By monitoring the Eu^{III} luminescence at the wavelength of the $^5D_0 \rightarrow {}^7F_2$ transition peak as the function of Eu^{III} added to an aqueous solution of ligand (50 μM), at a pH such that the competition of protons is negligible (pH = 7.0), a binding curve is obtained (Figure 3). Since the ligand concentration is well above the dissociation constant for lanthanide complexes, the titration curve is expected to break sharply when the stoichiometric quantity of Eu^{III} has been added. Figure 3 shows a typical plot of the relative Eu^{III} luminescence intensity versus equivalents of added Eu^{III} with L^2 as ligand.

The macrocyclic ligands L^1, L^2, and L^3 have a 1:1 stoichiometry that is consistent with the size of the cavity as well as the number of donor atoms.

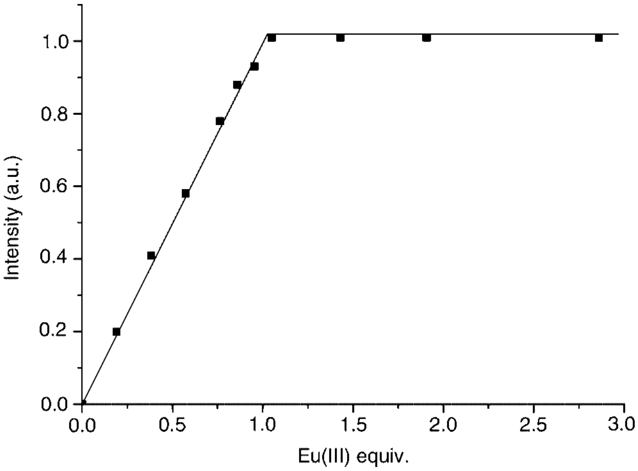

Figure 3. Intensities of the $^5D_0 \rightarrow {}^7F_2$ transition peak as the function of Eu^{III} added to an aqueous solution of ligand L^2 (50 µm), 0.085 m KCl and 0.015 m HEPES-buffered medium (pH = 7.0)

Luminescence Lifetimes, Quantum Yields

For each solution, the emission spectra are homothetical with I_{592}/I_{614} constant. Furthermore, a pulsed laser excitation source allows the measurement of characteristic Eu^{III} excited state lifetimes for each solution. The luminescence intensity of each europium complex decreases according to mono-exponential kinetics (Figure 4). Thus, under the conditions of our experiments, only 1:1 complexes for ligands L^1, L^2, and L^3 were present.

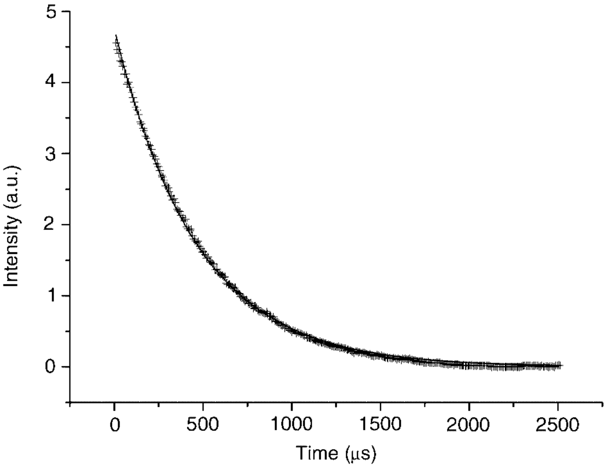

Figure 4. Excited-state luminescence decay for the system containing the macrocyclic ligand L^2 (50 µm) in the presence of EuCl$_3$ (60 µm) at pH = 5.28, [MES] = 0.015 m, [KCl] = 0.085 m

The luminescence lifetimes of Eu^{III} complexes with L^1, L^2, and L^3, and the overall quantum yields measured in H_2O and D_2O, are given in Table 2. From such measurements the estimated number of water molecules coordinated to the Eu^{III} complexes (Table 2), using the empirical relation proposed by Horrocks and co-workers,[20,21] Parker and co-workers,[22] or Kimura and co-workers,[23] show a decreasing degree of hydration with increasing ring size. The presence of 2.3, 1.6, and 1.4 coordinated water molecules for [L^1⊂Eu^{3+}], [L^2⊂Eu^{3+}], and [L^3⊂Eu^{3+}], respectively, agrees with the expected seven-coordinating nature of ligands since Eu^{III} prefers a coordination number of 8−9.

Table 2. Lifetimes of Eu^{III} complexes formed with L^1, L^2, and L^3, average number of water molecules coordinated to the complexes, and luminescence quantum yields

	Lifetimes τ [ms][a]		n H_2O[b]	n H_2O[c]	n H_2O[d]	Luminescence quantum yield[e]	
	H_2O	D_2O				H_2O	D_2O
[L^1⊂Eu^{3+}]	0.37	2.12	2.3	2.3		2.32.9%	19.1%
[L^2⊂Eu^{3+}]	0.43	1.35	1.7	1.7		1.94.6%	−
[L^3⊂Eu^{3+}]	0.48	1.39	1.4	1.3		1.62.4%	8.1%

[a] Measured at room temperature; excitation into the lowest-energy ligand-centered absorption band in correspondence with the hypersensitive $5D_0 \rightarrow 7F_2$ transition; experimental error 5%. [b] Number of coordinated H_2O molecules estimated using Horrock's equation:[20,21] $n = 1.05 \cdot (\tau^{-1}_{H2O} - \tau^{-1}_{D2O})$. [c] Number of coordinated H_2O molecules estimated using Parker's equation:[24] $n = 1.2 \cdot [(\tau^{-1}_{H2O} - \tau^{-1}_{D2O}) - 0.25]$. [d] Number of coordinated H_2O molecules estimated using Kimura's equation:[23] $n = 1.07 \cdot (\tau^{-1}_{H2O}) - 0.62)$. [e] Measured at room temperature with reference to quinine sulfate;[25] excitation in the lowest energy ligand-centered absorption band (269 nm); experimental error 10%.

Determination of the Stability Constants of L^1, L^2, and L^3 with Eu^{III}

Since the multidentate ligands L^1 to L^3 form 1:1 complexes with Eu^{III} the general complexation equilibria apply [Equation (1)].

$$[Eu^{3+}] + [L^{3-}] \rightleftarrows [EuL] \tag{1}$$

The equilibrium constant for Equation (1) can be expressed as in Equation (2).

$$K(Eu^{3+}) = \frac{[EuL]}{[Eu^{3+}][L^{3-}]} \tag{2}$$

Depending on its intrinsic basicity, each ligand has a different response to the proton competition that limits the metal-ion binding, leading to the conditional stability constants [Equation (3)].

$$K_{cond.}(Eu^{3+}) = \frac{[EuL]}{\left[Eu^{3+}\right]\left\{\left[L^{3-}\right]+\left[HL^{2-}\right]+\left[H_2L^{-}\right]+\left[H_3L\right]+\left[H_4L^{+}\right]\right\}} \tag{3}$$

The thermodynamics and conditional stability constants are related by Equation (4)

$$K_{cond.}(Eu^{3+}) = K(Eu^{3+})\alpha_H \tag{4}$$

with α_H defined by Equation (5)

$$\alpha_H^{-1} = 1 + K_{a1}\cdot[H^+] + K_{a1}\cdot K_{a2}\cdot[H^+]^2 + K_{a1}\cdot K_{a2}\cdot K_{a3}\cdot[H^+]^3 + K_{a1}\cdot K_{a2}\cdot K_{a3}\cdot K_{a4}\cdot[H^+]^4 \qquad (5)$$

and K_{a1}, K_{a2}, K_{a3}, and K_{a4} being the protonation constants of the studied ligand.

Provided a constant amount of energy is furnished to the studied system, the luminescence intensity is proportional to [EuL]. Consequently, the luminescence intensity may be expressed as a function of the pH and of the stability constant of the complex (K) by Equation (6)[11]

$$I = \frac{k'}{2}\left\{[Eu]_0 + [L]_0 + \frac{\alpha_H^{-1}}{K} - \left[\left([Eu]_0 + [L]_0 + \frac{\alpha_H^{-1}}{K}\right)^2 - 4[Eu]_0[L]_0\right]^{1/2}\right\} \qquad (6)$$

where $[Eu]^0$ and $[L]_0$ stand for the initial total concentrations of Eu^{III} and ligand respectively, k' is the proportionality constant between maximal intensity and $[Eu]_0$.

Plotting the luminescence intensity at the wavelength of the ${}^5D_0 \rightarrow {}^7F_2$ transition peak as a function of the pH after a suitable equilibration time, give a binding curve (Figure 5). The fitting (least-squares method) of the theoretical curve obtained from Equation (6) (Figure 5, solid curve) to the experimental data (Figure 5, squares) leads to a log$K$ value of 21.1, 13.7, and 10.7 for complexes with L^1, L^2, and L^3, respectively.

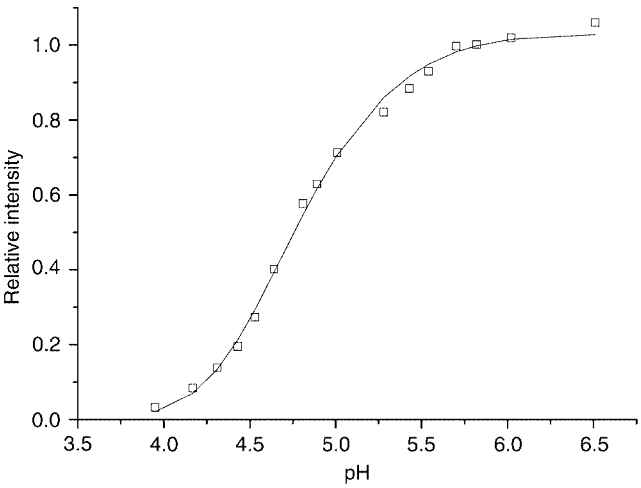

Figure 5. Binding curve obtained by monitoring the luminescence intensity (614 nm) of samples containing the macrocyclic ligand L^2 (50 μM) in the presence of $EuCl_3$ (50−60 μM) as a function of pH, [KCl] = 0.085 M, 4 < pH < 5 [HOMOPIPES] = 0.015 M, 5 < pH < 6.5 [MES] = 0.015 M; the luminescence resulted from Nd-YAG laser excitation at 266 nm; the squares represent actual data points and the solid line the theoretical fit of data with log$K$ = 13.7

Compared with L^1, an important diminution of the complexation constant is observed for L^2 and L^3 (Table 3). Thus, increasing the length of the acid group has a negative influence on the complexation of Eu^{III}.

Table 3. Stability constants (log K_{EuL}) of the complexes formed with the ligands L^1, L^2, L^3, and DOTA

Ln	L^1 [a]	L^2 [a]	L^3 [a]	DOTA
Eu^{III}	21.1	13.7	10.7	26.2 [b]
Gd^{III}	20.8 [c]			24.6 [d]

[a] 0.1 M KCl, 25 °C. [b] Ref.[12] 0.1 M KCl. [c] Ref.[8] [d] 0.1 M NaCl, ref.[26]

Conclusion

In conclusion, we report here the protonation constants of new N-acetate or N-propionate substituted azamacrocycles and an extended characterization of Eu^{III} complexes formed with these ligands based on time-resolved laser-induced Eu^{III} luminescence. This enabled us to determine the stoichiometry of the complexes, the luminescence quantum yield and the stability constant, which revealed the influence of the chelate ring size of the pendant arms on the stability constant of the Eu^{III} complex. This successful outcome has encouraged us to embark on a program to characterize various similar ligands with different macrocyclic and chelate ring sizes.

Experimental Section

Materials and Chemicals: All measurements were performed at 293 K and the solutions were prepared with deionized water (Millipore system). All glassware was thoroughly rinsed with water. The ionic strength of the solutions was adjusted to 0.1 M with KCl. Europium(III) chloride hexahydrate (Aldrich), sodium formate, 2-[N-(2-hydroxyethyl)piperazin-N'-yl]ethanesulfonic acid sodium salt (HEPES-Na), hexahydro-1H-1,4-diazepine-1,4-diylbis(2-ethanesulfonic acid) (Homo-PIPES) and 2-(N-morpholinyl)ethanesulfonic acid monohydrate (MES) were purchased as their purest form from Fluka. The potentiometric titrations were performed using an automatic titrator system DMS 716 Titrino (Metrohm) with a combined glass electrode (Metrohm, filled with saturated KCl solution) and connected to a microcomputer. $EuCl_3$ stock solutions (ca. 10 mM) were titrated by ICP-AES. The concentrations of the ligand stock solutions (ca. 0.1 M) were determined by titration with a standardized Eu^{III} solution at pH = 7 for L^1 and L^2 and at pH = 8 for L^3, on equilibrated samples using time-resolved laser-induced Eu^{III} luminescence.

Time-Resolved Laser-Induced Fluorescence: An Nd-YAG laser (Model Minilite, Continuum, Santa Clara, USA), operating at 266 nm (quadrupled) and delivering ca. 0.2 mJ of energy in a 4 ns pulse with a repetition rate of 15 Hz, was used as the excitation source. The laser output energy was monitored by a laser power meter (Scientech, Boulder, USA). The laser beam was directed into the 4-mL quartz cell of a "FLUO 2001" spectrofluorometer (Dilor, Lille, France). The radiation coming from the cell was focused on the polychromator's entrance slit. Taking into account the dispersion of the holographic grating used in the polychromator, the measurement range extended to approximately 200 nm into the visible spectrum with a resolution of 1 nm. An intensified photodiodes (1024) array, cooled by the Peltier effect (−30 °C) and positioned at the polychromator exit, was used as detector. Spectra were recorded by integration of the pulsed light signal from the intensifier. The integration time, adjustable from 1 to 99 s, allows for variation in detection sensitivity. Logic circuits, synchronized with the laser shot, allow the intensifier to be active with a determined time delay (from 0.1 to 999 μs) and during a determined aperture time (from 0.5 to 999 μs). The whole system was controlled by a microcomputer. Data analysis was performed using the iterative least-squares fitting procedure in Microsoft Excel program. Fluorescence quantum yields were determined at 293 K by comparison with that of quinine sulfate in aqueous sulfuric acid solution (1 N), for which a reference yield of 0.55 was taken.[25] Luminescence lifetimes (at 293 K) were determined at 600 nm by excitation with a B.M. Industries frequency-quadrupled Nd-YAG laser (266 nm, pulse duration 8 ns FWHM) using an oscilloscope Tektronix 9310 to monitor the output signal of the photomultiplier.

Synthesis of Ligands: The ligands L^1, L^2, and L^3 were synthesized as reported.[8,27,28]

Potentiometric Titrations: The electrodes were calibrated to read the pH by a classical method.[29] .The ligand (5 mL, 0.001 M) was titrated with standardized 0.01 M sodium hydroxide. Argon was bubbled through the solution to exclude CO_2 and O_2. Sodium hydroxide was prepared from 0.1 M NaOH (Prolabo) and standardized against potassium hydrogen phthalate. The carbonate content was checked by Gran's method. The titration for each ligand was carried out at least three times. Each titration consisted of about 70 points collected over the pH range of 2.5−10.9. The titration data were refined by the non-linear least-squares refinement program Hyperquad[15] to determine the protonation constants. The pK_a values were calculated from the cumulative constants determined with the program. The uncertainties in the pK_a values correspond to the added standard deviations in the cumulative constants.

Spectrophotometric Experiments

Preparation of Samples for the Stoichiometry Determination: The pH of an aqueous stock solution containing HEPES (sodium salt, 0.015 M), KCl (0.085 M), and ligand (50 μM) was adjusted to pH = 7 for L^1 and L^2 and to pH = 8 for L^3 with an aqueous solution of HCl. A series of 11 samples was prepared in separate sealed containers with concentrations of $EuCl_3$ ranging from 0 to 200 μM. After overnight incubation at 60 °C, the samples were allowed to cool to room temperature and then monitored by absorption spectroscopy until no further spectral change was detected (typically 24 h). The Eu^{III} excited state lifetime was monitored and the luminescence intensity of each sample was measured at the wavelength of the $5D_0 \rightarrow 7F_2$ transition peak.

Preparation of Samples for Lifetime and Quantum Yield Measurements: Samples containing HEPES (sodium salt, 0.015 M), KCl (0.085 M), ligand (50 μM), and $EuCl_3$ (75 μM) were prepared in H_2O (D_2O). The pH (pD) was adjusted with an aqueous solution of HCl (DCl) to pH = 7.0 (7.4) (pD = pH + 0.41).

Preparation of Samples Used To Determine the Stability Constant of the Eu^{III} Complex: An aqueous stock solution containing buffer (0.015 M), KCl (0.085 M), ligand (50 μM), and a slight excess of $EuCl_3$ (55 to 60 μM) was prepared. A series of 15 samples was produced in separate sealed containers at various pH by addition of an aqueous solution of HCl (KCl/HCl buffer for pH = 1−2, HCO_2Na/HCO_2H buffer for pH =2−4, HOMOPIPES buffer for pH = 4−5, MES buffer for pH = 5−6.5, and HEPES buffer for pH = 6.5−8). After overnight incubation at 60 °C, the samples were allowed to cool to room temperature, and then monitored by absorption spectroscopy until no further change was detected. At equilibrium the samples were irradiated, and the Eu^{III} excited state lifetime monitored and the luminescence intensity of each sample measured at the wavelength of the $5D_0 \rightarrow 7F_2$ transition peak.

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