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ARTICLE

AMPED: a new platform for picolinate based luminescent lanthanide chelates

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Claudia Guanci,[a] Giovanni Giovenzana,[a]* Luciano Lattuada,[b] Carlos Platas-Iglesias,[c] and Loïc J. Charbonnière[d]*

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The synthesis of a new nonacoordinating ligand based on an AMPED (6-amino-6-methylperhydro-1,4-diazepine) scaffold functionalized by three picolinate (6-carboxy-2-methylpyridine) arms is described. Coordination of lanthanide cations (Ln = Eu and Tb) was investigated by spectrophotometric titrations monitored by UV-Vis absorption and steady-state emission spectroscopy, showing the formation of [LnL] complexes in aqueous solutions. The corresponding Eu and Tb complexes were isolated and characterized, and their spectroscopic properties (luminescence quantum yields, excited state lifetimes) were determined in buffered water (TRIS/HCl, pH 7.4) and compared to the data reported in the literature for related systems. DFT modelling of the complexes showed the picolinate arms to be perfectly wrapped around the Ln^{3+} cations, affording an excellent shielding of the metal as confirmed by the determination of the hydration number of q = 0 for both complexes. The high resolution emission spectrum was used to determine the radiative lifetime of Eu in the complex (τ_{rad} = 3.05 ms) and the metal-centred luminescence quantum yield (0.20). The modest 0.10 overall luminescence quantum yield of the Eu complex is a consequence of an energy transfer with medium efficiency (0.50) and a low metal centred luminescence efficiency attributed in part to the presence of numerous NH and CH bonds in close proximity to the metal centre.

Introduction

Luminescent lanthanide (Ln) complexes have found a particular niche in spectroscopic applications combining elemental spectral signatures, long luminescence lifetimes, large Stokes' shifts,[1] and sensing[2] or upconversion properties.[3] Particular efforts have been devoted to the design of highly luminescent lanthanide tags[4] for their use in time-resolved luminescence analytical applications and microscopy.[5] Such complexes are basically constituted of three main components: i) a pre-organizing scaffold aiming at providing thermodynamically stable and kinetically inert Ln complexes; ii) antenna units, which collect the exciting photons and transfer the corresponding energy to the Ln excited states; and iii) an activated pending arm for the covalent grafting of the Ln-based label to the (bio)material of interest. Although the pioneering efforts have been mainly devoted to macropolycyclic scaffolds to ensure the stability of the complexes,[4a,6] pre-organised scaffolds based on macrocyclic moieties[7] or non-macrocyclic systems providing strong electrostatic interactions[8] also proved to be stable enough for bioanalytical applications, while being far less demanding in terms of synthetic efforts. Among the numerous examples dealing with macrocyclic structures, scaffolds based on tetraazacycloalkanes (in particular cyclen[9] but also cyclam[10]) and triazacycloalkanes (mainly triazacyclononane or TACN)[11] have been thoroughly investigated.

More recently, the synthesis of 6-amino-6-methylperhydro-1,4-diazepine (AMPED, Chart 1) was reported.[12] It soon

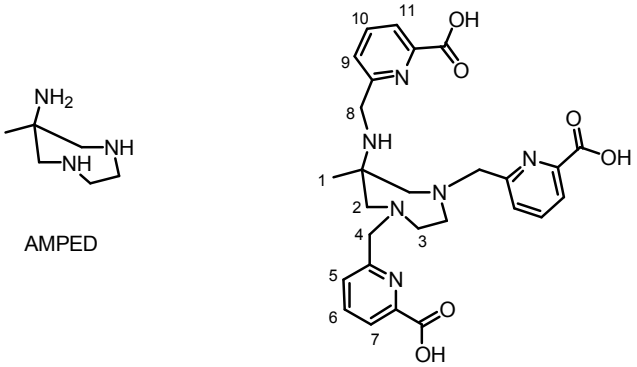

Chart 1. AMPED and the AMPED picolinate ligand LH_3 with H numbering.

appeared to be an interesting scaffold for the preparation of chelating agents, forming stable lanthanide complexes,[13] with a particular emphasis on Gd-based relaxation agents.[14] As an

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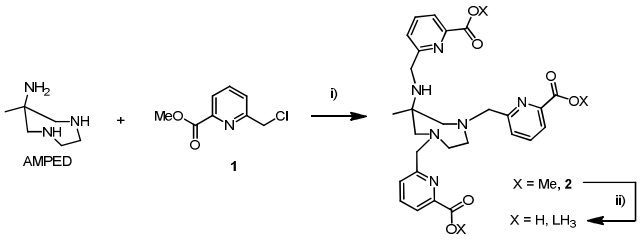
intrinsic feature, the structure of AMPED displays two possible entries into the introduction of an activated function for biolabelling; *i.e.*: the alkyl chain on the quaternary carbon atom[15] and possibly the regioselective sequential alkylation on the nitrogen atoms taking advantage of the differential reactivity of primary and secondary amines.[16] Considering its versatility, the potential of using AMPED as a scaffold to construct luminescent Ln complexes becomes obvious, providing that an adequate antenna was used. The picolinate arm appeared to be a typical substituent model as an evident choice, as it has been introduced on a plethora of scaffolds including podands,[17] linear[18] or cyclic polyamines.[15a,19] Moreover, the *para* position of the pyridyl ring can easily be modified by inclusion of unsaturated groups to extend the electronic delocalisation and to improve the antenna effect.[20]

In this contribution, we describe the synthesis of the AMPED based nonadentate ligand LH_3 (Chart 1), which has been designed for the complexation of Ln cations. The Eu^{3+} and Tb^{3+} complexes were prepared and characterized. The spectroscopic properties of these complexes were investigated using both absorption and emission electronic spectroscopy and DFT calculations.

Results and discussion

Scheme 1 shows the synthetic protocol followed to obtain ligand LH_3. AMPED was prepared according to the literature procedure[12] by a two-steps procedure involving a nitro-Mannich-type reaction with nitroethane, paraformaldehyde and dibenzylethylenediamine diacetate followed by reductive hydrogenation/debenzylation with H_2 over Pd/C. The picolinate precursor **1** was prepared according to a literature three steps procedure[21] from dipicolinic acid, which was first esterified into its dimethyl ester before partial reduction of one of the ester functions and chlorination with $SOCl_2$. Alkylation of AMPED with five equivalents of **1** was carried out in acetonitrile in the presence of potassium carbonate as a base with a modest 20% yield. Despite all our efforts, including addition of a large excess of **1**, it has not been possible to isolate the tetraalkylated compound corresponding to the bisalkylation of the primary amine of AMPED. Nevertheless, compound **2** was particularly interesting as the remaining secondary amine group could represent a suitable site for the introduction of an activating function for biolabeling.



Scheme 1. Synthesis of the ligand.(i) K_2CO_3, CH_3CN, r.t. 72h, 20%. ii) NaOH, H_2O, r.t. 14h, then HCl, 77%.)

Finally, basic hydrolysis of the ester functions followed by acidification of the medium afforded ligand LH_3 in a decent 77% yield.

Figure 1 represents the ^1H NMR spectrum of the ligand in D_2O. The aromatic region displays two sets of three peaks (two doublets and a triplet) integrating for three and six protons, respectively. This pattern is related to an average planar symmetry of the molecule in solution, with the symmetry plane passing through the secondary nitrogen atom, the quaternary aliphatic carbon atom and bisecting the bond joining the two adjacent methylene groups of the ring, pointing to a rapid pyramidal inversion at the secondary nitrogen atom. As a result of this symmetry, the endocyclic methylene groups were found as two sets of signals, each displaying an AB pattern resulting from a blocked conformation of the seven-membered ring cycle. The first AB spin system consists of the two doublets at 3.93 and 3.69 ppm, attributed to the H2 proton (see chart 1 for H numbering). Regarding the strong correlation observed between the doublet at 3.93 and peaks due to H1 (1.28 ppm) and H8 (4.51 ppm) in the NOESY spectrum (Figure S1), this signal was attributed to the equatorial H2 atom. The second AB pattern (3.36-3.58 ppm) was attributed to the two adjacent methylene groups of the cycle (H3). Finally, the exocyclic methylene bridges joining the two symmetrical picolinate arms H4, are observed as a third AB spin system at 4.35 ppm.

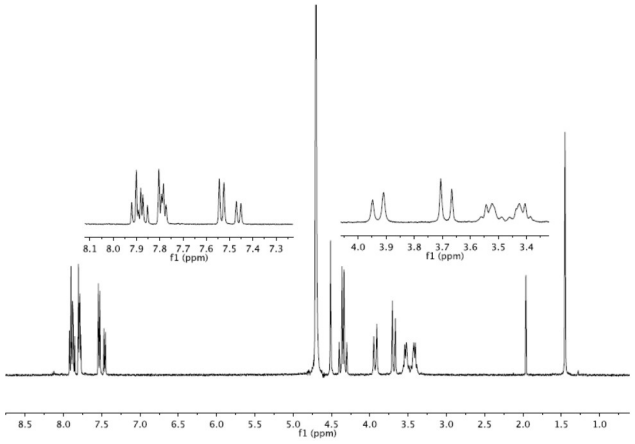


Figure 1. ^1H NMR spectrum of LH_3 in D_2O (15°C, 400 MHz).

The complexation of Eu and Tb was monitored by titration experiments in which the absorption and emission spectra of buffered solutions of the ligand in TRIS/HCl (0.01 M, pH = 7.4) were monitored as a function of increasing aliquots of the chloride salts of Ln. Figure 2 displays the evolution of the emission spectra during the titration with Tb. Upon addition of Tb, the excitation through the ligand π–π* absorption bands at 265 nm resulted in the observation of thin emission bands at 490, 543, 583 and 621 nm, with weaker signals at 653, 670 and 681 nm. These emission bands are typical of the $^5D_4 \rightarrow {}^7F_J$ transitions (J = 6 to 0 respectively) centred on Tb.[1] The intensity of these bands increased linearly upon Ln addition up to one equivalent, after which the emission intensity did not change anymore. This evolution points to the formation of a

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single complex species with a 1:1 (Tb:ligand) composition. The same behaviour was observed for Eu (Figure S2).

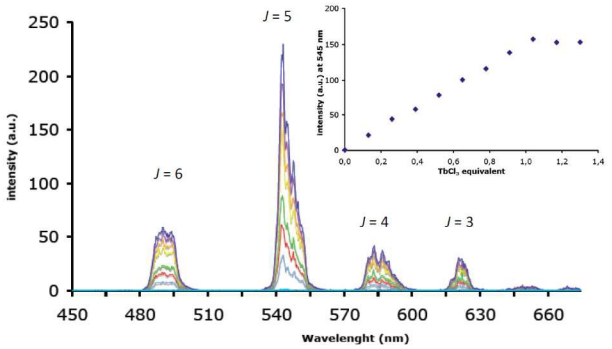

Figure 2. Evolution of the emission spectra of a solution of L upon addition of $TbCl_3 \cdot 6H_2O$ (λ_{exc} = 265 nm, TRIS/HCl, 0.01 M, pH = 7.4) with attribution of the $^5D_4 \rightarrow {}^7F_J$ transitions. Inset: Evolution of the emitted intensity at 545 nm.

On the basis of this composition, the [LnL] complexes were prepared by mixing equimolar concentrations of ligand and metal ion in water at pH 4.5 and heating for 4 hours at 80°C. The complexes were isolated by precipitation with THF from the water solutions. The electrospray mass spectra of the complexes (Figure S3 and S4) displayed the expected pattern corresponding to the [LnL] complexes, with the expected isotopic distribution corresponding to the ^{151}Eu and ^{153}Eu isotopes.

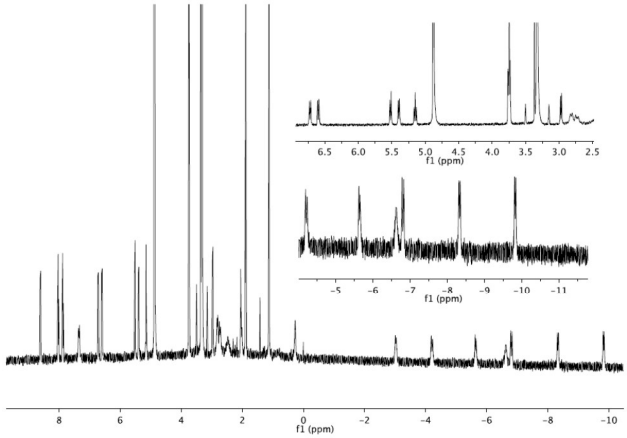

Figure 3. ^{1}H-NMR spectrum of [EuL] in D_2O (25°C, 400 MHz).

The ^{1}H NMR spectrum of the Eu complex in deuterated water showed the symmetry observed in the ligand to be disrupted by coordination to the metal ion. The spectrum clearly showed 22 signals corresponding each to one proton and a singlet of three protons. It is surmised that the lacking peak is hidden under the signals of the solvent. The coordination of the cation into the cavity is expected to induce a wrapping of the picolinate arms around the metal, resulting in a pseudo helicity of the complex, as confirmed by DFT modelling (*vide infra*). This induced chirality results in a lack of any symmetry element in the molecule.

The ^{1}H NMR signals of the ligand experience significant paramagnetic shifts upon coordination to the paramagnetic center. Besides, the nine signals attributed to the proton nuclei of the picolinate arms (8.61, 8.03, 7.88, 7.36, 6.72, 6.60, 5.52, 5.40, 5.15 and 2.97 ppm) present very similar linewidths, which is compatible with the coordination of the three picolinate pendant arms to the metal ion in solution.[19c]

The UV-Vis absorption spectra and steady-state emission spectra of the complexes are presented in Figure 4, while Table 1 summarizes the main spectroscopic properties of the complexes in water. The absorption spectra of the complexes are both dominated by an intense absorption band with a maximum at 273 nm, attributed to $\pi \rightarrow \pi^*$ transitions centered on the picolinate moieties (see below). Upon excitation into this band both complexes displayed the typical emission bands arising from the transitions $^5D_0 \rightarrow {}^7F_J$ (J = 0 to 4) for Eu and $^5D_4 \rightarrow {}^7F_J$ (J 0 to 6) for Tb.

Table 1. Absorption maximum (λ_{max}), metal centred excited state lifetime in water (τ_{H_2O}) and heavy water (τ_{D_2O}) at 298 K, overall luminescence quantum yield (ϕ_{H_2O}) and hydration number (q) for the [LnL] complexes (Ln = Eu and Tb).

	λ_{max} / nm (ε / $M^{-1}.cm^{-1}$)	τ_{H_2O} (ms)	τ_{D_2O} (ms)	ϕ_{H_2O}	q^a
[EuL]	273 (15900)	0.61	0.73	0.10[b]	0
[TbL]	273 (15600)	1.83	2.00	0.20[b]	0

[a] Calculated according to ref 22 and 25 (see text). [b] see experimental section for full details

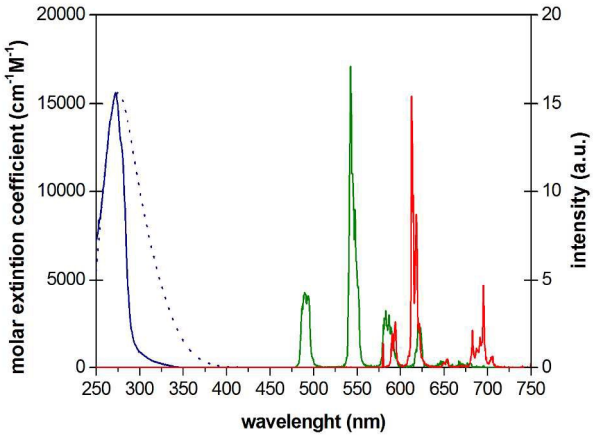

Figure 4. UV-Vis absorption spectrum of [TbL] (blue) and emission spectra of [EuL] (red) and [TbL] (green) in water. The absorption spectrum of [EuL] calculated using TDDFT is shown as a dotted line.

The excited state lifetimes of the complexes were recorded in water and deuterated water allowing for the determination of the hydration number, *i.e.* the number of water molecules in the first coordination sphere of the Ln cation, according to Horrocks methodology[25] using refined coefficients determined by Parker et al.[22] For both Eu and Tb, the analysis showed the

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coordination sphere to be fully saturated by the nine coordination sites of the ligand, leaving no space available for the coordination of water molecules, thereby affording an excellent protection of the luminescent cations towards non radiative deactivation. The luminescence quantum yield of the Eu complex (ϕ = 0.10) is in excellent agreement with that obtained for other nonacoordinated ligands containing three picolinate arms, such as the derivative of TACN (ϕ = 0.09),[26] or its phosphinate based analogues (ϕ = 0.09-0.07).[27] Surprisingly, the luminescence quantum yield of the Tb complex (0.20) is somehow smaller than that observed for similar compounds (0.43 for the TACN derivative[26] and up to 0.50-0.60 for phosphinate based TACN derivatives[27]). To further understand the energy transfer processes within the Eu complex, we calculated the radiative lifetime of Eu in the complex following the methodology developed by Werts and coworkers.[28] Assuming that the $^5D_0 \rightarrow {}^7F_1$ transition of Eu (from 577 to 601 nm, Figure 4) is of purely magnetic dipole origin, the radiative lifetime of Eu, τ_R, can be calculated with equation 1:

$$1/\tau_R = A_{MD,0} n^3 (I_{tot}/I_{MD}) \qquad (1)$$

in which, $A_{MD,0}$ is the spontaneous emission probability of the $^5D_0 \rightarrow {}^7F_1$ transition ($A_{MD,0}$ = 14.65 s^{-1}), n is the refractive index of the medium (1.333 for water at 589.3 nm) and I_{tot} and I_{MD} respectively correspond to the total area of the corrected emission spectrum and the part corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition. A value of 3.03 ms was obtained for τ_R, in good agreement with reported data of the literature.[28,29] From the radiative lifetime and knowing the luminescence lifetime of the Eu complex in water, τ_{H_2O}, one calculates the metal centered luminescence quantum yield, ϕ_{Eu} with equation 2:

$$\emptyset_{Eu} = \frac{\tau_{H_2O}}{\tau_R} \qquad (2)$$

which amounts to 0.20 in our complex. Considering the overall luminescence quantum yield (the quantum yield upon excitation into the ligand, ϕ_{H_2O} = 0.10), the sensitization efficiency η of the picolinate arms can be obtained with equation 3:

$$\phi_{H_2O} = \eta \times \phi_{Eu} \qquad (3)$$

The calculated sensitization efficiency amounts to 0.50, pointing to a modest efficiency of the energy transfer from the triplet excited state of the ligand to the Eu^{3+} cation. In absence of low temperature set up to measure the ligand centred triplet state, we turned our attention to DFT calculations (see below). On the basis of the optimized structure, the energy of the lowest-energy triplet state was found to be 364.9 nm (27 400 cm^{-1}), in good agreement with reported data for the trisdipicolinate TACN complexes (26670 to 27030 cm^{-1} at 77K).[26] This energy level is far higher than the $^5D_0$ (17 200 cm^{-1}) or $^5D_1$ (ca 18700 cm^{-1}) excited states of Eu(III), explaining a rather modest sensitization efficiency.[30]

DFT calculations. Following the methodology reported in recent computational studies,[31] the [EuL] complex was investigated by means of DFT calculations using the TPSSh functional and the large-core relativistic ECP of Dolg et al., which includes 52 electrons in the core for Eu^{3+}.The ligand coordinates to the Eu^{3+} ion using a N_6O_3 donor set composed of the three amine nitrogen atoms, the three nitrogen atoms of the pyridyl rings and three oxygen atoms of the carboxylate groups (Figure 5). The latter donor atoms provide the strongest interaction with the metal ion(Eu-O distances in the range 2.38-2.41 Å), followed by the nitrogen atoms of the pyridyl moieties (2.59-2.62 Å). The calculated distances between the Eu^{3+} ion and the amine nitrogen atoms of the ligand (2.66-2.83 Å) are only slightly longer than those observed in the solid state for the Gd^{3+} complex of AAZTA (2.60-2.78 Å), while following the sequence Ln-N1 < Ln-N3 < Ln-N2 (see Figure 5 for atom numbering).[32]

The N3-CH_2-CH_2-N dihedral angle (-33.2°) is close to those observed in the Eu^{3+}complex of the related AAZTA-CH_2CH_2OH ligand (-28.2°),[33] the Ga^{3+} complexes with hexadentate ligands based on the AMPED platform[34] and the Cu complex with AAZTA, resulting in twist-chair conformations of the 1,4-diazepine seven-membered ring. This torsion angle is somewhat smaller in the Gd^{3+} complex of AAZTA-C_2H_4COOBn (-20.8°)[35] and Cu(H_2AAZTA) (-23.7°),[36] approaching an eclipsed conformation in the Gd^{3+} complex of AAZTA (-2.9°),[32] which is characteristic of the chair conformation.

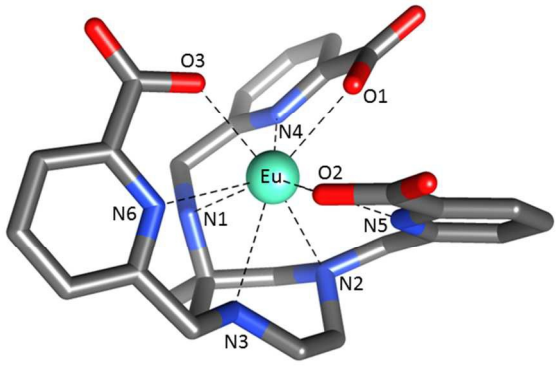

Figure 5. Structure of the [EuL] complex optimized in aqueous solution at the TPSSh/LCRECP/6-31G(d,p) level. Bond distances of the metal coordination environment: Eu-O1, 2.409 Å; Eu-O2, 2.382 Å; Eu-O3, 2.390 Å; Eu-N1, 2.658 Å; Eu-N2, 2.827 Å; Eu-N3, 2.722 Å; Eu-N4, 2.590 Å; Eu-N5, 2.620 Å; Eu-N1, 2.613 Å.

The assignment of a coordination polyhedron to describe the metal coordination environment in [EuL] is not straightforward. Among the different coordination polyhedra most frequently observed for nine-coordinate metal complexes are the monocapped square antiprism, the tricapped trigonal prism and the muffin.[37] These polyhedra provide shape measures S(A)= 3.41, 2.57 and 3.05, respectively (the shape measure S(A)=0 for a structure fully coincident in shape with the reference polyhedron, while the maximum allowed value of S(A) is 100).[38] Thus, the best description of the metal coordination environment in [EuL] is given by a distorted monocapped square antiprism.

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Aiming to gain insight into the excited states responsible for the absorption spectrum of EuL we carried out theoretical TDDFT calculations. The absorption profile obtained with TDDFT is in excellent agreement with the experimental absorption spectrum (Figure 4), with a calculated absorption maximum at 275 nm (273 nm in the experimental spectrum). The calculated absorption profile entails significant contributions from up to 14 excited states with oscillator strengths $f > 0.001$. According to our calculations the absorption band is dominated by excited state 30 (calculated at 267.6 nm, $f = 0.0205$), which presents important contributions of at least four excitations: HOMO-5 → LUMO+2, HOMO-6 → LUMO+1, HOMO-8 → LUMO+1 and HOMO-9→ LUMO. The MOs are dominated by contributions of π orbitals centred on the pyridyl and carboxylate moieties of the ligand. Besides, HOMO-6 and particularly HOMO-5 have significant contributions of the lone pairs of N atoms of the ligand (Figure S5). Thus, the absorption band of the [LnL] complexes can be assigned to a combination of π→π* and n→π* transitions centered on the ligand.

Experimental section

General Methods. Solvents and starting materials were purchased from Aldrich, Acros and Alfa Aesar and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 and Avance 400 spectrometers operating at 300 and 400 MHz for ^{1}H, respectively. Chemical shifts are reported in ppm, with residual protonated solvent as internal reference.[39] IR spectra were recorded on a Perkin Elmer Spectrum One Spectrophotometer as solid samples and only the most significant absorption bands are given in cm^{-1}. High Resolution Mass spectra were recorded by electrospray ionisation method on a microTOF LC Bruker Daltonics. Elemental analyses were recorded at the service central d'analyse of the University of Strasbourg.

Synthesis of the ligand. AMPED was prepared according to ref. 12, while compound **1** was prepared following the procedure reported in ref. 21.

Synthesis of compound **2**. To a suspension of AMPED (200 mg, 1.55 mmol) in CH_3CN (15 mL), dry K_2CO_3 (1.28 g, 6 eq., 9.29 mmol) and methyl 6-chloromethylpicolinate (1.44 g, 7.75 mmol, 5 eq.) were sequentially added. The reaction was stirred at room temperature for 4 days and monitored by TLC (CH_2Cl_2/MeOH/NH_3 90:9:1). The mixture was filtered to remove the salts and evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL), washed with brine (10 mL), dried over Na_2SO_4, filtered and evaporated under *vacuum*. The crude product was purified by flash chromatography column (CH_2Cl_2/MeOH/NH_3 99:0:1 to96:3:1) affording after evaporation a pale yellow solid (178 mg, 20%). ^{1}H-NMR($CDCl_3$, 298K, 400 MHz): δ 7.93 (d, 3H, ^3J = 8Hz), 7.84 (d, 2H, ^3J = 8Hz), 7.73 (t, 3H, ^3J = 8Hz), 7.52 (m, br, 1H), 3.94 (s, 9H), 3.92 (s, 4H), 3.73 (s, 2H), 2.83 (d, br, 2H, ^2J = 16Hz), 2.75-2.56 (m, 6H), 0.92 (s, 3H).^{13}C-NMR($CDCl_3$, 298K, 100.1 MHz): 165.8 ($2C_q$), 160.8 ($2C_q$), 147.1 ($2C_q$), 137.3 (CH), 137.2 (CH),126.5 (CH), 125.4 (CH), 123.6 (CH), 123.2(CH), 66.5 (CH_2), 66.0 (CH_2), 58.4 (CH_2), 56.5 (C_q), 52.9 (CH_3), 52.7 (CH_3), 47.5 (CH_2), 22.9 (CH_3). ES$^+$/MS: *m/z* calcd for $[C_{30}H_{36}N_6O_6+H]^+$, 577.277; found: 577.272. Found: C, 60.86; H, 6.19; N, 14.45%. Calc. for $C_{30}H_{36}N_6O_6\cdot H_2O$: C, 62.49; H, 14.57; N, 6.29.

Synthesis of **LH_3**. Compound **2** (60 mg, 0.104 mmol) was dissolved in a 1M NaOH solution (1.1 mL). The solution was stirred overnight at room temperature. After concentration under vacuum, the residue was dissolved in water and acidified to pH = 2 and evaporated to dryness under reduced pressure. The crude residue was purified by RP-FPLC CH_3CN(0.1%TFA)/H_2O(0.1% TFA) 0:100 to 100:0 affording the pure product as a white solid (67.7 mg, 55%). ^{1}H-NMR (D_2O, 298K, 400 MHz): δ 7.90 (t, 2H, ^3J = 8Hz), 7.87 (t, 1H, ^3J = 8Hz), 7.79 (d,2H, ^3J = 8Hz), 7.78 (d,1H, ^3J = 8Hz), 7.53 (d, 2H, 7.79 (d,2H, ^3J = 8Hz), = 8Hz), 7.46 (d, 1H, ^3J = 8Hz), 4.51 (s, 2H), 4.40-4.30 (AB spin system, 4H, δ_A = 4.38, δ_B = 4.32, ^2J = 16Hz), 3.95-3.67 (AB spin system, 4H, δ_A = 3.93, δ_B = 3.69, ^2J = 16Hz), 3.56-3.39 (m, 4H). ^{13}C-NMR (D_2O, 298K, 101 MHz): δ 166.9 (C_q), 166.3 (C_q) 162.8 (qd, $^2J_{CF}$ = 36Hz), 153.3 (C_q) 151.6 (C_q), 146.2 (C_q), 145.9 (C_q), 140.5 (CH), 140.0 (CH), 128.2 (CH), 126.3 (CH), 125.4 (CH), 125.3 (CH), 116.3 (qd, $^1J_{CF}$ = 289Hz), 61.7 (CH_2), 59.9 (CH_2), 53.0 (CH_2), 43.82 (CH_2), 24.5 (C_q), 18.1 (CH_3).ES$^+$/MS : *m/z* calcd for $[C_{27}H_{30}N_6O_6+H]^+$, 535.230; found: 535.232. Found: C, 37.45; H, 3.34; N, 7.57%. Calc. for $C_{27}H_{30}N_6O_6\cdot(CF_3CO_2H)_5\cdot 4H_2O$: C, 37.76; H, 3.68; N, 7.14.

[EuL]: LH_3 (20.0 mg, 0.017 mmol) was dissolved in ultrapure water (1mL) and $EuCl_3\cdot 6H_2O$ (7.0 mg, 0.019 mmol) was added. The pH was adjusted to 4.50 with NaOH 0.1M and the solution was stirred at 80°C for 4h. The reaction was monitored by RP-TLC CH_3CN(0.1% TFA)/H_2O(0.1% TFA) 1:1 observing a fluorescent red spot at 254 nm. After 4h at 80°C the mixture was cooled at room temperature and the pH adjusted to 7 with NaOH 0.1M. The solution was concentrated and the complex was finally purified by precipitation with THF affording 8.1 mg of EuL as a white solid (yield 70%). ^{1}H-NMR (D_2O, 298K, 400 MHz): δ 8.61 (d, J = 8Hz, 1H), 8.03 (t, J = 8Hz, 1H), 7.88 (t, J = 8Hz, 1H), 7.35 (d, br, J = 16Hz, 1H), 6.72 (d, J = 8Hz, 1H), 6.60 (d, J = 8Hz, 1H), 5.52 (d, J = 8Hz, 1H), 5.40 (d, J = 8Hz, 1H), 5.15 (t, J = 8Hz), 2.97 (d, J = 8Hz, , 1H), 2.81 (d, J = 12Hz, 1H), 2.73 (d, J = 16Hz, 1H), 2.48 (s, br, 1H), 2.05 (s, br, 1H), 1.13 (s, 3H), 0.27 (s, br, 1H), -3.03 (s, br, 1H), -4.20 (d, J = 16Hz, 1H), -5.63 (d, J = 16Hz, 1H), -6.64 (s, br, 1H), -6.81 (d, J = 16Hz, 1H), -8.32 (d, J = 16Hz, 1H), -9.82 (d, J = 16Hz, 1H). ES$^+$/MS: *m/z* calcd for $[C_{27}H_{27}EuN_6NaO_6]^+$: 705.108 (85%), 707.110 (100%); found 705.027 (76%), 707.028 (100%).

[TbL]: LH_3 (20 mg, 0.017 mmol) was dissolved in ultrapure water (1 mL) and $TbCl_3.6H_2O$ (7.1 mg, 0.019 mmol) was added. The pH was adjusted to 4.5 with NaOH 0.1M and the solution was stirred at 80°C for 4h. The reaction was monitored by RP-TLC CH_3CN(0.1% TFA)/H_2O(0.1% TFA) 1:1 showing a fluorescent green spot at 254 nm. After 4h at 80°C the

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mixture was cooled at room temperature and the pH adjusted to 7.0 with NaOH 0.1 M. The solution was concentrated and the complex was precipitated by addition of THF affording 7.1 mg of [TbL] as a white solid (60 %). ES^+/MS: *m/z* calcd for $[C_{27}H_{27}N_6NaO_6T_b]^+$: 713.114 (100%); found 713.024 (100%).

Spectroscopy. UV-Vis absorption spectra were recorded on a Specord 205 (Analytik Jena) or a Perkin Elmer lambda 950 spectrometer. Steady-state luminescence emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrometer working with a continuous 450 W Xe lamp. Detection was performed with a Hamamatsu R928 photomultiplier. All spectra were corrected for the instrumental response. When necessary, a 399 nm cut off filter was used to eliminate the second order artifacts. Phosphorescence decays were measured on the same instrument working in the phosphorescence mode, with 50 µs delay time and a 100 ms integration window or working in the Time Correlated Single Photon Counting (TCSPC) Lifetime Spectroscopy mode, both using a Xenon flash lamp as the excitation source. Monoexponential decay profiles were fitted with the FAST program from Edinburgh Instruments or with the Data station software from Jobin Yvon. Estimated errors on lifetimes are ±10%. Luminescence quantum yields are the average of those obtained with two distinct references and were measured according to conventional procedures, with optically diluted solutions (optical density < 0.05), using rhodamine 6G in water (ϕ = 76%)[23a] and a previously reported Tb complex (ϕ = 31%)[23b] as references for Tb and $[Ru(bipy)_3]Cl_2$ in water (ϕ = 4.0%)[24a] and $[Eu(pic)_3]^{3-}$ (ϕ = 13.5% in TRIS pH 7.4)[24b] for Eu. Estimated errors are ± 15% and deviations were less than 10% from one reference to the other.

DFT calculations. Full geometry optimizations of the [EuL] system were performed in aqueous solution employing DFT within the hybrid meta-GGA approximation with the TPSSh exchange-correlation functional,[40] and the Gaussian 09 package (Revision B.01).[41] In these calculations we used the large-core relativistic effective core potential (LCRECP) of Dolg *et al.* and the related [5s4p3d]-GTO valence basis set for Eu,[42] while C, H, N and O atoms were described with the standard 6-31G(d,p) basis set for. In the LCRECP approach, the 46+4f^6 electrons of Eu^{3+} are included in the core, leaving the outermost 11 electrons to be treated explicitly. Thus, LCRECP calculations were conducted on a pseudo-singlet state configuration. No symmetry constraints have been imposed during the optimizations. The default values for the integration grid (75 radial shells and 302 angular points) and the SCF energy convergence criteria (10^{-8}) were used in all calculations. The stationary points found on the potential energy surfaces as a result of the geometry optimizations have been tested to represent energy minima rather than saddle points via frequency analysis. Time-dependent density functional theory (TDDFT)[43] was used for the calculation of the 40 lowest energy singlet-singlet electronic transitions and the lowest-lying singlet-triplet transition of [EuL] in aqueous solution. The calculated absorption spectrum profile was obtained using half-widths at half height of 0.333 eV (2685.8 cm^{-1}). Solvent effects (water) were evaluated by using the integral equation formalism variant of the polarizable continuum model (IEFPCM),[44] as implemented in Gaussian 09.

Conclusion

Recent reports[4] have highlighted (if needed) that there is still some place for improvements of luminescent lanthanide complexes and their applications as labels in bioanalytical applications. If much of these efforts are directed towards the optimization of the antennas[4,20] or the use of nanoscopic scaffolds[45] less are devoted to the search of new scaffolds. In that respect, AMPED appeared to be particularly attractive with a cyclic structure affording pre-organisation and the possibility to introduce antenna arms and putatively two possibilities to append a dangling function for bioconjugation. Introduction of three picolinate strands on the AMPED cycle led to the formation of a potentially nonadentate ligand, which was shown to be perfectly suited for the coordination of lanthanide cations. Complexation with Eu and Tb led to the formation of luminescent complexes with photo-physical properties close to that observed for C_3 symmetrical analogues. Surprisingly, different efforts to alkylate the secondary nitrogen atom of the ligand were unsuccessful up to now in our hands. An alternative to the introduction of the labelling function may be found in the pre-functionalisation of the quaternary carbon atom of the AMPED structure.[15]

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Notes and references

[a] *Dipartimento di Scienze del Farmaco, Università del Piemonte Orientale "A. Avogadro", Largo Donegani 2/3, 28100 Novara, Italy. E.mail: giovenzana@pharm.unipmn.it*
[b] *Bracco Imaging spa, Bracco Research Centre, Via Ribes 5, 10010 Colleretto Giacosa (TO), Italy.*
[c] *Departamento de Química Fundamental, Universidade da Coruña, Campus da Zapateira-Rúa da Fraga 10, 15008 A Coruña, Spain.*
[d] *Laboratoire d'Ingénierie Moléculaire Appliquée à l'Analyse, Institut Pluridisciplinaire Hubert Curien (IPHC, UMR 7178, CNRS/Université de Strasbourg), ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex. France. Email: l.charbonn@unistra.fr*

† Electronic Supplementary Information (ESI) available: ^1H-^1H Noesy spectrum of LH_3, spectrofluorimetric titration of LH_3 by $EuCl_3$, ES/MS spectra of the Eu and Tb complexes and Views of the frontier MOs of [EuL] obtained from DFT calculations in aqueous solution (5 Figures). See DOI: 10.1039/b000000x/

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