Tripodal diglycolamides as highly efficient extractants for f-elements

Dominik Jańczewski,^{*ab*} David N. Reinhoudt,^{*a*} Willem Verboom,^{*ac*} Clément Hill,^{*d*} Cécile Allignol^{*d*} and Marie-Thérèse Duchesne^{*d*}

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A series of new ligands bearing three diglycolamide functions preorganized at the C-pivot and trialkylphenyl platforms was synthesized. They are very efficient extractants for Am^{3+} and Eu^{3+} with an up to five times relative extraction ability for Eu^{3+} . The distribution coefficients are up to 1000 times increased upon alkylation or arylation of the *N*-position of the diglycolamide moieties. The tripodal diglycolamides show a 1 : 1 metal to ligand stoichiometry as proven with three independent methods for the complexation of the 3-pentyl *N*-substituted diglycolamide ligand with Eu^{3+} ($K = 2.5 \times 10^5 \text{ M}^{-1}$ in acetonitrile–water). A cage-like cryptand, containing three diglycolamide units, was prepared using a Eu^{3+} templated synthesis. However, it does not exhibit improved extraction properties.

Introduction

Despite political, financial, and scientific efforts to explore new renewable energy sources, nuclear electricity remains the main sustainable replacement for that generated from fossil fuels. A current topic of ongoing research is the reprocessing of the spent nuclear fuel produced by atomic power plants worldwide. Presently, plutonium and uranium are effectively removed from waste streams by the PUREX (Plutonium Uranium Extraction) process.¹ The most commonly used TRUEX (TransUranium EXtraction)² process for the recovery of the remaining highly radiotoxic trivalent *trans*-plutonium actinides cannot properly differentiate between the actinides and the much more abundant lanthanides. Isolation of the long-living radiotoxic actinides (10^3-10^5 years) is necessary to differentiate the radioactive wastes, and consequently to reduce the cost affecting handling, treatment, and storage.³

There are a few types of extracting ionophores, compatible with highly acidic conditions, studied as potential ligands for the liquid/liquid–actinide/lanthanide separation. They contain both different ligating groups such as phosphorus–oxygen,⁴ amide–oxygen,⁵ or nitrogen⁶ type donors and different arrangements of these functions at various platforms such as for example: tripodal type,⁷ calixarenes⁸ or cavitands.⁹

Diglycolamides have drawn attention as very effective ionophores for the complexation of f-elements.¹⁰ They act as tridentate binding groups¹¹ thanks to the presence of an additional oxygen atom between the carbonyl groups and therefore display a very high affinity toward actinides and lanthanides¹² compared to other diamides. Except for the work of Scott and co-workers^{13,14} related to the trityl platform, to the best of our knowledge there are no reports on preorganized diglycolamides containing more than one ligating group in a single ionophore.

In this paper we report on the synthesis and extraction behavior of two new classes of efficient actinide and lanthanide ligands, having diglycolamide functions, build upon the tripodal C-pivot and trialkylbenzene platforms.

Results and discussion

Synthesis

The tripodal amines 1a,¹⁵ 1b,c¹⁶ 1d¹⁷ and 4a,b,¹⁶ acting as platform for the construction of ligands, were synthesized by previously described reduction strategies. Reaction of digly-colic anhydride with *N*-methyl-*N*-butylamine gave glycolamic acid 2 in 78%. Subsequent attachment of 2 to the C-pivot (1a–d) and trialkylphenyl amines 4a,b using peptide (DCC) coupling conditions afforded ligands 3a–d (Scheme 1) and 5a,b (Scheme 2), respectively.

All compounds show in the ¹H NMR spectra a characteristic series of signals for the C(O)CH₂O protons in the 4.0–4.3 ppm region, namely three singlets when three secondary amide groups are present (**3a** and **5a**,**b**) and more complex multiplets for compounds with six tertiary amide groups (**3b–d**).

To study the influence of more shielding on the extraction behavior, cryptand 7 was prepared, consisting of a combination of a tripodal secondary amide derivative of **1a** and a tripodal tertiary amide derivative of **1c** (Scheme 3). Diglycolic anhydride was reacted with tripodal amine **1c** to give the corresponding tricarboxylic acid, that for purification reasons was esterified with methanol to give the tripodal ester **6** in 52% yield. Saponification of **6** and subsequent reaction of the resulting tricarboxylic acid with tripodal amine **1a** in the presence of DCC and Eu(NO₃)₃ gave cryptand **7** in 9% yield.¹⁸ In this reaction the presence of Eu(NO₃)₃ is essential, the Eu³⁺ acting as a template cation, since it strongly coordinates to the

^a Laboratory of Supramolecular Chemistry and Technology, Mesa⁺ Research Institute for Nanotechnology, University of Twente, P. O. Box 217, 7500 AE Enschede, The Netherlands. E-mail:

w.verboom@utwente.nl; Fax: +31489 4645; Tel: +31 53489 2977 ^b Institute of Materials Research and Engineering, 3 Research Link, Singapore, 117602, Singapore

^c Laboratory of Molecular Nanofabrication, Mesa⁺ Research Institute for Nanotechnology, University of Twente, P. O. Box 217, 7500 AE Enschede, The Netherlands

^d Commissariat à l' Energie Atomique, CEA-Valrho, DRCP/SCPS/ LCSE, bât. 399, Bp 17171, 30207 Bagnols-sur-Cèze, France



C-pivot tripodal glycolamide arms. Cryptand 7 has a rather complicated ¹H NMR spectrum, but its formation was clearly evidenced by its high resolution FAB mass spectrum showing a distinct signal at m/z 1153.7220 (M + K). Despite many efforts using different coupling strategies, the synthesis of a corresponding cryptand, containing tertiary amide moieties (like *e.g.* 1c) at both sites, was not successful.

Extraction

To investigate the ability of the tripodal glycolamide ligands **3a–d**, **5a,b** and **7** to extract Am^{3+} and Eu^{3+} from acidic aqueous solutions to an organic phase, trace level extraction tests were carried out using 1,1,2,2-tetrachloroethane (TCE) and *n*-octanol as the organic diluents. The results are summarized in Table 1.

Compared to the previously investigated CMP(O)s and malonamides,¹⁶ similar in structure but armed with different ligating groups, the diglycolamides are much more effective





extractants and reach much higher *D* values at comparable conditions. The *D*-values for ligands **3b–d**, with *N*-alkyl or aryl substituted amide groups, are 20 to 1000 times larger than that of unsubstituted ligand **3a**. The highest extraction performance is comparable to that reported by Scott and co-workers for tripodal diglycolamides constructed upon the trityl platform.^{13,14} In general, the C-pivot diglycolamides **3a–d** show a pronounced relative extraction ability toward Eu³⁺ extracting it up to five times more efficient than Am³⁺ (**3b**). The trialk-ylbenzene platform derived ligands **5a,b**, using the preorganization concept proposed by Anslyn and co-workers,¹⁹ extract better than **3a**, however, not as well as the *N*-substituted ligands **3b–d**. They also display a lower relative extraction ability.²⁰

Closing a tripodal structure into a preorganized cage is less beneficial than one would expect. The extraction efficiency of cryptand 7, having features of both ligands 3a and 3c, lies between these two. Unfortunately, we were not able to obtain a cryptand closed at both sides with *N*-substituted amides, which probably would be more efficient. All investigated ligands extract better at the higher nitric acid concentration, which is prerequisite for back extraction of the ligand and potential applications.

Complexation stoichiometry

To investigate the ligand/metal stoichiometry, a fluorescence spectroscopy titration of $Eu(NO_3)_3$ with ligand **3c** in CH₃CN–H₂O solution was performed (Fig. 1). The initial, very low luminescence of Eu³⁺ in the presence of water is strongly increased already upon addition of the first portion of

Table 1 Distribution and separation coefficients for ligands 3a-d, 5a,b and 7

Ligand			Solvent/HNO ₃ initial conc.				
	Cana M		ТСЕ		n-Octanol		
	Conc./M		1 M	3 M		1 M	3 M
3a	4.8×10^{-2}	$D_{\rm Am}{}^a$	2.9×10^{-2}	0.74	$D_{\rm Am}$	2.5	6.8
		$D_{\rm Eu}$	8.3×10^{-2}	3.2	$D_{\rm Eu}$	3.5	8.9
	2	$S_{{ m Eu}/{ m Am}}{}^b$	2.9	4.3	$S_{{ m Eu}/{ m Am}}$	1.4	1.3
3b	3.6×10^{-2}	$D_{\rm Am}$	8.9	143	D_{Am}	100	184
		D_{Eu}	33	797	D_{Eu}	125	219
		$S_{{ m Eu}/{ m Am}}$	3.7	5.6	$S_{{ m Eu}/{ m Am}}$	1.25	1.2
3c	7×10^{-2}	$D_{\rm Am}$	43	с	D_{Am}	1380	$> 10^{3}$
		D_{Eu}	130	с	D_{Eu}	780	$> 10^{3}$
		$S_{\rm Eu/Am}$	3.0	С	$S_{\rm Eu/Am}$	0.6	—
3d	7.7×10^{-2}	$D_{\rm Am}$	12	141	$D_{\rm Am}$	311	346
		$D_{\rm Eu}$	11	344	$D_{\rm Eu}$	884	1164
		$S_{\rm Eu/Am}$	0.9	2.4	$S_{\rm Eu/Am}$	2.8	3.4
5a	4.2×10^{-2}	$D_{\rm Am}$	14	55	$D_{\rm Am}$	3.1	9.1
		$D_{\rm Eu}$	31	49	$D_{\rm Eu}$	3.0	9.9
		$S_{\rm Eu/Am}$	2.2	0.9	$S_{\rm Eu/Am}$	1.0	1.1
5b	3.9×10^{-2}	$D_{\rm Am}$	26	100	$D_{\rm Am}$	10.2	23
		$D_{\rm Eu}$	84	102	$D_{\rm Eu}$	8.9	26
		$S_{\rm Eu/Am}$	3.2	1.0	$S_{\rm Fu/Am}$	0.9	1.1
7	5.3×10^{-2}	$D_{\rm Am}$	0.19	2.6	$D_{\rm Am}$	2.0	9.2
		$D_{\rm Fu}$	0.15	3.6	$D_{\rm Fu}$	5.0	25
		$S_{\rm Fu/Am}$	0.8	1.4	$S_{\rm Fu/Am}$	2.5	2.7

^{*a*} Ligand efficiency *D*: distribution of a metal ion between the organic and water phase after extraction. ^{*b*} Ligand selectivity *S*: ratio $D_{\text{Eu}}/D_{\text{Am}}$. ^{*c*} Not determined.

the ligand. Fig. 1(b) clearly shows the 1 : 1 stoichiometry of the complex; fitting of the data gave a binding constant $K = 2.5 \times 10^5 \text{ M}^{-1}$.



Fig. 1 (a) Fluorescence spectroscopy titration of $Eu(NO_3)_3$ with ligand **3c** in CH₃CN–H₂O = 5 : 1; excitation at 230 nm. (b) Integration of the signal at 603–635 nm, fitting data with a model.



Fig. 2 (a) Molecular ion of the $[3c \cdot Eu(NO_3)_2]^+$ complex in the mass spectrum; (b) Distribution as function of the concentration of ligand **3c** in *n*-octanol.

The same stoichiometry was also confirmed by MS soft ionization. The mass spectrum of a 1 : 1 mixture of ligand 3cwith Eu(NO₃)₃ shows a stable complex in the gas phase with a molecular ion formed by dissociation of one nitrate anion (Fig. 2(a)). The stoichiometry of the extraction with ligand 3cin *n*-octanol was also determined from the slope of the curve of the logarithm of the distribution coefficient *vs.* the logarithm of the concentration of 3c. In this way values for Am³⁺ and Eu³⁺ of 1.05 and 1.09, respectively, were obtained, which in the case of Eu³⁺ is in good agreement with the stoichiometries determined with the other methods (Fig. 2(b)).

Conclusions

New tripodal diglycolamide ligands, based on the C-pivot and trialkylphenyl platforms, were synthesized and their extraction

behavior investigated. They completely fill the metal coordination sphere and form 1 : 1 complexes as proven for the complexation of Eu^{3+} by ligand **3c**. The different tripodal ligands display very high distribution coefficients for Am^{3+} and Eu^{3+} extraction, particularly upon substitution of the amide NH with an alkyl or aryl groups (**3b–d**). They are up to five times more selective toward Eu^{3+} than Am^{3+} . The high complexation ability was successfully used for the synthesis of tripodal cryptand receptor **7**, however its extraction performance was less than expected.

Experimental

¹H and ¹³C NMR spectra were recorded on a Varian Unity INOVA 300 MHz or a Varian Unity 400 WB NMR spectrometer. Fast atom bombardment (FAB) mass spectra were measured on a Finnigan MAT 90 spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. Low fragmentation spectra of the $3c \cdot Eu(NO_3)_3$ complex were taken with a Micromass LCT-electro spray time of flight spectrometer with a cone-voltage of 75 V. All solvents were purified by standard procedures. All other chemicals were analytically pure and were used without further purification.

Glycolamic acid 2

To a cold solution (0 °C) of diglycolic anhydride (19.1 g, 148 mmol) in dry THF (200 mL), N-methyl-N-butylamine was added (18.2 mL, 147 mmol). The reaction mixture was allowed to warm up to room temperature and stirred for 48 h. Subsequently, the solvent was evaporated and the remaining oil was dissolved in AcOEt (200 mL). The resulting solution was washed with 1 M HCl (20 mL) and H₂O (2 \times 20 mL). Evaporation of the solvent afforded product 2 as an oil (23.6 g, 78%). δ_H (300 MHz; CDCl₃) 4.40 (s, 0.9 H, C(O)CH₂O), 4.37 (s, 1.1 H, C(O)CH₂O), 4.20 (s, 2 H, C(O)CH₂O), 3.43 (t, 1.1 H, J 7.2, NCH₂), 3.13 (t, 0.9 H, J 7.5, NCH₂), 3.00 (s, 1.4 H NCH₃), 2.90 (s, 1.6 H NCH₃), 1.48-1.62, 1.24-1.40 (m, 4 H, NCH₂C₂H₄CH₃), 0.97, (t, 3 H, J7.2, NCH₂C₂H₄CH₃), 0.95 (t, 3 H, J 7.2, NCH₂C₂H₄CH₃); $\delta_{\rm H}$ (75 MHz; CDCl₃) 172.1, 172.0, 171.0, 73.0, 71.5, 71.2, 48.8, 34.1, 39.9, 30.3, 29.2, 20.2, 20.1, 14.0; m/z (FAB) 204.1301 ([M + H]⁺. C₉H₁₈NO₄ requires 204.1236).

General procedure for the synthesis of diglycolamide ligands 3a-d and 5a,b

A mixture of glycolamic acid **2** and DCC in dry THF (100 mL) was stirred for 1 h at room temperature. After addition of the appropriate tripodal amine (**1a–d** and **4a,b**) stirring was continued for an additional 16 h at 30 °C. After filtration of the precipitate and evaporation of the solvent gave an oil that subsequently was purified with column chromatography (SiO₂, CH₂Cl₂–MeOH–AcOH = 20 : 1 : 0 \rightarrow 10 : 3 : 1). The salts containing products were dissolved in CHCl₃ (50 mL). The resulting solutions were washed with 1 M HCl (20 mL) and H₂O (3 \times 20 mL) to give, after solvent evaporation, the pure diglycolamic ligands.

C-Pivot ligand 3a. Reaction of glycolamic acid 2 (3.19 g, 15.7 mmol) with DCC (3.49 g, 16.9 mmol) and amine 1a

(1.05 g, 3.42 mmol) gave product **3a** (0.74 g, 25%). $\delta_{\rm H}$ (300 MHz; CDCl₃) 7.48 (br, 3 H, CH₂NHCO), 4.25 (s, 2.7 H, C(O)CH₂O), 4.22 (s, 3.3 H, C(O)CH₂O), 4.05 (s, 6 H, C(O)CH₂O), 3.33–3.46 (m, 15 H, OCH₂CH₂CH₂CH₂N, NC-H₂C₂H₄CH₃), 3.27 (s, 6 H, CCH₂O), 3.16 (t, 3 H, J 7.5, NCH₂C₂H₄CH₃), 2.93 (s, 4.2 H, NCH₃), 2.90 (s, 4.8 H, NCH₃), 1.72–1.84 (m, 6 H, OCH₂CH₂CH₂N), 1.27–1.61 (m, 14 H, NCH₂C₂H₄CH₃), 0.83 (t, 3 H, J 7.5, CH₂C₂H₄CH₃), 0.83 (t, 3 H, J 7.5, CH₂CH₃); $\delta_{\rm C}$ (100 MHz; CDCl₃) 169.3, 168.3, 168.2, 71.6, 71.5, 71.3, 69.6, 69.4, 48.5, 47.7, 43.0, 36.6, 33.7, 33.3, 30.3, 29.5, 29.1, 22.9, 19.9, 19.8, 13.8, 13.7, 7.7; *m*/*z* (FAB) 899.5466 ([M + K]⁺. C₄₂H₈₀N₆O₁₂K requires 899.5471).

C-Pivot ligand 3b. Reaction of glycolamic acid **2** (1.41 g, 6.92 mmol) with DCC (1.49 g, 7.23 mmol) and amine **1b** (0.47 g, 0.99 mmol) gave product **3b** (0.36 g, 35%). $\delta_{\rm H}$ (300 MHz; CDCl₃) 4.25–4.31 (m, 12 H, COCH₂O), 3.15–3.45 (m, 30 H, CH₂OCH₂CH₂CH₂N, NCH₂C₂H₄CH₃), 2.97 (s, 4.7 H, NCH₃), 2.91 (s, 4.3 H, NCH₃), 1.70–1.85 (m, 6 H, OCH₂C-H₂CH₂N), 1.26–1.52 (m, 26 H, NCH₂C₂H₄CH₃, CH₃CH₂C₂C), 0.91–0.95 (m, 18 H, NCH₂C₂H₄CH₃), 0.84 (t, 3 H, J 7.5, CCH₂CH₃); $\delta_{\rm C}$ (100 MHz; CDCl₃) 168.9–168.7, 71.7, 71.5, 69.8, 69.7, 69.3, 69.2, 69.1, 48.9, 47.7, 47.3, 45.7, 44.0, 43.6, 43.2, 36.4, 34.3, 33.3, 31.2, 30.6, 29.8, 29.3, 28.1, 23.4, 20.3, 20.1, 20.0, 14.0, 8.0; *m/z* (FAB) 1067.7097 ([M + K]⁺. C₅₄H₁₀₄N₆O₁₂K requires 1067.7349).

C-Pivot ligand 3c. Reaction of glycolamic acid **2** (4.50 g, 22.2 mmol) with DCC (4.58 g, 22.2 mmol) and amine **1c** (2.95 g, 5.71 mmol) gave product **3c** (1.39 g, 23%). $\delta_{\rm H}$ (300 MHz; CDCl₃) 4.30–4.36 (m, 12 H, C(O)CH₂O), 3.15–3.45 (m, 27 H, CH₂O, CH₂N, CHN), 2.95–2.98 (m, 5 H, NCH₃), 2.91 (s, 4 H, NCH₃), 1.72–1.90 (m, 6 H, OCH₂CH₂CH₃), 1.22–1.57 (m, 26 H, CH₂CH₃, C₂H₄CH₃), 0.82–0.95 (m, 30 H, CH₂CH₃); $\delta_{\rm C}$ (75 MHz; CDCl₃) 170.3, 170.2, 169.9, 169.8, 169.0, 168.8, 71.7, 69.8, 69.4, 69.3, 68.9, 60.3, 58.8, 49.0, 47.8, 43.4, 40.7, 39.0, 34.4, 33.4, 31.4, 30.6, 29.3, 29.2, 26.5, 25.8, 23.6, 20.2, 20.1, 14.0, 11.4, 11.3, 8.1; *m/z* (FAB) 1109.7562 ([M + K]⁺. C₅₇H₁₁₀N₆O₁₂K requires 1109.7819).

C-Pivot ligand 3d. Reaction of glycolamic acid **2** (1.25 g, 6.13 mmol) with DCC (0.85 g, 4.12 mmol) and amine **1d** (0.52 g, 0.90 mmol) gave product **3d** (0.52 g, 51%). $\delta_{\rm H}$ (300 MHz; CDCl₃) 7.17 (d, 6 H, *J* 8.1, Ph), 7.00 (d, 6 H, *J* 8.1, Ph), 4.24–4.27 (m, 6 H, OCH₂C(O)), 3.91 (s, 6 H, OCH₂C(O)), 3.67 (t, 6 H, *J* 7.8, OCH₂, NCH₂), 3.22–3.32 (m, 12 H OCH₂, NCH₂), 3.05 (s, 6 H, CCH₂O, NCH₃), 2.96 (s, 5 H, CCH₂O, NCH₃), 2.85 (s, 4 H, CCH₂O, NCH₃), 2.35 (s, 9 H, PhCH₃), 1.72 (m, 6 H, OCH₂CH₂CH₂N), 1.40–1.58, 1.13–1.32 (m, 14 H, CH₂CH₃, C₂H₄CH₃), 0.86–0.94 (m, 9 H, C₂H₄CH₃), 0.66 (t, 3 H, *J* 7.5 Hz, CH₂CH₃); $\delta_{\rm C}$ (75 MHz; CDCl₃) 169.2, 169.0, 138.6, 138.2, 130.8, 128.0, 71.5, 70.2, 69.8, 69.0, 68.9, 49.1, 47.8, 47.3, 43.2, 34.6, 33.4, 30.6, 29.3, 28.2, 23.2, 21.3, 20.2, 20.1, 14.0, 7.9; *m*/*z* (FAB) 1169.6860 ([M + K]⁺. C₆₃H₉₈N₆O₁₂K requires 1169.6880).

Trialkylphenyl ligand 5a. Reaction of glycolamic acid **2** (2.06 g, 10.1 mmol) with DCC (2.14 g, 10.4 mmol) and amine **4a** (0.58 g, 2.31 mmol) gave product **5a** (0.52 g, 28%). $\delta_{\rm H}$

(300 MHz; CDCl₃) 7.65 (br s, 3 H, CH₂NHCO), 4.26 (s, 3 H, C(O)CH₂O), 4.24 (s, 3 H, C(O)CH₂O), 4.08 (s, 6 H, C(O)CH₂O), 3.32–3.42 (m, 9 H, PhCH₂CH₂N, NC- $H_2C_2H_4CH_3$), 3.16 (t, 3 H, J 7.5, NCH₂C₂H₄CH₃), 2.90–2.97 (m, 15 H, PhCH₂CH₂N, NCH₃), 2.40 (s, 9 H, PhCH₃), 1.43–1.57, 1.25–1.38 (m, 12 H, NCH₂C₂H₄CH₃), 0.91–0.98 (m, 9 H, NCH₂C₂H₄CH₃); δ_C (100 MHz; CDCl₃) 169.4, 168.4, 168.3, 133.8, 133.6, 71.83, 71.77, 69.7, 69.4, 48.5, 47.8, 38.2, 33.7, 33.7, 33.3, 30.7, 30.3, 29.1, 19.95, 19.88, 16.0, 13.8; m/z (FAB) 843.4746 ([M + K]⁺. C₄₂H₇₂N₆O₉K requires 843.4998).

Trialkylphenyl ligand 5b. Reaction of glycolamic acid **2** (2.98 g, 14.6 mmol) with DCC (2.27 g, 11.0 mmol) and amine **4b** (0.81 g, 2.76 mmol) gave product **5b** (1.27 g, 54%). $\delta_{\rm H}$ (300 MHz; CDCl₃) 7.78 (br s, 3 H, CH₂NHCO), 4.28 (s, 3 H, C(O)CH₂O), 4.26 (s, 3 H, C(O)CH₂O), 4.11 (s, 6 H, C(O)CH₂O), 3.37–3.41 (m, 9 H, PhCH₂CH₂N, NC-H₂C₂H₄CH₃), 3.16 (t, 3 H, *J* 7.5, NCH₂C₂H₄CH₃) 2.72–2.96 (m, 21 H, PhCH₂CH₂N, PhCH₂CH₃, NCH₃), 1.47–1.60, 1.26–1.38 (m, 12 H, NCH₂C₂H₄CH₃), 1.17 (t, 9 H, *J* 7.0, PhCH₂CH₃), 0.91–0.98 (m, 9 H, NCH₂C₂H₄CH₃); $\delta_{\rm C}$ (100 MHz; CDCl₃) 169.7, 168.6, 140.7, 132.6, 72.04, 71.98, 69.9, 69.7, 48.7, 48.1, 40.3, 34.0, 33.6, 30.6, 29.51, 29.48, 29.4, 22.7, 20.20, 20.17, 16.0, 14.0; *m/z* (FAB) 885.5600 ([M + K]⁺. C₄₅H₇₈N₆O₉K requires 885.5467).

Tripodal ester 6. To a cold (0 $^{\circ}$ C) solution of amine 1c (8.7 g, 16.9 mmol) in THF (200 mL) were added diglycolic anhydride (22.6 g, 194.9 mmol) followed by triethylamine (20 mL, 143 mmol). The mixture was warmed up to room temperature and stirred for 16 h. After neutralisation with 3 M HCl to pH 1-2 the solvent was evaporated. A solution of the remaining oil and a catalytic amount of H₂SO₄ in MeOH (250 mL) was refluxed for 16 h using a Soxhlet apparatus containing 3 Å molecular sieves to absorb the formed H2O. After addition of NaHCO₃ (2 g) and evaporation of the MeOH, the resulting residue was separated with column chromatography (SiO₂; CH_2Cl_2 -MeOH = 100 : 6) to give pure ester 6 as an oil (8.0 g, 52%). δ_H (300 MHz; CDCl₃) 4.27 (s, 1.7 H, C(O)CH₂OCH₂-C(O)), 4.21-4.24, (m, 5.7 H, C(O)CH₂OCH₂C(O)), 4.17 (s, 4.6 H, $C(O)CH_2OCH_2C(O)$, 3.67–3.70 (m, 9 H, OCH_3), 3.26-3.38, 3.09-3.20 (m, 21 H, CH₂O, CH₂NCH), 1.68-1.84, 1.28–1.54 (m, 20 H, CH₂CH₃, CH₂CH₂CH₂), 0.75–0.84 (m, 21 H, CH₂CH₃); δ_C (75 MHz; CDCl₃) 170.7, 170.6, 169.5, 169.2, 71.9, 71.6, 70.0, 69.8, 69.4, 68.8, 68.2, 60.4, 58.8, 52.0, 43.4, 52.0, 43.4, 40.7, 38.9, 31.5, 29.2, 26.5, 25.8, 23.5, 11.4, 11.3, 8.0; m/z (FAB) 944.5371 ([M + K]⁺. C₄₅H₈₃N₃O₁₅K requires 944.5461).

Cryptand 7. A solution of ester 7 (2.84 g, 3.14 mmol) and LiOH (0.68 g, 28.2 mmol) in a mixture of MeOH (50 mL) and H_2O (20 mL) was stirred for 4 h at room temperature. Subsequently, it was acidified with conc. HCl to pH 1. After evaporation of the solvent the residue was dissolved in AcOEt (50 mL) and the solution washed with H_2O (2 × 5 mL). Solvent evaporation and long vacuum drying gave an oil, which was subsequently dissolved in dry THF (500 mL). DCC (3.8 g, 18.4 mmol) followed by Eu(NO₃)₃ (1.40 g, 3.14 mmol), amine **1a** (0.96 g, 3.14 mmol) and a catalytic amount of

diisopropylethylamine were added to this solution at -18°C. The mixture was slowly warmed to room temperature for 12 h and than stirred for 20 h at 40 °C. After solvent evaporation the resulting solid was purified with triple column chromatography (SiO₂, CH₂Cl₂–MeOH–AcOH = 50 : 2 : 0 \rightarrow 10 : 4 : 1). The salts containing product was dissolved in CHCl₃ (50 mL). The resulting solution was washed with 1 M HCl (20 mL) and H₂O (3 \times 20 mL) to give, after solvent evaporation, cryptand 7 (0.30 g, 9%). $\delta_{\rm H}$ (300 MHz; CDCl₃) 8.25-8.39, 7.18-7.32 (m, 3 H, NH), 4.18-4.35, 3.96-4.12 (m, 12 H, OCH₂C(O)), 3.03–3.55 (m, 39 H, NCH₂, NCH, OCH₂), 1.62-1.94, 1.13-1.62 (m, 28 H, OCH₂CH₂CH₂N, CH₂CH₃), 0.79–0.89 (m, 24 H, CH_2CH_3); δ_C (75 MHz; $CDCl_3$) 169.3-169.9, 72.7-68.6, 60.4, 59.2, 43.4, 43.3, 40.6, 39.0, 36.6, 33.9, 31.7, 29.9, 29.6, 29.3, 26.6, 25.9, 25.1, 23.7, 23.2, 11.5, 11.4, 8.1, 8.0; m/z (FAB) 1153.7220 ([M + K]⁺. C₅₇H₁₀₆N₆O₁₅K requires 1153.7353).

Titration

The photoluminescence titration experiment was carried on a Edinburgh XE-900 spectrofluorometer. The experiment was directly carried out in the spectrophotometric cell by addition of a solution of **3c** (12.9 mM) and Eu(NO₃)₃·6H₂O (0.325 mM) in CH₃CN-H₂O = 5 : 1 to a solution of Eu(NO₃)₃·6H₂O (0.325 mM) in CH₃CN-H₂O = 5 : 1, maintaining in this way a constant Eu³⁺ concentration during the experiment. A spectrum was recorded 5 min upon addition of the ligand. A binding model was constructed assuming the formation of LM, LM₂ and LM₃ complexes. However, data analysis revealed that LM₂ and LM₃ complexes only exist in a very low concentration and therefore can be omitted.

Extraction experiments

Liquid–liquid extraction experiments were performed using either 1 or 3 M nitric acid solutions, spiked with 152 Eu(III) and 241 Am(III), as the aqueous solutions, and solutions of compounds **3a–d**, **5a,b** or **7**, dissolved at various concentrations in 1,1,2,2-tetrachloroethane (TCE) or *n*-octanol, as the organic solutions.

Organic and aqueous phases ($V_{org} = V_{aq} = 200 \ \mu$ L) were mixed in 2 mL Eppendorf micro-tubes, thermostated at 25 ± 0.5 °C and shaken for 60 min with a vortex (Vibrax VXR) IKA device. Tubes were centrifuged and 40 μ L of each phase were diluted either in 560 μ L of TCE or *n*-octanol (organic samples), or in 560 μ L of molar nitric acid (aqueous samples). 500 μ L of these samples were used for radiometric analyses on a Canberra Eurisys highly pure Ge gamma detector.

The acid contents of the initial and final aqueous solutions were determined by potentiometric titration of 100 μ L samples, using a METROHM 751 GPD Titrino device and a 0.1 M NaOH solution.

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