Tripodal diglycolamides as highly efficient extractants for f-elements

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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+} ($K = 2.5 \times 10^5$ 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 nitrogen[6] type donors and different arrangements of these functions at various platforms such as for example: tripodal type,[7] calixarenes[8] or cavitands.[9]

Diglycolamides have drawn attention as very effective ionophores for the complexation of f-elements.[10] They act as tridentate binding groups[11] thanks to the presence of an additional oxygen atom between the carbonyl groups and therefore display a very high affinity toward actinides and lanthanides[12] 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,c**[16] **1d**[17] and **4a,b**,[16] acting as platform for the construction of ligands, were synthesized by previously described reduction strategies. Reaction of diglycolic 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 ^{1}H NMR spectra a characteristic series of signals for the $C(O)CH_2O$ 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 $Eu(NO_3)_3$ gave cryptand **7** in 9% yield.[18] In this reaction the presence of $Eu(NO_3)_3$ is essential, the Eu^{3+} acting as a template cation, since it strongly coordinates to the

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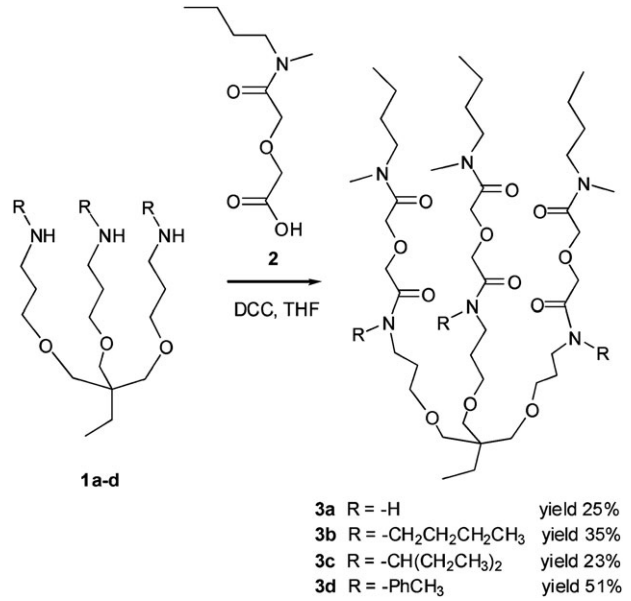


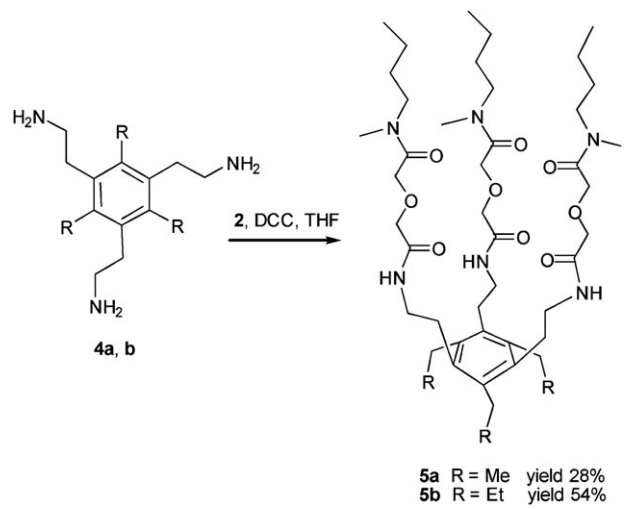
Scheme 1

C-pivot tripodal glycolamide arms. Cryptand **7** has a rather complicated ^{1}H 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.

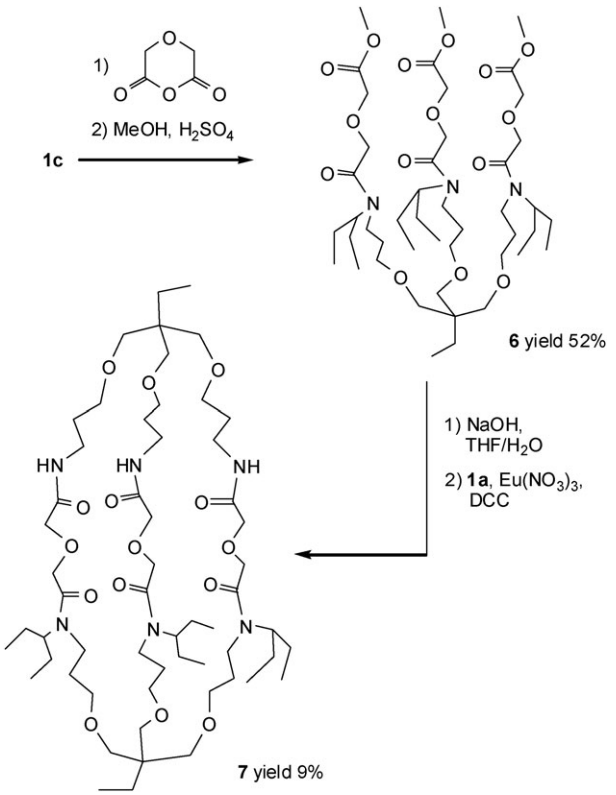
Extraction

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



Scheme 2



Scheme 3

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 Eu^{3+} extracting it up to five times more efficient than Am^{3+} (**3b**). The trialkylbenzene 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 CH_3CN–H_2O solution was performed (Fig. 1). The initial, very low luminescence of Eu^{3+} 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	Conc./M		Solvent/HNO_3 initial conc.				
			TCE			*n*-Octanol	
			1 M	3 M		1 M	3 M
3a	4.8×10^{-2}	D_{Am} [a]	2.9×10^{-2}	0.74	D_{Am}	2.5	6.8
		D_{Eu}	8.3×10^{-2}	3.2	D_{Eu}	3.5	8.9
		$S_{Eu/Am}$ [b]	**2.9**	**4.3**	$S_{Eu/Am}$	**1.4**	**1.3**
3b	3.6×10^{-2}	D_{Am}	8.9	143	D_{Am}	100	184
		D_{Eu}	33	797	D_{Eu}	125	219
		$S_{Eu/Am}$	**3.7**	**5.6**	$S_{Eu/Am}$	**1.25**	**1.2**
3c	7×10^{-2}	D_{Am}	43	[c]	D_{Am}	1380	$>10^3$
		D_{Eu}	130	[c]	D_{Eu}	780	$>10^3$
		$S_{Eu/Am}$	**3.0**	[c]	$S_{Eu/Am}$	**0.6**	—
3d	7.7×10^{-2}	D_{Am}	12	141	D_{Am}	311	346
		D_{Eu}	11	344	D_{Eu}	884	1164
		$S_{Eu/Am}$	**0.9**	**2.4**	$S_{Eu/Am}$	**2.8**	**3.4**
5a	4.2×10^{-2}	D_{Am}	14	55	D_{Am}	3.1	9.1
		D_{Eu}	31	49	D_{Eu}	3.0	9.9
		$S_{Eu/Am}$	**2.2**	**0.9**	$S_{Eu/Am}$	**1.0**	**1.1**
5b	3.9×10^{-2}	D_{Am}	26	100	D_{Am}	10.2	23
		D_{Eu}	84	102	D_{Eu}	8.9	26
		$S_{Eu/Am}$	**3.2**	**1.0**	$S_{Eu/Am}$	**0.9**	**1.1**
7	5.3×10^{-2}	D_{Am}	0.19	2.6	D_{Am}	2.0	9.2
		D_{Eu}	0.15	3.6	D_{Eu}	5.0	25
		$S_{Eu/Am}$	**0.8**	**1.4**	$S_{Eu/Am}$	**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_{Eu}/D_{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 $K = 2.5 \times 10^5\ M^{-1}$.

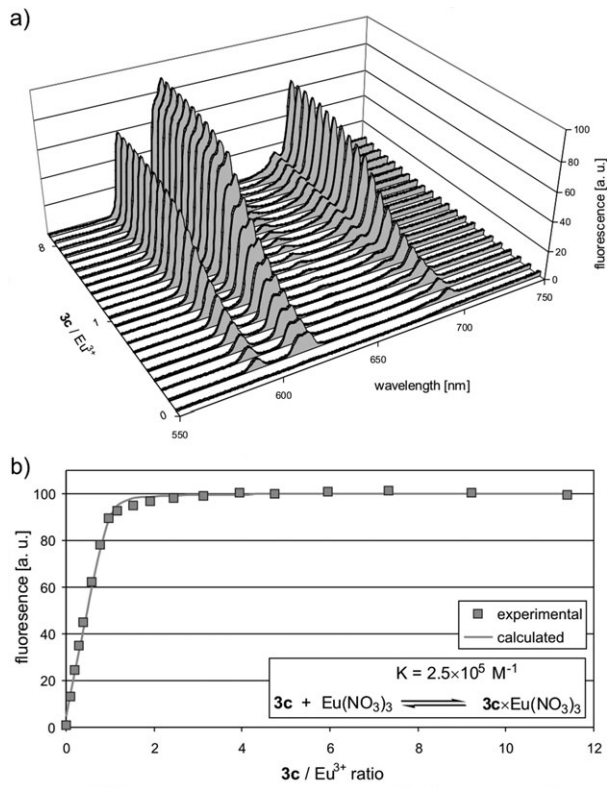


Fig. 1 (a) Fluorescence spectroscopy titration of $Eu(NO_3)_3$ with ligand **3c** in CH_3CN–H_2O = 5 : 1; excitation at 230 nm. (b) Integration of the signal at 603–635 nm, fitting data with a model.

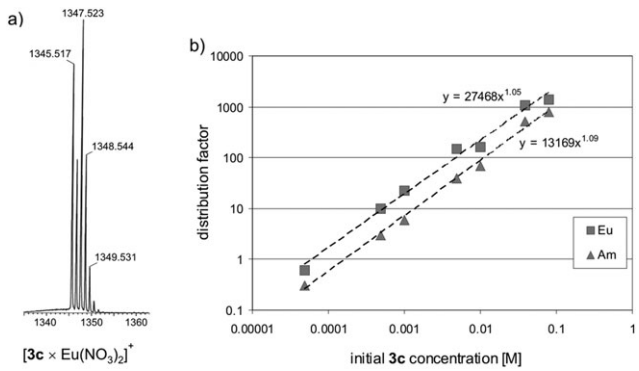


Fig. 2 (a) Molecular ion of the $[\mathbf{3c}{\cdot}Eu(NO_3)_2]^+$ complex in the mass spectrum; (b) Distribution as function of the concentration of ligand **3c** in *n*-octanol.

The same stoichiometry was also confirmed by MS soft ionization. The mass spectrum of a 1 : 1 mixture of ligand **3c** with $Eu(NO_3)_3$ 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 **3c** in *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 Am^{3+} and Eu^{3+} of 1.05 and 1.09, respectively, were obtained, which in the case of Eu^{3+} 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 ^{13}C 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**·$Eu(NO_3)_3$ 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 H_2O (2 × 20 mL). Evaporation of the solvent afforded product **2** as an oil (23.6 g, 78%). δ_H (300 MHz; $CDCl_3$) 4.40 (s, 0.9 H, $C(O)CH_2O$), 4.37 (s, 1.1 H, $C(O)CH_2O$), 4.20 (s, 2 H, $C(O)CH_2O$), 3.43 (t, 1.1 H, *J* 7.2, NCH_2), 3.13 (t, 0.9 H, *J* 7.5, NCH_2), 3.00 (s, 1.4 H NCH_3), 2.90 (s, 1.6 H NCH_3), 1.48–1.62, 1.24–1.40 (m, 4 H, $NCH_2C_2H_4CH_3$), 0.97, (t, 3 H, *J* 7.2, $NCH_2C_2H_4CH_3$), 0.95 (t, 3 H, *J* 7.2, $NCH_2C_2H_4CH_3$); δ_H (75 MHz; $CDCl_3$) 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 ($[M + H]^+$. $C_9H_{18}NO_4$ 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 (SiO_2, CH_2Cl_2–MeOH–AcOH = 20 : 1 : 0 → 10 : 3 : 1). The salts containing products were dissolved in $CHCl_3$ (50 mL). The resulting solutions were washed with 1 M HCl (20 mL) and H_2O (3 × 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%). δ_H (300 MHz; $CDCl_3$) 7.48 (br, 3 H, CH_2NHCO), 4.25 (s, 2.7 H, $C(O)CH_2O$), 4.22 (s, 3.3 H, $C(O)CH_2O$), 4.05 (s, 6 H, $C(O)CH_2O$), 3.33–3.46 (m, 15 H, $OCH_2CH_2CH_2N$, $NCH_2C_2H_4CH_3$), 3.27 (s, 6 H, CCH_2O), 3.16 (t, 3 H, *J* 7.5, $NCH_2C_2H_4CH_3$), 2.93 (s, 4.2 H, NCH_3), 2.90 (s, 4.8 H, NCH_3), 1.72–1.84 (m, 6 H, $OCH_2CH_2CH_2N$), 1.27–1.61 (m, 14 H, $NCH_2C_2H_4CH_3$, CH_3CH_2C), 0.91–0.98 (m, 9 H, $NCH_2C_2H_4CH_3$), 0.83 (t, 3 H, *J* 7.5, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 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 ($[M + K]^+$. $C_{42}H_{80}N_6O_{12}K$ 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%). δ_H (300 MHz; $CDCl_3$) 4.25–4.31 (m, 12 H, $COCH_2O$), 3.15–3.45 (m, 30 H, $CH_2OCH_2CH_2CH_2N$, $NCH_2C_2H_4CH_3$), 2.97 (s, 4.7 H, NCH_3), 2.91 (s, 4.3 H, NCH_3), 1.70–1.85 (m, 6 H, $OCH_2CH_2CH_2N$), 1.26–1.52 (m, 26 H, $NCH_2C_2H_4CH_3$, CH_3CH_2C), 0.91–0.95 (m, 18 H, $NCH_2C_2H_4CH_3$), 0.84 (t, 3 H, *J* 7.5, CCH_2CH_3); δ_C (100 MHz; $CDCl_3$) 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 ($[M + K]^+$. $C_{54}H_{104}N_6O_{12}K$ 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%). δ_H (300 MHz; $CDCl_3$) 4.30–4.36 (m, 12 H, $C(O)CH_2O$), 3.15–3.45 (m, 27 H, CH_2O, CH_2N, CHN), 2.95–2.98 (m, 5 H, NCH_3), 2.91 (s, 4 H, NCH_3), 1.72–1.90 (m, 6 H, $OCH_2CH_2CH_3$), 1.22–1.57 (m, 26 H, CH_2CH_3, $C_2H_4CH_3$), 0.82–0.95 (m, 30 H, CH_2CH_3); δ_C (75 MHz; $CDCl_3$) 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 ($[M + K]^+$. $C_{57}H_{110}N_6O_{12}K$ 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%). δ_H (300 MHz; $CDCl_3$) 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, $OCH_2C(O)$), 3.91 (s, 6 H, $OCH_2C(O)$), 3.67 (t, 6 H, *J* 7.8, OCH_2, NCH_2), 3.22–3.32 (m, 12 H OCH_2, NCH_2), 3.05 (s, 6 H, CCH_2O, NCH_3), 2.96 (s, 5 H, CCH_2O, NCH_3), 2.85 (s, 4 H, CCH_2O, NCH_3), 2.35 (s, 9 H, $PhCH_3$), 1.72 (m, 6 H, $OCH_2CH_2CH_2N$), 1.40–1.58, 1.13–1.32 (m, 14 H, CH_2CH_3, $C_2H_4CH_3$), 0.86–0.94 (m, 9 H, $C_2H_4CH_3$), 0.66 (t, 3 H, *J* 7.5 Hz, CH_2CH_3); δ_C (75 MHz; $CDCl_3$) 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 ($[M + K]^+$. $C_{63}H_{98}N_6O_{12}K$ 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%). δ_H

(300 MHz; $CDCl_3$) 7.65 (br s, 3 H, CH_2NHCO), 4.26 (s, 3 H, $C(O)CH_2O$), 4.24 (s, 3 H, $C(O)CH_2O$), 4.08 (s, 6 H, $C(O)CH_2O$), 3.32–3.42 (m, 9 H, $PhCH_2CH_2N$, $NCH_2C_2H_4CH_3$), 3.16 (t, 3 H, *J* 7.5, $NCH_2C_2H_4CH_3$), 2.90–2.97 (m, 15 H, $PhCH_2CH_2N$, NCH_3), 2.40 (s, 9 H, $PhCH_3$), 1.43–1.57, 1.25–1.38 (m, 12 H, $NCH_2C_2H_4CH_3$), 0.91–0.98 (m, 9 H, $NCH_2C_2H_4CH_3$); δ_C (100 MHz; $CDCl_3$) 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 ($[M + K]^+$. $C_{42}H_{72}N_6O_9K$ 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%). δ_H (300 MHz; $CDCl_3$) 7.78 (br s, 3 H, CH_2NHCO), 4.28 (s, 3 H, $C(O)CH_2O$), 4.26 (s, 3 H, $C(O)CH_2O$), 4.11 (s, 6 H, $C(O)CH_2O$), 3.37–3.41 (m, 9 H, $PhCH_2CH_2N$, $NCH_2C_2H_4CH_3$), 3.16 (t, 3 H, *J* 7.5, $NCH_2C_2H_4CH_3$) 2.72–2.96 (m, 21 H, $PhCH_2CH_2N$, $PhCH_2CH_3$, NCH_3), 1.47–1.60, 1.26–1.38 (m, 12 H, $NCH_2C_2H_4CH_3$), 1.17 (t, 9 H, *J* 7.0, $PhCH_2CH_3$), 0.91–0.98 (m, 9 H, $NCH_2C_2H_4CH_3$); δ_C (100 MHz; $CDCl_3$) 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 ($[M + K]^+$. $C_{45}H_{78}N_6O_9K$ requires 885.5467).

Tripodal ester 6. To a cold (0 °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 H_2SO_4 in MeOH (250 mL) was refluxed for 16 h using a Soxhlet apparatus containing 3 Å molecular sieves to absorb the formed H_2O. After addition of $NaHCO_3$ (2 g) and evaporation of the MeOH, the resulting residue was separated with column chromatography (SiO_2; CH_2Cl_2–MeOH = 100 : 6) to give pure ester **6** as an oil (8.0 g, 52%). δ_H (300 MHz; $CDCl_3$) 4.27 (s, 1.7 H, $C(O)CH_2OCH_2C(O)$), 4.21–4.24, (m, 5.7 H, $C(O)CH_2OCH_2C(O)$), 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, CH_2O, CH_2NCH), 1.68–1.84, 1.28–1.54 (m, 20 H, CH_2CH_3, $CH_2CH_2CH_2$), 0.75–0.84 (m, 21 H, CH_2CH_3); δ_C (75 MHz; $CDCl_3$) 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 ($[M + K]^+$. $C_{45}H_{83}N_3O_{15}K$ 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 $Eu(NO_3)_3$ (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 (SiO_2, CH_2Cl_2–MeOH–AcOH = 50 : 2 : 0 → 10 : 4 : 1). The salts containing product was dissolved in $CHCl_3$ (50 mL). The resulting solution was washed with 1 M HCl (20 mL) and H_2O (3 × 20 mL) to give, after solvent evaporation, cryptand **7** (0.30 g, 9%). δ_H (300 MHz; $CDCl_3$) 8.25–8.39, 7.18–7.32 (m, 3 H, NH), 4.18–4.35, 3.96–4.12 (m, 12 H, $OCH_2C(O)$), 3.03–3.55 (m, 39 H, NCH_2, NCH, OCH_2), 1.62–1.94, 1.13–1.62 (m, 28 H, $OCH_2CH_2CH_2N$, CH_2CH_3), 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 ($[M + K]^+$. $C_{57}H_{106}N_6O_{15}K$ 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 $Eu(NO_3)_3{\cdot}6H_2O$ (0.325 mM) in CH_3CN–H_2O = 5 : 1 to a solution of $Eu(NO_3)_3{\cdot}6H_2O$ (0.325 mM) in CH_3CN–H_2O = 5 : 1, maintaining in this way a constant Eu^{3+} 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, LM_2 and LM_3 complexes. However, data analysis revealed that LM_2 and LM_3 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 μL) 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 μL of each phase were diluted either in 560 μL of TCE or *n*-octanol (organic samples), or in 560 μL of molar nitric acid (aqueous samples). 500 μL 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 μL samples, using a METROHM 751 GPD Titrino device and a 0.1 M NaOH solution.

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