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Calix[6]arene-Picolinamide Extractants for Radioactive Waste Treatment: Effect of Additional Carboxy Binding Sites in the Pyridine 6-Positions on Complexation, Extraction Efficiency and An/Ln Separation

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Dedicated to Professor Saverio Florio on the occasion of his 70th birthday

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The effect of the presence of an additional ester or amide carboxy group in the 6-position of the pyridine nuclei of calixarene-based picolinamide ligands on the extraction and complexation properties of lanthanide(III) and actinide(III) metal ions was studied. For this purpose, six new ligands **1**–**6** were synthesized; their conformational properties were studied both in solution and in the solid state, and their binding properties towards lanthanide (Ln^{III}) and actinide (An^{III}) metal ions were determined under extracting conditions simulating those present in radioactive waste. In the presence of BrCosan as synergizer, a rather high efficiency in the extraction of trivalent metal ions by these ligands was observed even at $[HNO_3] > 2$–3 M. Complexation of Ln^{III} metal ions was also studied under homogeneous conditions (methanol solution), both in chloride and nitrate media, by using spectrophotometry and calorimetry. A comparison with the data obtained with ligands **L1**–**L3**, lacking the additional binding sites in the 6-position of the pyridine nuclei, is reported and the effects of the structure of the ligands on the stoichiometry of the complexes, coordination of the metal ions, basicity of the pyridine binding groups and efficiency and selectivity in the extractions are also discussed.

Introduction

Since the last decade, the chemistry of the nuclear fuel cycle[1] has focussed on the difficult and ambitious goal of separating actinides from lanthanides in solutions derived from nuclear fuel reprocessing plants. This separation, in fact, would allow the long-lived minor actinides (Np, Am, Cm) to be transmutated in fast nuclear reactors or dedicated devices, which would therefore minimize radiotoxicity in the ultimate waste, making nuclear power plants more efficient and sustainable.[2–5] A rather selective solvent extraction process based on heterocyclic polynitrogen ligands[6] has been proposed and tested for An^{III}/Ln^{III} separation from 1 M nitric acid solutions,[7] but new ligands are still needed that could work at even higher nitric acid concentrations.

It was demonstrated that the preorganisation of binding groups on macrocycles[8] such as calixarenes,[9–15] resorcarenes[16] or tripodal scaffolds[17,18] strongly enhances the efficiency in extraction. We previously found that calixarene-based picolinamide ligands (e.g., **L1**–**L3**) are rather efficient and selective (separation factors $SF_{Am/Eu} = D_{Am}/D_{Eu} \leq 11.4$), at least up to $[HNO_3] = 10^{-2}/10^{-3}$ M.[9] More recently, we also showed that calixarene-based picolinamide ligands having electron-withdrawing groups in the *para* position of the pyridine nuclei are able to extract trivalent metal ions into the organic phase even at higher nitric acid concentrations.[19] Although it is well known that the introduction of additional binding sites such as carboxylic acid, ester or amide groups in the *ortho* position to the heterocy-

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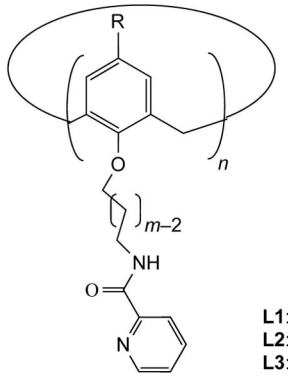
clic N atom of pyridine,[20,21] bipyridine[22] and phenanthroline[23] strongly increases their coordination ability toward highly charged lanthanide and actinide metal ions, nothing is known, to the best of our knowledge, on their effect on An/Ln selectivity. We have therefore synthesised a series of novel calixarene-based picolinamide ligands **1**–**6** bearing additional carboxylic ester, amide and acid moieties in the 6-position of the pyridine nuclei and studied how these substituents affect An/Ln selectivity and the efficiency of extraction at low pH values.

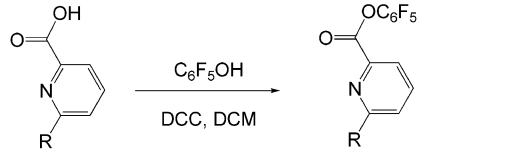


L1: *n* = 6, R = H, *m* = 3
L2: *n* = 4, R = H, *m* = 3
L3: *n* = 4, R = *t*Bu, *m* = 4

Results and Discussion

Synthesis and Conformations of the Ligands

We previously demonstrated[9] that lower-rim picolinamide calix[*n*]arenes (e.g., **L1**–**L3**) can be efficiently synthesised through reaction with the pentafluorophenyl esters of picolinic acids. Following a similar strategy, we prepared pentafluorophenyl esters **11**–**14** (Scheme 1) by treating picolinic acids (**7–10**) modified in the 6-position with methyl ester, benzyl ester, diethylacetamido or acetylamino groups, respectively, with dicyclohexylcarbodiimide (DCC) and pentafluorophenol (68–99% yield).

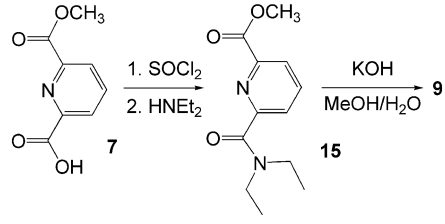


7: R = $COOCH_3$
8: R = $COOCH_2C_6H_5$
9: R = $CONEt_2$
10: R = $NHCOCH_3$

11: R = $COOCH_3$
12: R = $COOCH_2C_6H_5$
13: R = $CONEt_2$
14: R = $NHCOCH_3$

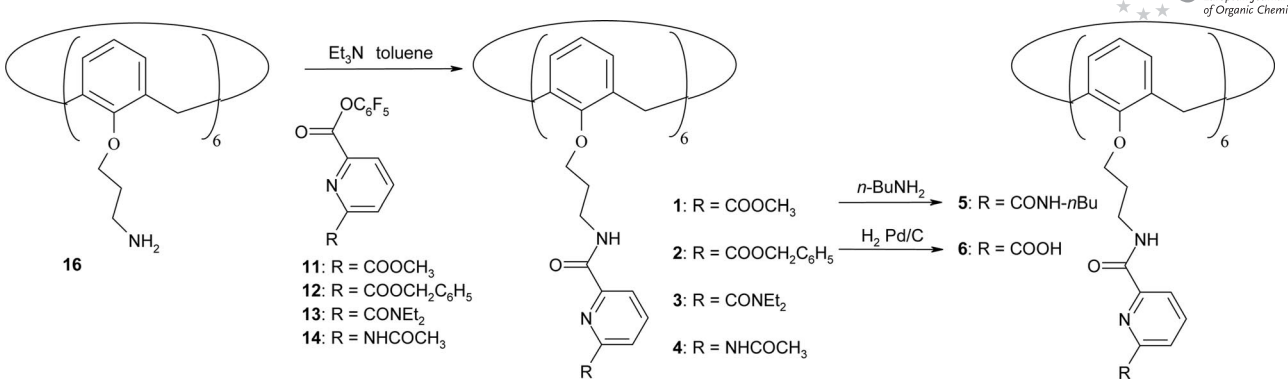
Scheme 1.

Compounds **7**,[24] **8**[25] and **10**[24] were prepared according to literature procedures, whereas monoamido derivative **9** of dipicolinic acid was synthesised according to Scheme 2. The monomethyl ester of dipicolinic acid **7** was transformed into the acyl chloride and subsequently into the monoamido-monomethyl ester derivative **15**, which was hydrolysed to compound **9** with KOH in aqueous methanol (76% overall yield). Reaction of 3-aminopropyloxycalix[6]arene **16** with active esters **11**–**14** at 90 °C in toluene for 24 h (Scheme 3) afforded final ligands **1**–**4** in 76–88% yield. Finally, secondary butyl amide derivative **5** was obtained (66%) by heating methyl ester **1** at reflux in neat butylamine for 5 d, whereas hexaacid **6** was easily isolated (88%) by hydrogenolysis of benzyl ester **2**. Hexaacid **6** is completely insoluble in both polar and apolar organic solvents, and it shows moderate solubility only in acetone/alcohol mixtures. The peaks in the ^1H NMR spectra of compounds **1**–**5** in $CDCl_3$ at room temperature are very broad because of extensive H-bonding between the picolinamide groups at the lower rim of the calixarenes. At room temperature in [D_6]-DMSO, the resonances in the ^1H NMR spectra become slightly sharper as a result of H-bond breaking. Sharp singlets and multiplets could be found only when the spectra were recorded at high temperatures in this solvent. The presence of singlets for the methylene bridge ($ArCH_2Ar$) protons around 3.9 ppm clearly indicates fast interconversion between different conformations for these compounds. Low-temperature ^1H NMR spectra in $CDCl_3$ were also registered for compound **5**, which showed that the calixarene was blocked in a single conformation at –10 °C. Two doublets (δ = 4.48 and 3.42 ppm, 4 H each) and a singlet (δ = 3.90 ppm, 4 H) are present for the methylene bridge ($ArCH_2Ar$) protons, which together with all the other signals are indicative of a centre of symmetry in the molecule (Figures S1–S5, Supporting Information), thus suggesting a 1,2,3-alternate structure for **5** in solution. The ^{13}C NMR spectra, on the other hand, are usually sharp in [D_6]DMSO at room temperature (see Supporting Information). A single crystal, suitable for X-ray diffraction studies, was obtained for compound **2**. In Figure 1, the molecular structure of complex **2**·$2H_2O$ is illustrated, showing the macrocycle to be in a conformation quite similar to that determined for ligand **5** in solution. This confirms, once again, that the 1,2,3-alternate structure is rather common and highly preferred for hexasubstituted calix[6]arene macrocycles.[9,19] Complex **2**·$2H_2O$ is centrosymmetric and the conformation of the calix[6]arene basket is unequivocally defined by the conformational parameters[26,27] ϕ and χ and by the dihedral angles[28] δ reported in Table 1. As a result of the inversion centre, the opposite phenolic rings are antiparallel in pairs (**A** is antiparallel to **A**′ and so on).



Scheme 2.

The orientation of the amide chains at the calixarene subunits **A** and **B**, extended far from the calix[6]arene basket, is determined by the two intramolecular N1A–H···N2A and N1B–H···N2B hydrogen bonds (see Table 2 for geometrical parameters of hydrogen bonds), whereas the amide



Scheme 3.

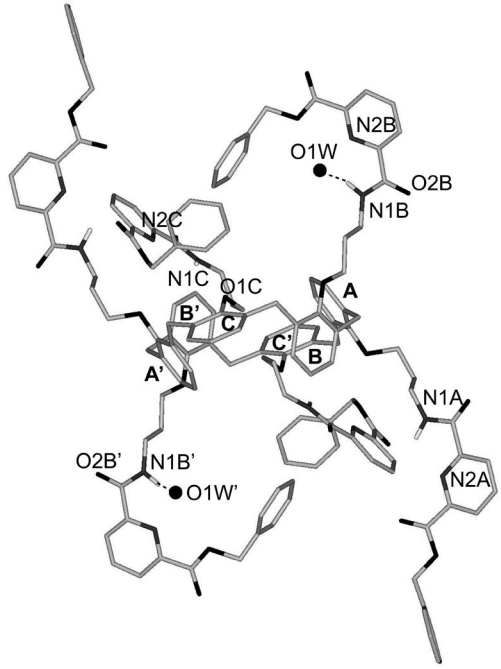


Figure 1. Perspective view of the molecular structure of complex **2**·2H_2O (primed atoms are related to the unprimed ones by the centre of symmetry). Only hydrogen bonds (dotted lines) with water molecules (black spheres) have been evidenced. Atoms are as follows: C, light grey; N, grey; O, black, H, white. For a coloured picture see Figure S6 in the Supporting Information.

Table 1. Conformational parameters ϕ and χ (the symbolic representation of the molecular conformation is C_i +–, ++, –+), and dihedral angles δ [°] between the reference plane R (the weighted least-squares plane through the CH_2 bridging groups) and the planes of the aromatic rings (A,B,C,A′,B′,C′) in the molecular structure of **2**·2H_2O.

Conformational parameters			Dihedral angles	
	ϕ (°)	χ (°)		δ (°)
C–B	95.1(6)	–23.4(5)	A–R	302.8(1)
B–A	87.2(4)	73.6(6)	B–R	69.8(1)
A–C′	–19.4(5)	104.1(5)	C–R	138.5(1)
C′–B′	–23.4(5)	95.1(6)	A′–R	360-δ_{A-R}
B′–A′	–87.2(4)	–73.6(6)	B′–R	360-δ_{B-R}
A′–C	19.4(5)	–104.1(5)	C′–R	360-δ_{C-R}

chain at the calixarene subunit **C** is folded close to the calix[6]arene basket due to the intramolecular hydrogen bond N1C–H···O1C.

Table 2. Geometrical parameters for hydrogen-bonding interactions found in the structure of **2**·2H_2O.

Donor–H···Acceptor	H···A (Å)	D···A (Å)	D–H···A (°)
N1B–H···O1W	2.133(9)	3.038(9)	156.6(3)
N1C–H···O1C	2.206(2)	2.839(4)	122.4(2)
N1A–H···N2A	2.212(3)	2.660(3)	107.3(2)
N1B–H···N2B	2.310(3)	2.668(4)	101.2(2)
N1C–H···N2C	2.314(3)	2.738(4)	106.0(2)

Two water molecules, O1W and the centrosymmetric one O1W′, are linked to the host by the strong intermolecular hydrogen bonds N1B–H···O1W and N1B′–H···O1W′. The role of the water molecules is pivotal in the crystal packing. In fact, as shown in Figure 2, in the symmetry-extended structure, each water molecule acts as a hydrogen-bond acceptor from the N1B–H group of one complex, and contemporarily it acts as a hydrogen-bond donor towards the oxygen atom O2B of the first neighbouring complex. Then, because of the centre of symmetry, the complexes are self-assembled in 1D polymeric chains in which pairs of nearest

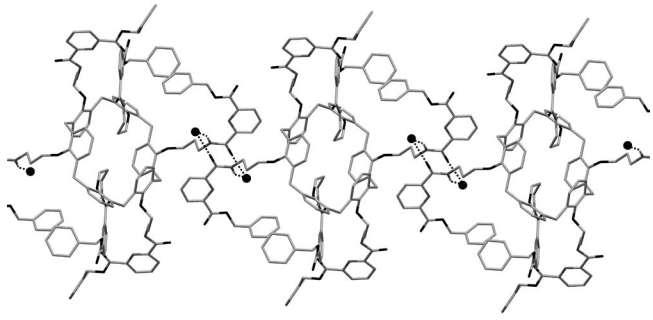


Figure 2. Perspective view of the polymeric self-assembly of **2**·2H_2O in the crystal lattice. Only hydrogen bonds (dotted lines) with water molecules (black spheres) have been evidenced. Atoms are as follows: C, light grey; N, grey; O, black, H, white. For a coloured picture see Figure S7 in the Supporting Information.

neighbouring complexes along each polymeric chain are held together by four hydrogen bonds with two water molecules.

Extraction Properties

Novel calix[6]arene-based picolinamide derivatives **1**–**6** were studied in the extraction of americium and europium from acidic solutions, with or without a synergistic agent. In the present work, a large lipophilic cobalt bisdicarbollide anion (BrCosan, Figure 3) was used as a synergizer. The data were collected according to the procedure described in the Experimental Section.

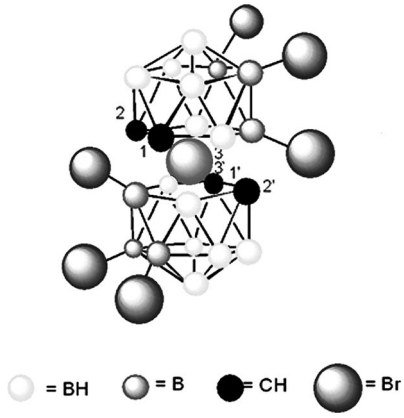


Figure 3. Molecular structure of the BrCosan anion (for a coloured picture see Figure S8 in the Supporting Information).

First, we tested the compounds in *o*-nitrophenyl hexyl ether (NPHE), a diluent already considered in previous studies for industrial process applications. The preliminary tests outlined solubility problems in this solvent for some of the ligands and difficulties in the extraction tests due to the formation of a third phase. For these reasons, we considered different diluents, such as alcohols, ketones or ethers, and their mixtures, to select a diluent in which all the ligands were soluble (Table 3).

The addition of different amounts of acetophenone (methyl phenyl ketone/ACP) to NPHE enabled most of these difficulties to be overcome. Anyway, it was not possible to find a proper solvent mixture for hexaacid **6**. Therefore, extraction tests with ligand **6** were not continued. Then, different NPHE/ACP mixtures were considered and a strong influence of the diluent composition on the extracting properties was observed. Table 4 reports the distribution coefficients (D_M) and the separation factor ($SF_{Am/Eu}$) for all the ligands as a function of the percentage of NPHE in the diluent mixture. In general, the D_{Am} and D_{Eu} values strongly increase by increasing the percentage of NPHE, as expected by the increase in the polarity of the medium passing from ACP (17.9 D) to NPHE (25.7 D). In particular, the greatest improvements in the D_M values were observed for ligands **1**, **3** and **5**. Moreover, for ligands **3** and **4**, the extraction of Am^{III} and Eu^{III} is similarly influenced and the selectivity remains constant, whereas for ligands **1**, **2** and **5** the variation in the mixture composition affects much more the extraction of Am^{III}, leading to higher separation factors.

Table 3. Solubility and third-phase formation issues of the extractants in the different diluents.

Diluent	Solubility		Third-phase
	Soluble	Insoluble	formation
NPHE	**1**–**5**	**6**	**2**,[a] **3**, **4**, **5**[a]
Methyl hexyl ketone		**1**–**6**	
1-Octanol	**1**, **2**, **6**	**3**, **5**	**6**[a]
NPHE/ACP, 70:30	**1**–**5**	**6**	**3**,[b] **4**,[b] **5**[b]
NPHE/ACP, 50:50	**1**–**5**	**6**	**4**[b]
NPHE/ACP, 20:80	**1**–**5**	**6**	**4**[b]

[a] It was impossible to reach complete phase separation. [b] The formation of a negligible third phase was observed.

The effect of the concentration of the synergizer on the extracting properties of the new ligands was considered by testing the molecules at increasing concentrations of the lipophilic anion. All the ligands are poorer extractants in the absence of the synergizer. Other studies in the literature showed that calixarenes in combination with lipophilic anions exhibit a synergistic effect in the extraction of trivalent metal ions.[9,29] Figures 4, 5 and 6 show the effect of the BrCosan concentration on the extraction capability of ligands **1**, **2** and **5**, respectively, in a mixture of NPHE/ACP (70:30). The results underline that the ligand/synergizer ratio strongly affects the extraction efficiency with a comparable effect for Am^{III} and Eu^{III}. An increase of two orders of magnitude in D_M was observed when [BrCosan] passed from 1 to 6 mM. Similar experiments, carried out in the absence of any calixarene ligand and with the only BrCosan in the organic phase, clearly showed that the synergizer alone does not significantly extract An^{III} or Ln^{III} ions (Table S1, Supporting Information). On the contrary, the separation factors are influenced to a lesser extent.

Table 4. D_{Am}, D_{Eu} and $SF_{Am/Eu}$ as a function of the percentage of NPHE in the mixture. Experimental conditions: [ligand] = 1 mM, [BrCosan] = 1.5 mM, diluent = NPHE/ACP and $[H^+]$ = 0.1 M.

	20% NPHE			50% NPHE			70% NPHE			100% NPHE		
	D_{Am}	D_{Eu}	$SF_{Am/Eu}$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
1	0.0035	0.0015	2.31	0.191	0.063	3.05	9.61	2.85	3.37	1058	322.02	3.28
2	0.057	0.028	2.01	0.214	0.096	2.22	8.95	2.51	3.57	_[a]	_[a]	_[a]
3	0.126	0.093	1.35	41.99	31.87	1.32	4552	3706	1.23	>>5000	>>5000	–
4	0.0082	0.0117	0.70	0.081	0.122	0.66	0.84	1.29	0.65	1.61	2.53	0.64
5	0.058	0.043	1.35	4.99	2.69	1.86	212.91	92.89	2.29	_[a]	_[a]	_[a]

[a] Data not available due to incomplete phase separation.

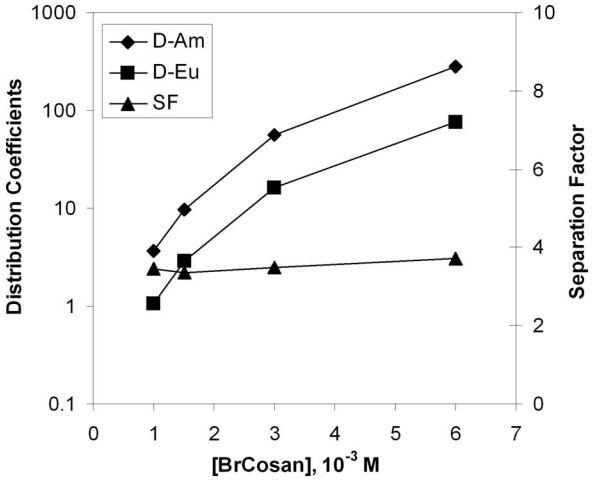


Figure 4. Extraction of Am^{III} and Eu^{III} from nitric acid (0.1 M) at 25 °C by ligand **1** as a function of the concentration of BrCosan.

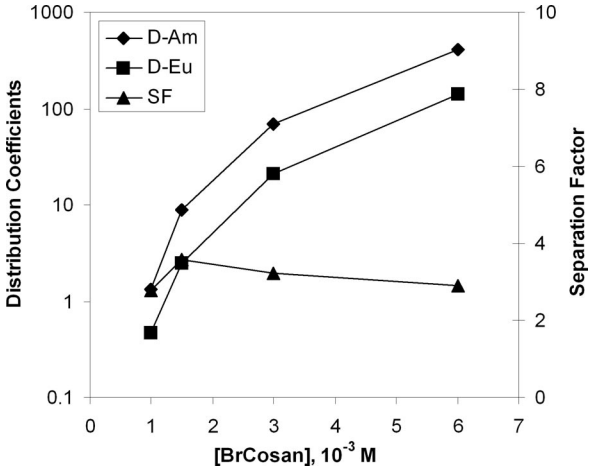


Figure 5. Extraction of Am^{III} and Eu^{III} from nitric acid (0.1 M) at 25 °C by ligand **2** as a function of the concentration of BrCosan.

Finally, it was observed that the synergism between the ligand and the dicarbollide anion is affected by the diluent. As shown in Table 5, in particular for ligand **2**, the distribution coefficients for Am and Eu increase by a factor 2 in the mixture NPHE/ACP, 20:80, and by a factor 8 in the mixture 70:30, when the synergizer concentration was doubled.

To assess the influence of the acidity of the aqueous phase on the extracting properties of the new picolinamide extractants, we performed a series of liquid–liquid extraction tests in NPHE/ACP (70:30) by varying $[H^+]$ between 0.01 and 1 M (Table 6). All the ligands showed a remarkable

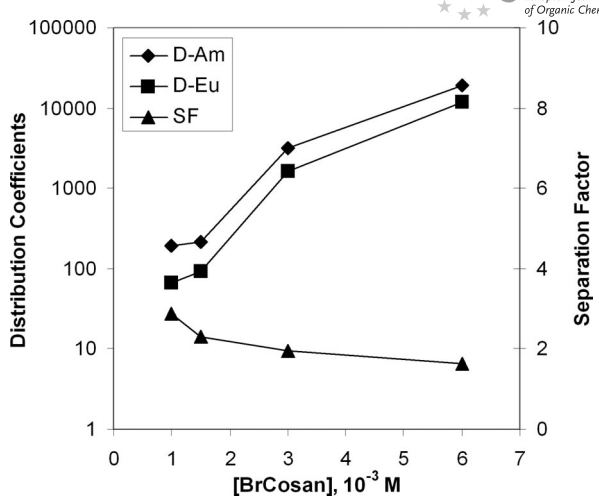


Figure 6. Extraction of Am^{III} and Eu^{III} from nitric acid (0.1 M) at 25 °C by ligand **5** as a function of the concentration of BrCosan.

decrease in the values of D_M upon increasing the concentration of HNO_3 as a result of the protonation of the pyridine nitrogen atoms of the picolinamide binding groups. However, some general important considerations can be drawn from all these results. Ligand **3**, functionalised with a tertiary amide, shows the highest extraction efficiency among all the ligands. This behaviour is expected and explained by the fact that the amide C=O oxygen atom is much more basic and therefore coordinating. At the same time, this ligand is among the less selective. Similar behaviour was observed for ligand **5**, functionalised with a secondary amide. It shows high distribution coefficients at $[H^+] = 0.1$ M, even if lower than those of ligand **3**, but a slightly higher selectivity.

Ligands **1** and **2**, functionalised with methyl and benzyl esters, respectively, show rather similar behaviour, both having a markedly high selectivity and a decrease in the values of D_M by nearly two orders of magnitude on passing from $[H^+] = 0.01$ to 0.1 M. Picolindiamide ligands **3** and **5** display higher chelating ability towards trivalent Ln^{III} and An^{III} metal ions compared to monoester-monoamide derivatives **1** and **2**. This is due to the higher basicity of both the pyridine N atom and the additional amide carbonyl group. The much higher coordination ability of picolindiamide ligands **3** and **5** strongly reduces the competition with the proton (even if the latter is at least six orders of magnitude more concentrated than the cations) and allows these ligands to be rather efficient extracting agents even at $[H^+] \geq 1$ M (Tables 6 and 7). Ligand **4** also possesses two amide groups per pyridine nuclei, but the $CH_3C=O$ group does not give

Table 5. Comparison of the extracting properties in two different diluent mixtures (NPHE/ACP, 20:80 and 70:30) with increasing concentration of BrCosan. Experimental conditions: [ligand] = 1 mM and $[H^+] = 0.1$ M.

	1				**2**				**5**			
[BrCosan]	NPHE/ACP, 20:80		NPHE/ACP, 70:30		NPHE/ACP, 20:80		NPHE/ACP, 70:30		NPHE/ACP, 20:80		NPHE/ACP, 70:30	
	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}
0.0015 M	0.0035	0.0015	9.61	2.85	0.057	0.028	8.95	2.51	0.058	0.043	212.91	92.89
0.003 M	0.0178	0.0074	56.61	16.17	0.107	0.051	68.64	21.2	0.956	0.637	3151	1625

Table 6. Distribution coefficients and separation factors of the ligands studied as a function of the acidity of the aqueous phase. [ligand] = 1 mM, [BrCosan] = 1.5 mM, diluent = NPHE/ACP, 70:30.

	$[H^+]$	**1**	**2**	**3**	**4**	**5**
D_{Am}	0.01	952.45	933.31	>>5000	893.63	>>5000
	0.05	–	37.58	–	–	–
	0.1	9.61	8.95	4552	0.84	212.91
	0.5	–	–	–	–	12.03
	1	0.004	0.024	1.55	0.0011	2.52
D_{Eu}	0.01	396.27	534.48	>>5000	1337	>>5000
	0.05	–	12.41	–	–	–
	0.1	2.85	2.51	3706	1.29	92.89
	0.5	–	–	–	–	3.36
	1	0.0014	0.009	1.29	0.0017	1.77
$SF_{Am/Eu}$	0.01	2.40	1.75	–	0.67	–
	0.05	–	3.03	–	–	–
	0.1	3.37	3.57	1.23	0.65	2.29
	0.5	–	–	–	–	3.60
	1	2.86	2.75	1.20	0.65	1.43

rise to such an efficient chelating effect with the heterocyclic N atom. Selectivity for ligand **4** is also inverted compared to that of the other ligands, as it extracts Ln^{III} better than An^{III}.

Table 7. Comparison among ligands **L1**–**L3** and newly synthesised **1** and **3** in NPHE. The concentrations of the ligand and the synergizer were changed due to solubility problems.

	$[H^+]$	**L1**[a]	**L2**[b]	**L3**[b]	**1**[a]	**3**[c]
D_{Am}	0.001	–	16.3	173	–	–
	0.005	277.95	–	–	–	–
	0.1	0.0317	–	–	>>1000	>>1000
	2	–	–	–	42.22	–
	2.5	–	–	–	–	88.32
	3	–	–	–	8.94	–
D_{Eu}	0.001	–	1.43	19.6	–	–
	0.005	35.15	–	–	–	–
	0.1	0.00878	–	–	>>1000	>>1000
	2		–	–	13.39	–
	2.5		–	–	–	84.06
	3	–	–	–	3.02	–
$SF_{Am/Eu}$	0.001	–	11.4	8.8	–	–
	0.005	7.91	–	–	–	–
	0.1	3.73	–	–	–	–
	2	–	–	–	3.16	–
	2.5	–	–	–	–	1.05
	3	–	–	–	2.89	–

[a] [**1**] = [**L1**] = 1 mM and [BrCosan] = 3 mM. [b] [L] = 10 mM and [BrCosan] = 3 mM. [c] [**3**] = 1 mM and [BrCosan] = 1.8 mM.

Moreover, the electron-donating ability of the CH_3CONH nitrogen atom certainly strongly increases the basicity of the pyridine N atom, which is probably already protonated at $[H^+] \geq 0.1$ M. This behaviour resembles that of previously studied ligands **L1**–**L3** in NPHE under the same experimental conditions (Table 7).[9,30] Ligands **L1**–**L3** showed interesting extracting properties, both in efficiency and selectivity, but only at very low concentrations of the acid ($[H^+] \leq 0.005$ M). On the contrary, in the case of newly synthesised ligands **1** and **3**, the distribution coefficients are still well above unity at $[H^+] = 2.5$ M.[31] Moreover, whereas the selectivity of ligands **L1**–**L3** ranges between 7.9 and 11.4 at very low $[H^+]$ but strongly decreases with a slight increase in the acidity of the aqueous phase (see data for **L1** at $[H^+] = 0.005$ and 0.1 M), the separation factors of ligands **1** and **3** around 3 and 1, respectively, seem to be constant even at high concentrations of nitric acid.

Complexation Properties in Methanol

The complexation properties of the best extracting ligands **3** and **5** with La^{3+}, Eu^{3+} and Yb^{3+} chlorides were studied in methanol by using UV/absorption spectrophotometry. For comparison purpose, the properties of **L1**–**L3** were also investigated. In all cases the spectrophotometric titrations led to significant spectral changes, especially with the hexamers. The complexation of $LaCl_3$ by ligand **5** is illustrated in Figure 7 as an example. The stability constants and stoichiometry of the complexes were calculated from the absorbance variations by the Specfit software. The results, corresponding in each case to at least three independent experiments, are given in Table 8.

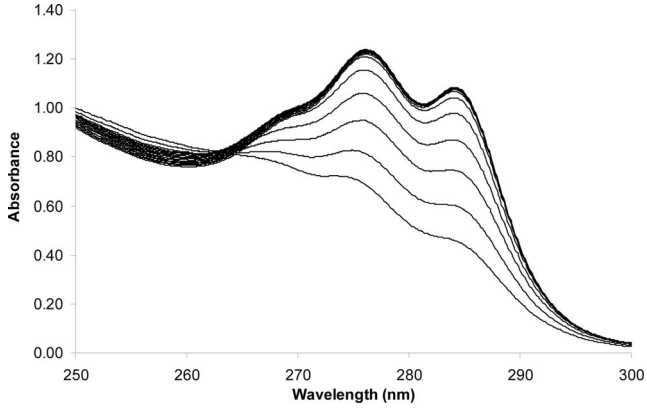


Figure 7. Spectrophotometric titration of ligand **5** ([ligand] = 2.17×10^{-5} M), lower spectrum, by a solution of $LaCl_3$ in methanol ($0 \leq [La]/[ligand] \leq 8.5$).

Table 8. Overall stability constants ($\log\beta_{xy} \pm \sigma$) of lanthanide complexes with ligands **3**, **5** and **L1**–**L3** in methanol ($[Et_4NCl] \times 10^{-2}$ M, 25 °C).

Ligand	Complex	La^{3+}	Eu^{3+}	Yb^{3+}
3	1:1	6.4 ± 0.2	5.3 ± 0.2	6.00 ± 0.05
	2:1	10.9 ± 0.2	10.5 ± 0.2	11.7 ± 0.1
5	1:1	5.6 ± 0.4	4.6 ± 0.2	5.0 ± 0.3
	2:1	10.5 ± 0.4	10.3 ± 0.2	11.3 ± 0.2
L1	1:1	5.3 ± 0.1	5.9 ± 0.2	5.9 ± 0.2
		(2.72 ± 0.05)[a]	(3.03 ± 0.03)[a]	
	1:2	9.4 ± 0.4	11.1 ± 0.7	11.0 ± 0.5
L2	1:1	5.1 ± 0.2	5.3 ± 0.5	5.7 ± 0.5
	1:2	9.6 ± 0.3	9.9 ± 0.2	10.0 ± 0.5
L3	1:1	5.2 ± 0.1	5.4 ± 0.1	5.6 ± 0.2
	1:2	8.8 ± 0.1	9.0 ± 0.2	9.5 ± 0.2

[a] 1:1 complexes in nitrate medium (nitrate salts and Et_4NNO_3 as supporting electrolyte).

In all cases two complexes have been found in agreement with the number of absorbing species found by the factor analysis routine included in the program: four absorbing

species were observed with Eu^{3+} corresponding to the ligand, the metal and two complexes, whereas only three species with La^{3+} and Yb^{3+} as these ions do not absorb in the investigated region. The results show that the stoichiometry of the complexes differs from one ligand to another: 1:1 and 2:1 (Ln/L) complexes are formed with **3** and **5**, whereas 1:1 and 1:2 complexes are formed with hexamer **L1** and tetramers **L2** and **L3**. The distribution curves corresponding to the La^{3+}–**5** system are given in Figure 8. They show the coexistence of the two 1:1 and 2:1 complexes in a wide concentration range. Tetramers **L2** and **L3** form complexes of similar stability (within experimental error), indicating that neither the upper rim substituent nor the linker length between the calixarene and the picolinamide binding group play an important role in the binding efficiency. The complexes of hexamer **L1** are slightly more stable. The stepwise stability constants for the 1:2 complexes of **L1**–**L3** ($\log K_2 = \log\beta_{12} - \log\beta_{11}$ = 3.6–5.2) are lower than the $\log\beta_{11}$ values (ranging between 5.1 and 5.9) for the 1:1 complexes.

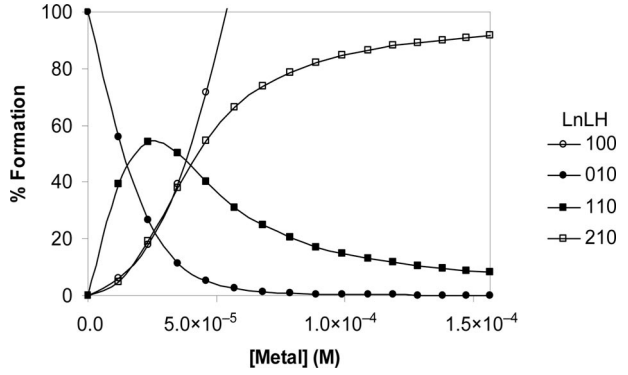


Figure 8. Speciation curves (LnLH species) corresponding to the system La^{3+}–**5** ([ligand] = 2.17×10^{-5} M).

These ligands do not display any remarkable selectivity among lanthanides, although the trend is a slight increase in stability from La^{3+} to Yb^{3+}, which is consistent with the increase in the charge density on the cations and in agreement with the "classical" behaviour of lanthanide chelates. The presence of an additional amide function on the picolinamide ring as in **3** and **5** does not significantly modify the stability of the 1:1 complexes: La^{3+} forms more stable complexes with **3** and **5** ($\log\beta$ = 6.4 and 5.6, respectively) than with **L1** ($\log\beta$ = 5.3), whereas the opposite trend is found with Eu^{3+}, which forms less stable complexes with **3** and **5** ($\log\beta$ = 5.3 and 4.6) than with **L1** ($\log\beta$ = 5.9). However, completely different are the types of complexes formed besides the 1:1 species: ligands **3** and **5**, having three donor atoms per picolinamide chain, form only 2:1 (Ln/L) complexes, whereas ligands **L1**–**L3** possessing only an oxygen and a nitrogen donor atom give 1:2 species. The higher number of binding sites ($3 \times 6 = 18$) present on picolindiamides **3** and **5** compared to **L1** ($2 \times 6 = 12$) or **L2** and **L3** ($2 \times 4 = 8$) clearly allows the binding of two high coordination number lanthanide cations. With ligands **3** and **5** the stability order of the 1:1 complexes is $La^{3+} > Yb^{3+} > Eu^{3+}$, in contrast with the sequence observed with **L1**–**L3** ($Yb^{3+} > Eu^{3+} > La^{3+}$). However, the logarithms of the stepwise stability constants of the 2:1 complexes increase in the series, from 4.5 (La^{3+}) to 5.2 (Eu^{3+}) and 5.7 (Yb^{3+}) with **3** and from 4.9 (La^{3+}) to 5.7 (Eu^{3+}) and 6.3 (Yb^{3+}) with **5**. A positive cooperative effect is found for the formation of the 2:1 complexes only for **5** with Eu^{3+} and Yb^{3+}. It is interesting to note that, despite the very small spectral changes observed during the spectrophotometric titrations of La^{3+} and Eu^{3+} nitrates with **L1** in the presence of Et_4NNO_3, the stability constants of the 1:1 complexes could be determined. These values are much lower than those obtained in chloride medium (Table 8), showing a competition effect between the ligand and the nitrate anion.

Calorimetric titrations have been performed with **3** and **5** and europium chloride. The results are given in Table 9 and globally show a good agreement with the data obtained by spectrophotometry in terms of both stoichiometry and stability of the complexes. With the two ligands, the formation of the 1:1 complex is characterised by strongly positive $T\Delta S_{11}$ values and very small $-\Delta H_{11}$ values, which is consistent with important desolvation effects upon complexation. On the contrary, the formation of the 2:1 complex is enthalpy driven, as shown by highly favourable values of the stepwise enthalpy changes (e.g., $\Delta H_2 = \Delta H_{21} - \Delta H_{11}$ = –58.7 kJ mol^{-1} with **3**), whereas the corresponding entropy values are negative and unfavourable (e.g., $T\Delta S_2 = T\Delta S_{21} - T\Delta S_{11}$ = –34 kJ mol^{-1} with **3**). This may indicate strong interactions with the binding groups and/or strong rearrangement of the ligand upon binding of the second cation.

Table 9. Stability constants ($\log\beta_{xy}$) and overall complexation thermodynamic parameters (kJ mol^{-1}) of europium chloride by ligands **3** and **5**.

Complexes (Eu/L)	Thermodynamic parameter	**3**	**5**
1:1	$\log\beta_{11}$	5.4 ± 0.2 (5.3)[a]	5.7 ± 0.5 (4.6)[a]
	$-\Delta G_{11}$	31 ± 1	32 ± 3
	$-\Delta H_{11}$	2.29 ± 0.05	2.2 ± 0.6
	$T\Delta S_{11}$	28 ± 1	30 ± 3
2:1	$\log\beta_{21}$	9.7 ± 0.3 (10.5)[a]	10.8 ± 0.3 (10.3)[a]
	$-\Delta G_{21}$	55 ± 2	62 ± 2
	$-\Delta H_{21}$	61 ± 4	40 ± 6
	$T\Delta S_{21}$	–6 ± 5	22 ± 8

[a] Spectrophotometric results.

The fact that the ΔH_{21} value is more negative (–61 kJ mol^{-1}) for **3** bearing tertiary amides than for **5** bearing secondary amides (–40 kJ mol^{-1}) supports the assumption that also the amide functions in the 6-position of the pyridine ring are involved in cation binding. Such a difference in the enthalpy contribution has already been shown for alkali and alkaline earth metal ion complexes with calix[4]arene derivatives substituted with both secondary and tertiary amides.[32,33]

Conclusions

Calixarene-based picolinamide ligands proved to be quite efficient complexing agents for trivalent lanthanide

and actinide ions. In homogeneous solution (methanol), it was found that the stoichiometry of the complexes is strongly dependent on the size of the macrocycle or the substitution of the pyridine nuclei. For unsubstituted picolinamide binding groups (no substituents in the pyridine 6-position, X_6 = H), 1:1 and 1:2 (Ln/L) complexes are formed with calix[6]arene (**L1**) and calix[4]arenes (**L2** and **L3**). It is likely that the reduced number of donor atoms induces the participation of the two macrocycles to complete the coordination sphere of the Ln^{III} metal ion. On the other hand, when picolinamide nuclei of calix[6]arenes are substituted in the 6-position with an additional binding group [X_6 = -CO(N)R^1R^2, in ligands **3** or **5**], in addition to the 1:1 species 2:1, (Ln/L) complexes also form. In this case, three donor atoms are present for each picolindiamide chelating unit allowing two metal ions with a high coordination number such as Ln^{III} to be bound. The calorimetric data are in nice agreement with the spectrophotometric results both in terms of stoichiometry and stability of the complexes. In extraction experiments, the newly synthesised calix[6]arene ligands **1**–**5**, bearing additional carboxy groups in the 6-positions of the picolinamide nuclei, showed remarkable efficiency in the extraction of both Eu^{3+} and Am^{3+} ions, even at the very high concentrations of nitric acid that are used for the treatment of nuclear waste. Compared to ligands **L1**–**L3** lacking the 6-substituents and which are effective only at $[HNO_3] \leq 0.05$ M, ligands **1**–**5** proved to be much more efficient: for instance, at $[H^+]$ = 0.1 M, the value of D_M for **3** is six orders of magnitude higher than that of **L1**. This is due, on one side, to the better chelation offered by the tridentate picolindiamide moiety compared to the bidentate picolinamide one and, on the other side, to the decrease in the basicity of the pyridine N atom due to the presence of an additional electron-withdrawing group in the *ortho* position, which disfavours H^+ binding and favours Ln^{3+} binding. The inversion of atom attachment of the amide group from the carboxy group [X_6 = -C(O)N] of ligand **3** or **5** to the N atom [X_6 = -NC(O)] changes the electronic effects on the pyridine N atom and increases its basicity, so that compound **4** is at least 300 times less efficient already at pH 1. Finally, amide derivatives **3** and **5** are by far more efficient than ester compounds **1** and **2**. An opposite effect is found on the selectivity between An and Ln: diamides **3** and **5** are less selective than monoamide-monoesters **1** and **2**. In conclusion, as a general trend, the introduction of additional carboxy substituents in the 6-position of the picolinamide ligands supported on a calixarene scaffold strongly increases the efficiency of extraction even at very high concentrations of HNO_3 in the water layer but, simultaneously, also lowers the separation factors $SF_{Am/Eu}$ compared to previously synthesised picolinamide-based calixarene extractants (e.g., **L1**–**L3**). Owing to the particular extraction conditions used (solvents, synergizer and acidity) and to the stoichiometry of the complexes formed by these multicoordinate ligands[8] in homogeneous solution, a direct comparison with acyclic ligands is not feasible. However, compared with lower-rim calix[4]arene tetracarbamoylmethyldiphenylphosphane oxide derivatives, calix[6]arenes **3** and **5** form 1:1 complexes in methanol of similar stabilities ($\log\beta$ = 4.6–6.4 vs. $\log\beta$ = 5.0–6.4[34]) and have comparable values of $SF_{Am/Eu}$ in extraction,[35] whereas calix[4]arenes **L2** and **L3** form slightly less stable complexes in methanol ($\log\beta$ = 5.1–5.7) but are considerably more selective in extraction ($SF_{Am/Eu}$ up to 11.4).

Experimental Section

General Remarks: Melting points were determined with an Electrothermal apparatus in sealed capillaries under an atmosphere of nitrogen. ^1H and ^{13}C NMR spectra were recorded with Bruker spectrometers AC300 (^1H: 300 MHz, ^{13}C: 75 MHz) with residual signals of partially deuterated solvents as internal standard. Mass spectra were obtained in the ESI mode with a Micromass 4LCZ or in the CI (CH_4) mode with Finnigan Mat SSQ710 spectrometers. TLC was performed on precoated silica gel Merck 60 F_{254}. All solvents were purified by standard procedures; dry solvents were obtained by literature methods and stored over molecular sieves. All reactions were carried out under an atmosphere of nitrogen. Dipicolinic acid monomethyl ester (**7**),[24] dipicolinic acid monobenzyl ester (**8**),[25] 6-acetylamino picolinic acid (**10**)[24,36] and hexakis(3-aminopropoxy)calix[6]arene (**16**)[9] were prepared according to the procedure reported in the literature.

2-(Methoxycarbonyl)-6-[(*N*,*N*-diethylamino)carbonyl]pyridine (15): To a sample of monomethyl dipicolinate (**7**; 1.5 g, 8.28 mmol) in a round-bottomed flask cooled with an ice bath was slowly added thionyl chloride (20 mL) and a drop of DMF. The suspension was stirred at 60 °C until all the solid dissolved (1 h). Thionyl chloride was removed under reduced pressure and then dry DCM (30 mL) was added. This solution was cooled with an ice bath and then diethylamine (4.3 mL, 41.6 mmol) was added. The solution was stirred at 40 °C for 2 h and then quenched with a solution of NH_4Cl. The organic layer was separated and washed with water (2 × 30 mL). DCM was then removed under reduced pressure to give a light brown oil. Yield: 1.91 g (98%). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.11 (d, ^3J = 7.6 Hz, 1 H, Py-H3), 7.90 (t, ^3J = 7.6 Hz, 1 H, Py-H4), 7.79 (d, J = 7.6 Hz, 1 H, Py-H5), 3.95 (s, 3 H, OCH_3), 3.53 and 3.37 (2q, ^3J = 6.9 Hz, 2 H each, NCH_2), 1.24 and 1.21 (2t, ^3J = 6.9 Hz, 3 H each, NCH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 167.3 (COO), 165.2 (CON), 154.9 (Py-C2), 146.3 (Py-C6), 137.8 (Py-C4), 126.7 (Py-C5), 125.4 (Py-C3), 52.7 (OCH_3), 43.5 and 40.6 (NCH_2), 14.1 and 12.7 (NCH_2CH_3) ppm. MS (ESI+): m/z = 259.4 $[M + Na]^+$. $C_{12}H_{16}N_2O_3$ (236.27).

2-(Hydroxycarbonyl)-6-[(*N*,*N*-diethylamino)carbonyl]pyridine (9):[37,38] A suspension of compound **15** (1.91 g, 8.08 mmol) in a mixture of MeOH/H_2O (1:1, 80 mL) was cooled to 0 °C and then KOH (0.91 g, 16.16 mmol) was added. After 2 h stirring, the reaction mixture was quenched with 0.2 M aqueous HCl to pH 4. The aqueous phase was extracted with EtOAc (3 × 50 mL). The solvent was removed from the combined organic extract under reduced pressure, and product **9** was obtained by precipitation with Et_2O. Yield: 1.40 g (78%). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.25 (d, ^3J = 7.8 Hz, 1 H, Py-H3), 8.04 (t, ^3J = 7.8 Hz, 1 H, Py-H4), 7.82 (d, J = 7.8 Hz, 1 H, Py-H5), 3.58 and 3.30 (2q, ^3J = 6.9 Hz, 2 H each, NCH_2), 1.28 and 1.19 (2t, ^3J = 6.9 Hz, 3 H each, NCH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 167.4 (COO), 165.1 (CON), 153.8 (Py-C2), 144.9 (Py-C6), 139.3 (Py-C4), 127.1 (Py-C5), 124.3 (Py-C3), 43.1 and 40.2 (NCH_2), 14.3 and 12.7 (NCH_2CH_3) ppm. MS (ESI+): m/z = 245.4 $[M + Na]^+$. $C_{11}H_{14}N_2O_3$ (222.24).

General Procedure for the Synthesis of Pentafluorophenyl Esters 11–14: To a suspension of acid **7**–**10** (3.00 mmol) in dry DCM (20 mL) was added dicyclohexylcarbodiimmide (DCC; 0.68 g, 3.30 mmol) and pentafluorophenol (0.61 g, 3.30 mmol). After 3–8 h, the resulting white solid of dicyclohexylurea (DCU) was filtered off and washed carefully with DCM. The solvent was removed from the combined filtrates under reduced pressure, and the product was purified from this crude as reported below for the single compounds.

2-(2,3,4,5,6-Pentafluorophenoxycarbonyl)-6-(methoxycarbonyl)pyridine (11): Reaction time, 3 h. Pure compound was obtained by crystallisation from hexane/DCM (9:1). Yield: 1.65 g (83%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.45 and 8.43 (2d, ^3J = 7.8 Hz, 1 H each, Py-H5 and Py-H3), 8.13 (t, ^3J = 7.8 Hz, 1 H, Py-H4), 4.05 (s, 3 H, OCH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 164.6 (COOMe), 160.5 (COO), 148.9 (Py-C6), 145.3 (Py-C2), 141.06 (dd, J = 250, 9 Hz, C2-C_6F_5), 140.3 (dt, J = 140, 12 Hz, C4-C_6F_5), 138.3 (Py-C4), 136.9 (dt, J = 140, 9 Hz, C3-C_6F_5), 129.1 (Py-C3 and Py-C5), 125.0 (t, J = 8 Hz, C_1-C_6F_5), 53.2 (OCH_3) ppm. MS (ESI+): m/z = 686.5 [M + Na]$^+$.$C_{34}H_{38}F_5N_3O_5$ (663.67).

2-(2,3,4,5,6-Pentafluorophenoxycarbonyl)-6-(benzyloxycarbonyl)pyridine (12): Reaction time, 8 h. Pure compound was obtained by crystallisation from Et_2O. Yield: 1.55 g (70%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.43 and 8.38 (2d, ^3J = 7.6 Hz, 1 H each, Py-H5 and Py-H3), 8.09 (t, ^3J = 7.6 Hz, 1 H, Py-H4), 7.49 (d, ^3J = 7.6 Hz, BnH), 7.39 (m, 3 H, BnH), 5.49 (s, 2 H, OCH_2) ppm. MS (ESI+): m/z = 762.6 [M + Na]$^+$. $C_{40}H_{42}F_5N_3O_5$ (739.77).

2-(2,3,4,5,6-Pentafluorophenoxycarbonyl)-6-[(*N*,*N*-diethylamino)carbonyl]pyridine (13): Reaction time, 3 h. After a first trituration in DCM, the resulting solid was purified by flash chromatography (SiO_2; hexane/EtOAc, 1:1 to 1:2). Yield: 2.09 g (99%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.31 (dd, J = 7.2, 2.1 Hz, 1 H, Py-H5), 8.1–8.0 (m, 2 H, Py-H4 and Py-H3), 3.59 and 3.46 (2q, ^3J = 7.2 Hz, 2 H each, NCH_2CH_3), 1.32 (m, 6 H, NCH_2CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 166.6 (COO), 160.8 (CON), 155.3 (Py-C6), 143.3 (Py-C2), 141.3 (dd, J = 235, 9 Hz, C2-C_6F_5), 139.5 (dt, J = 130, 12 Hz, C4-C_6F_5), 138.3 (Py-C4), 137.9 (dt, J = 135, 9 Hz, C3-C_6F_5), 128.3 (Py-C3), 125.6 (Py-C5), 124.8 (t, J = 8 Hz, C1-C_6F_5), 43.8 and 40.9 (NCH_2CH_3), 14.1 and 12.6 (NCH_2CH_3) ppm. MS (ESI+): m/z = 727.8 [M + Na]$^+$. $C_{37}H_{45}F_5N_4O_4$ (704.77).

2-(2,3,4,5,6-Pentafluorophenoxycarbonyl)-6-(acetylamino)pyridine (14): Reaction time, 4 h. Pure compound was obtained by flash chromatography (SiO_2; DCM/EtOAc, 20:1 to 4:1). Yield: 1.36 g (68%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.54 (d, ^3J = 7.8 Hz, 1 H, Py-H5), 8.32 (s, 1 H, NH), 8.01 (d, ^3J = 7.8 Hz, 1 H, Py-H3), 7.94 (t, ^3J = 7.8 Hz, 1 H, Py-H4), 2.23 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 169.0 (CON), 160.8 (COO), 151.7 (Py-C6), 142.9 (Py-C2), 141.9 (dd, J = 230, 9 Hz, C2-C_6F_5), 140.2 (dt, J = 135, 12 Hz, C4-C_6F_5), 139.7 (Py-C4), 137.0 (dt, J = 130, 9 Hz, C3-C_6F_5), 125.1 (t, J = 8 Hz, C1-C_6F_5), 122.5 (Py-C3), 119.1 (Py-C5), 24.5 (CH_3CO) ppm. MS (+): m/z = 685.4 [M + Na]$^+$. $C_{34}H_{39}F_5N_4O_4$ (662.69).

General Procedure for the Synthesis of Ligands 1–4: To a solution of hexaaminocalix[6]arene **16** (1.00 g, 1.02 mmol) in dry toluene (75 mL) was added the proper pentafluorophenyl ester **11**–**14** (6.73 mmol) and triethylamine (0.4 mL, 3.1 mmol). This mixture was heated at 90 °C in a sealed tube under an atmosphere of nitrogen for 24 h. The solvent was then removed under reduced pressure, and the reaction was quenched with 2 M $NaHCO_3$ (50 mL). The product was extracted in DCM (2 × 30 mL), and the combined organic layer was washed with water (2 × 50 mL). The solvent was then removed under reduced pressure, and the residue was purified as reported below for the single products.

37,38,39,40,41,42-Hexakis{3-[(pyridine-6-methoxycarbonyl-2-carboxy)amino]propoxy}calix[6]arene (1): The product was recrystallised from hexane. Yield: 1.640 g (82%); m.p. 184–185 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.40 (br. s, 12 H, NH and PyH), 8.18 (d, ^2J = 7.5 Hz, 6 H, PyH), 7.96 (t, ^2J = 7.5 Hz, 6 H, PyH), 7.30–6.90 (br. s, 18 H, ArH), 3.95–3.55 (br. s, 42 H, $ArCH_2Ar$, OCH_3, OCH_2), 3.10–2.90 (br. s, 12 H, NCH_2), 2.05 (br. s, 12 H, OCH_2CH_2) ppm. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 8.51 (s, 6 H, NH), 8.21–8.08 (m, 18 H, PyH), 7.2–6.7 (br. s, 18 H, ArH), 3.73 (s, 42 H, $ArCH_2Ar$, OCH_3, OCH_2), 3.35 (br. s, 12 H, NCH_2), 1.80 (br. s, 12 H, OCH_2CH_2) ppm. ^{13}C{^{1}H} NMR ([D_6]DMSO, 75 MHz): δ = 164.4 (COO), 162.7 (CON), 154.3 (Ar_{ipso}), 149.9 (Py-C2), 146.2 (Py-C6), 139.1 (Py-C4), 134.1 (Ar_{ortho}), 126.8 (Ar_{meta}), 124.9 (Py-C3, Py-C5), 123.3 (Ar_{para}), 70.8 ($OCH_2CH_2CH_2$), 52.3 (OCH_3), 36.7 ($OCH_2CH_2CH_2$), 29.7 and 29.5 ($OCH_2CH_2CH_2$ and $ArCH_2Ar$) ppm. MS (ESI+): m/z = 1980.1 [M + Na]$^+$, 1001.8 [M + 2Na]$^{2+}$. $C_{108}H_{108}N_{12}O_{24}$·2$H_2O$ (1994.11): calcd. C 65.05, H 5.66, N 8.43; found C 64.89, H 5.54, N 8.52.

37,38,39,40,41,42-Hexakis{3-[(pyridine-6-benzyloxycarbonyl-2-carboxy)amino]propoxy}calix[6]arene (2): The product was purified by crystallisation from hexane/AcOEt (3:1). Yield: 1.185 g (86%); m.p. 125–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.39 (br. s, 12 H, Py-H3 and NH), 8.16 (br. s, 6 H, Py-H5), 7.92 (t, ^3J = 7.5 Hz, 6 H, Py-H4), 7.32–7.28 (s, 30 H, PhH), 7.30–6.85 (br. s, 18 H, ArH), 5.34 (br. s, 12 H, CH_2Ph), 3.90–3.15 (br. s, 42 H, $ArCH_2Ar$, OCH_2, CH_2N), 2.00 (br. s, 12 H, OCH_2CH_2) ppm. ^{1}H NMR (300 MHz, [D_6]DMSO, 373 K): δ = 8.21–8.18 (m, 12 H, Py-H3 and NH), 8.13–8.03 (m, 12 H, Py-H4, Py-H5), 7.40–7.27 (m, 30 H, PhH), 6.88 (d, ^3J = 7.5 Hz, 12 H, ArH_{meta}), 6.79 (t, ^3J = 7.5 Hz, 6 H, ArH_{para}), 5.32 (s, 12 H, OCH_2Ph), 3.91 (s, 12 H, $ArCH_2Ar$), 3.43 (t, ^3J = 5.7 Hz, 12 H, $OCH_2CH_2CH_2$), 3.33 (q, ^3J = 6.6 Hz, 12 H, $OCH_2CH_2CH_2$), 1.57 (quint., ^3J = 6.6 Hz, 12 H, OCH_2CH_2) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]DMSO, 298 K): δ = 163.6 (COO), 162.7 (CON), 154.2 (Ar_{ipso}), 150.1 (Py-C2), 146.1 (Py-C6), 139.1 (Py-C4), 135.6 (Ph-C1), 134.0 (Ar_{ortho}), 128.2, 127.9 and 127.7 (Ph-C2, Ph-C6), 127.0 (Ar_{meta}), 125.0 (Py-C3, Py-C5), 123.3 (Ar_{para}), 70.6 ($OCH_2CH_2CH_2$), 66.5 (OCH_2Ph), 36.7 ($OCH_2CH_2CH_2$), 29.6 ($OCH_2CH_2CH_2$ and $ArCH_2Ar$) ppm. MS (ESI+): m/z = 2437.4 [M + Na]$^+$. $C_{144}H_{132}N_{12}O_{24}$ (2414.65): calcd. C 71.63, H 5.51, N 6.96; found C 71.42, H 5.64, N 7.02.

37,38,39,40,41,42-Hexakis{3-[(pyridine-6-*N*,*N*-diethylaminocarbonyl-2-carboxy)amino]propoxy}calix[6]arene (3): The product was purified by precipitation with Et_2O and column chromatography (SiO_2; 100% AcOEt to 50% AcOEt/MeOH). Yield: 1.21 g (76%); m.p. 169–170 °C. ^{1}H NMR (300 MHz, [D_6]DMSO, 298 K): δ = 8.54 (br. s, 6 H, NH), 8.01 (m, 12 H, Py-H3, Py-H4), 7.65 (m, 6 H, Py-H5), 7.20 (br. s, 12 H, ArH_{meta}), 6.78 (br. s, 6 H, ArH_{para}), 3.74 (br. s, 12 H, $ArCH_2Ar$), 3.45–3.00 (br. s, 48 H, $OCH_2CH_2CH_2$ and NCH_2CH_3), 1.85 (br. s, 12 H, OCH_2CH_2), 1.04 and 0.94 (s, 18 H each, NCH_2CH_3) ppm. ^{1}H NMR (300 MHz, [D_6]DMSO, 345 K): δ = 8.24 (t, ^3J = 5.7 Hz, 6 H, NH), 8.06–7.98 (m, 12 H, Py-H3,H4), 7.62 (dd, ^3J = 6.6 Hz, ^4J = 1.5 Hz, 6 H, Py-H5), 6.92 (d, ^3J = 7.2 Hz, 12 H, ArH_{meta}), 6.80 (t, ^3J = 7.2 Hz, 6 H, ArH_{para}), 3.89 (s, 12 H, $ArCH_2Ar$), 3.40–3.10 (br. s, 48 H, $OCH_2CH_2CH_2$ and NCH_2CH_3), 1.48 (br. s, 12 H, OCH_2CH_2), 1.04 (br. s, 36 H, NCH_2CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]DMSO, 298 K): δ = 166.9 ($CONEt_2$), 162.9 (CONH), 154.1 (Ar_{ipso}), 153.7 (Py-C6), 148.6 (Py-C2), 138.7 (Py-C4), 134.1 (Ar_{ortho}), 127.0 (Ar_{meta}), 124.6 (Py-C5), 123.2 (Ar_{para}), 121.9 (Py-C3), 70.6 ($OCH_2CH_2CH_2$), 42.3 (NCH_2), 36.6 ($OCH_2CH_2CH_2$), 29.5 ($OCH_2CH_2CH_2$ and Ar-

CH_2Ar), 13.7 and 12.5 (NCH_2CH_3) ppm. MS (ESI+): m/z = 2226.4 $[M + Na]^+$. $C_{126}H_{150}N_{18}O_{18}$ (2204.65): calcd. C 68.64, H 6.86, N 11.44; found C 68.73, H 6.95, N 11.51.

37,38,39,40,41,42-Hexakis{3-[(pyridine-6-acetylamino-2-carboxy)-amino]propoxy}calix[6]arene (4): The product was purified by precipitation with Et_2O/DCM (8:1). Yield: 0.615 g (88%); m.p. 218–220 °C. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.50–8.40 (m, 18 H, NH and Py-H5), 7.82 (d, ^3J = 6.9 Hz, 6 H, Py-H3), 7.74 (t, ^3J = 6.9 Hz, Py-H4), 6.85 (br. s, 18 H, ArH), 3.9–3.3 (br. s, 36 H, $ArCH_2Ar$, $OCH_2CH_2CH_2$), 2.08 (s, 18 H, CH_3CO), 1.73 (br. s, 12 H, OCH_2CH_2) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): δ = 169.2 (CH_3CO), 164.0 (CON), 154.4 (Ar_{ipso}), 150.2 (Py-C2), 147.8 (Py-C6), 139.7 (Py-C4), 134.0 (Ar_{ortho}), 129.1 (Ar_{meta}), 124.0 (Ar_{para}), 117.5 (Py-C5), 116.5 (Py-C3), 71.2 ($OCH_2CH_2CH_2$), 37.2 ($OCH_2CH_2CH_2$), 29.9 ($OCH_2CH_2CH_2$ and $ArCH_2Ar$), 24.4 (CH_3CO) ppm. MS (ESI+): m/z = 1974.3 $[M + Na]^+$. $C_{108}H_{114}N_{18}O_{18}$ (1952.17): calcd. C 66.45, H 5.89, N 12.91; found C 66.31, H 5.97, N 13.03.

37,38,39,40,41,42-Hexakis{3-[(pyridine-6-*N*-butylaminocarbonyl-2-carboxy)amino]propoxy}calix[6]arene (5): A suspension of the hexamethyl ester **1** (0.150 g, 0.077 mmol) in neat butylamine (10 mL) was stirred in a closed tube at 90 °C for 5 d. Then, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (SiO_2; acetone) and then crystallised from Et_2O. Yield: 0.075 g (66%); m.p. 165–166 °C. ^1H NMR (300 MHz, [D$_6$]DMSO, 373 K): δ = 8.86 and 8.66 (br. s, 6 H each, NH), 8.14 (d, ^3J = 7.8 Hz, 12 H, Py-H3, Py-H5), 8.03 (t, ^3J = 7.8 Hz, 6 H, Py-H4), 6.83 (d, ^3J = 7.5 Hz, 12 H, ArH_{meta}), 6.72 (t, ^3J = 7.5 Hz, 6 H, ArH_{para}), 3.92 (s, 12 H, $ArCH_2Ar$), 3.57 (t, ^3J = 6.6 Hz, 12 H, $OCH_2CH_2CH_2$), 3.39 and 3.24 (q, ^3J = 6.9 Hz, 12 H each, NCH_2CH_3), 2.92 (br. s, 12 H, $OCH_2CH_2CH_2$), 1.72 (quint., ^3J = 7.1 Hz, 12 H, OCH_2CH_2), 1.47 and 1.29 (quint. and sext., ^3J = 7.2 Hz, 12 H each, $NCH_2CH_2CH_2$), 0.84 (t, ^3J = 7.2 Hz, 18 H each, $NCH_2CH_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]DMSO, 298 K): δ = 163.1 and 162.8 (CONH), 154.2 (Ar_{ipso}), 148.7 and 148.6 (Py-C6 and Py-C2), 139.3 (Py-C4), 134.0 (Ar_{ortho}), 128.6 (Ar_{meta}), 124.0 (Py-C5 and Py-C3), 123.6 (Ar_{para}), 71.0 ($OCH_2CH_2CH_2$), 38.5 and 36.4 (NCH_2), 31.4 (NCH_2CH_2), 30.0 and 29.5 ($OCH_2CH_2CH_2$ and $ArCH_2Ar$), 19.6 (CH_2CH_3), 13.6 (CH_2CH_3) ppm. MS (ESI+): m/z = 2226.4 $[M + Na]^+$. $C_{126}H_{150}N_{18}O_{18}$ (2204.65): calcd. C 68.64, H 6.86, N 11.44; found C 68.51, H 6.99, N 11.65.

37,38,39,40,41,42-Hexakis{3-[(pyridine-6-hydroxycarbonyl-2-carboxy)amino]propoxy}calix[6]arene (6): To a suspension of hexabenzyl ester **2** (0.70 g, 0.290 mmol) in acetone/EtOH (1:1, 100 mL) was added a catalytic amount of Pd/C, and the mixture was stirred in a Parr apparatus under 3 bar H_2 pressure for 1 week. Then the catalyst was removed by filtration, and the solvents were removed from the filtrate. The residue was crystallised from DCM/Et_2O (1:4), and the product collected as a white powder. Yield: 0.48 g (88%); m.p. 225 °C (decomp.). ^1H NMR (300 MHz, [D$_6$]acetone/CD_3OD = 1:1, 298 K): δ = 8.27 (d, ^3J = 7.5 Hz, 6 H, Py-H3), 8.19 (d, ^3J = 7.5 Hz, 6 H, Py-H5), 8.09 (t, ^3J = 7.5 Hz, 6 H, Py-H4), 6.91 (br. s, 12 H, ArH_{meta}), 6.80 (br. s, 6 H, ArH_{para}), 3.91 (s, 12 H, $ArCH_2Ar$), 3.47 (br. s, 24 H, $OCH_2CH_2CH_2$), 1.67 (br. s, 12 H, OCH_2CH_2) ppm. ^1H NMR (300 MHz, [D$_6$]DMSO, 373 K): δ = 8.67 (t, ^3J = 7.8, 5.4 Hz, 6 H each, NH), 8.20 (d, ^3J = 7.2 Hz, 6 H, Py-H3), 8.16–8.06 (m, 12 H, Py-H4, Py-H5), 6.85 (d, ^3J = 7.5 Hz, 12 H, ArH_{meta}), 6.73 (t, ^3J = 7.5 Hz, 6 H, ArH_{para}), 3.94 (s, 12 H, $ArCH_2Ar$), 3.54 (t, ^3J = 6.5 Hz, 12 H, $OCH_2CH_2CH_2$), 3.50–3.35 (m, 24 H, $OCH_2CH_2CH_2$), 1.68 (quint., ^3J = 6.9 Hz, 12 H, OCH_2CH_2) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]DMSO, 298 K): δ = 164.9 (COOH), 162.8 (CONH), 154.4 (Ar_{ipso}), 149.4 (Py-C2), 146.4 (Py-C6), 139.5 (Py-C4), 134.1 (Ar_{ortho}), 128.7 (Ar_{meta}), 126.4 (Py-C5), 125.0 (Py-C3), 123.4 (Ar_{para}), 70.7 ($OCH_2CH_2CH_2$), 36.5 (NCH_2), 29.8 ($OCH_2CH_2CH_2$ and $ArCH_2Ar$) ppm. MS (ESI+): m/z = 1895.9 $[M + Na]^+$. $C_{102}H_{96}N_{12}O_{24}$ (1873.92): calcd. C 65.38, H 5.16, N 8.97; found C 65.26, H 5.25, N 9.01.

Extraction Experiments: The organic solutions were prepared by dissolving the ligands and the synergizer in the considered diluents. The ligand concentration was set to 1 mM. The synergizer concentration was varied between 1 and 6 mM. The aqueous solutions were prepared by spiking aqueous nitric acid with a stock solution of ^{241}Am and ^{152}Eu. The specific activity of Am and Eu in the aqueous solutions was about 4000 kBq/L, whereas the acidity ranged between 0.01 and 1 M. Liquid–liquid extraction experiments were performed by contacting the same volume (500 μL) of each phase in a single-use microtest tube. The samples were shaken for 1 h at room temperature. Complete separation of the phases was ensured by letting the samples settle for 5 min and then by spinning the tubes in a centrifuge for 10 min. After centrifugation, an aliquot of 200 μL of each phase was taken and analysed by γ-spectrometry by using a NaI(Tl) detector. The measurement times were set to obtain a relative standard deviation of the counting statistics, which is less than 1%. The efficiency of the extractant systems is described by the distribution coefficients, D_M, calculated as the ratio between the cation γ activity in the organic and aqueous phase, whereas the selectivity for Am^{III} over Eu^{III} is expressed by the separation factor, $SF_{Am/Eu}$, defined as the ratio of distribution coefficients D_{Am}/D_{Eu}.

Complexation Experiments: The overall stability constants β_{xy} defined as concentration ratios and corresponding to the complexation equilibria $xLn^{3+} + yL \leftrightarrow Ln_xL_y^{3x+}$ (where Ln is the lanthanide cation and L the ligand) were determined in methanol by UV absorption spectrophotometry at 25 °C and constant ionic strength provided by 0.01 M Et_4NCl in all cases and by 0.01 M Et_4NNO_3 in the case of lanthanum and europium nitrates with **L1**. The ligand concentrations were in the range $2.0–5.0 \times 10^{-5}$ M and the spectra, recorded with a Shimadzu UV-2101 PC spectrophotometer, were treated by the program Specfit, which also allowed the distribution curves to be established.[39] Lanthanides were provided as chloride or nitrate salts (Alfa Aesar), which were dried for 24 h before use. Microcalorimetric titrations were performed at 25 °C by using a 2277 Thermal Activity Monitor Microcalorimeter (Thermometric) according to the procedure already reported.[40] Heats of complexation were recorded after addition of 15×15 μL aliquots of 10^{-2} M europium chloride in methanol on 2.7 mL of $1.0–1.5 \times 10^{-4}$ M ligand solutions in the same solvent. The enthalpy of complexation (ΔH_{xy}) and the stability constants were refined simultaneously from these data after correction for the dilution by using the ligand binding analysis program DIGITAM version 4.1.[41] The corresponding values of the entropy contribution ($T\Delta S_{xy}$) were then calculated from the equation $\Delta G_{xy} = \Delta H_{xy} - T\Delta S_{xy}$, knowing $\Delta G = -RT\ln \beta_{xy}$.

X-ray Crystallographic Study: Data were collected with a Siemens AED diffractometer equipped with graphite monochromated Cu-K_α radiation source (λ = 1.54178 Å). Intensity data were collected at 293 K and corrected for Lorentz and polarisation effects and for absorption effects. The crystal data and the most relevant experimental parameters used in the X-ray measurements and in the crystal structure analyses are reported in Table 10. The structure was solved by direct methods by using SIR2004[42] and refined by full-matrix least-squares methods on F_2 by using the SHELXL-97 program.[43] The complex lies on a crystallographic centre of sym-

metry. All the non-hydrogen atoms were treated with anisotropic atomic displacements except the atoms of the terminal amido groups at the calixarene subunits B and C and the guest water molecule, which were all treated with isotropic atomic displacements. The hydrogen atoms were placed at their calculated positions with geometrical constraint C–H 0.96 Å and refined "riding" on their corresponding parent atoms. The hydrogen atoms of the guest water molecule were not located in final Fourier ΔF map and were not included in the refinement. CCDC-757083 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 10. Crystal data and structure refinement for **2**·2H_2O.

	2·2H_2O
Empirical formula	$C_{144}H_{132}N_{12}O_{24}$·2$H_2O$
Formula weight	1225.36
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	17.652(2)
b (Å)	19.060(2)
c (Å)	10.408(2)
α (°)	95.110(9)
β (°)	100.21(1)
γ (°)	108.059(6)
V (Å^3)	3237.5(8)
Z	1
$D_{calcd.}$ (g/cm^3)	1.257
F(000)	1292
Temperature (K)	293
θ Range (°)	8.0, 140.0
Index ranges	$-21 \le h \le 17$
	$-23 \le k$ 23
	$-4 \le l \le 12$
Refl. measured	13022
Indep. refl.	12252 (R_{int} = 0.0569)
Obs. refl. [$F_0 > 4\sigma(F_0)$]	3962
Data/restr./param.	12252/18/756
Final R indices[a]	R_1 = 0.0571
(Obs. data)	wR_2 = 0.1896
Goodness of fit S[b]	0.758
Min. and max. residual ρ [e/Å^3]	0.36, –0.33

[a] $R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 \, / \, \Sigma wF_o^4]^{1/2}$. [b] Goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2 \, / \, (n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

Supporting Information (see footnote on the first page of this article): VT-, COSY and HSQC NMR experiments for ligand **5**; perspective views (in colour) of the molecular structure and polymeric self-assembly of ligand **2**; coloured molecular structure of the Br-Cosan anion; table with the extracting properties of BrCosan at different concentrations in the absence of the ligand.

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