CMP(O) tripodands: synthesis, potentiometric studies and extractions

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Received (in Montpellier, France) 11th January 2006, Accepted 23rd February 2006
First published as an Advance Article on the web 21st March 2006
DOI: 10.1039/b600412a

Ligand systems containing three carbamoylmethylphosphonate (CMP) or -phosphine oxide (CMPO) moieties attached to a tripodal platform have been synthesized for metal complexation and subsequent extraction from HNO_3 solutions. The incorporation into ion selective electrodes (ISE) and picrate extractions with Na^+, K^+, Ag^+, Ca^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Eu^{3+} and Fe^{3+} shows that CMPO tripodand **3** is very selective for Eu^{3+} and forms a very stable complex ($\log \beta_{ML} = 28.3$). Liquid–liquid extractions performed with Eu^{3+} and Am^{3+} show reasonable extraction properties of the CMP(O) tripodands **3**, **11** and **13** in 1,1,2,2-tetrachloroethane, while in 1-octanol for all tripodands studied the distribution coefficients are low. Upon addition of the synergistic agent hexabrominated cobalt bis(dicarbollide) anion (bromo-COSAN) the distribution coefficients for Am^{3+} and Eu^{3+} extraction increase considerably for CMP(O) tripodands **3** and **4**. Covalently linked COSAN only enhances the extraction of Am^{3+} and Eu^{3+} at 0.001–0.01 M HNO_3. The functionalization of dendrimer coated magnetic silica particles with CMP(O) tripodands led to very effective particles (**31** and **32**) for Am^{3+} and Eu^{3+} removal from 0.01 M HNO_3 solutions.

Introduction

Carbamoylmethylphosphonate (CMP) and -phosphine oxide (CMPO) ligands are well known for the extraction of Am^{3+} and Eu^{3+} from nuclear waste.[1] Their attachment to molecular platforms as calixarenes[2–4] and cavitands[5] led to high extraction efficiencies and selectivities. In most cases these platforms contain four ligating sites. However, only three CMPO moieties are necessary for the coordination of a metal ion. To the best of our knowledge, there is only one example of a tripodal platform, *viz*. a trityl skeleton, with CMPO moieties,[6] while in general the number of tripodal ligands for actinide and/or lanthanide complexation is limited.[7]

Recently, we reported the synthesis, extraction and sensing behaviour of trimethylolpropane-based tripodal ionophores with picolin(thio)amide and *N*-acyl(thio)urea ligating sites.[8] This paper mainly deals with the behavior of the corresponding CMP(O) derivatives **3** and **4** and some derivatives thereof. In addition, the use of CMP(O) tripodands on magnetic silica particles is studied in magnetically assisted chemical separation.

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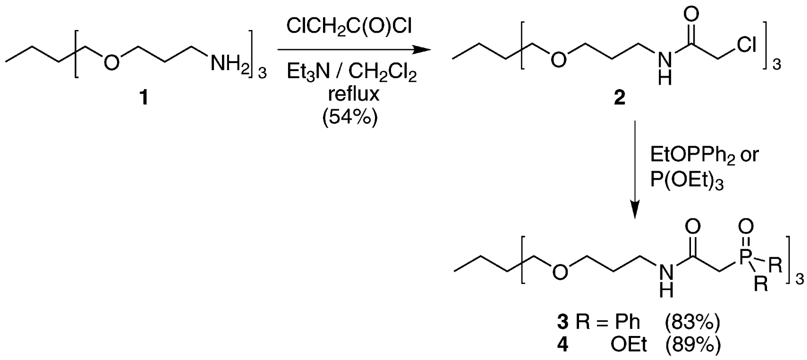
Results and discussion

Synthesis

The synthesis of the tripodal CMP(O) compounds is depicted in Scheme 1. The ligating sites are introduced on the tripodal scaffold *via* two steps starting from 1,1,1-tris[(aminopropoxy)methyl]propane (**1**), the synthesis of which has been described previously.[8] Acylation of amine **1** with chloroacetyl chloride and Et_3N as a base in CH_2Cl_2 afforded 1,1,1-tris[(chloroacetamidopropoxy)methyl]propane (**2**) in 54% yield. Arbusov reaction of **2** with ethyl diphenylphosphinite gave tris[(diphenylcarbamoyl)methylphosphine oxide *N*-propoxy)-methyl]propane (**3**) (CMPO tripodand) as a brown solid in 83% yield. Tris[(diethylcarbamoylmethylphosphonate *N*-propoxy)methyl]propane (**4**) (CMP tripodand) was obtained in 89% yield *via* an Arbusov reaction with triethyl phosphite.

The ^1H NMR spectra of CMPO tripodand **3** and CMP tripodand **4** exhibit characteristic signals for the CMP(O) methylene hydrogens at 3.40 ppm ($^2J_{PH}$ = 13.2 Hz) and 2.85 ppm ($^2J_{PH}$ = 20.8 Hz), respectively.

In order to introduce an extra functionality, which can be used as a handle for the coupling to COSAN moieties or magnetic silica particles, carbamate **5** was prepared following a literature procedure, starting from the commercially available 1,1,1-tris(hydroxymethyl)aminomethane.[9] For the introduction of the CMP(O) moieties the same strategy as for CMP(O) tripodands **3** and **4** was followed. Acylation of carbamate **5** followed by an Arbusov reaction gave **7** and **8** in 94 and 60% yield, respectively. The terminal amino group, which was protected by the Cbz (benzyloxycarbonyl) group, was deprotected by catalytic hydrogenation affording the target compounds **9** and **10** in 87 and 85% yield, respectively (Scheme 2).



Scheme 1

^{1}H NMR spectroscopy confirmed the formation of **9** and **10** by the absence of the signal at ~5.3 ppm of the CH_2 of the Cbz groups in **7** and **8**, and the presence of aromatic signals for CMPO tripodand **9** and ethoxy signals of CMP tripodand **10**.

In order to increase the solubility of compounds **3** and **4**, especially CMP tripodand **4**, long alkyl chains were attached *via* the terminal amino group of CMP(O) tripodands **9** and **10** (Scheme 3). The terminal amino group is at a sterically hindered position, which influences its reactivity. A nine carbon chain was introduced *via* an acylation reaction with nonanoyl chloride to give CMPO tripodand **11** and CMP tripodand **12** in 30 and 34% yield, respectively. CMP(O) tripodands **13** and **14**, which have a fourteen carbon chain, were obtained in 23 and 33% yield, respectively, by reaction of CMPO tripodand **9** and CMP tripodand **10** with myristoyl chloride. The tripodands **15** and **16**, which have a handle for the connection of COSAN moieties, were prepared by reaction of **9** and **10** with 6-chlorohexanoyl chloride in 68 and 27% yield, respectively. The formation of CMP(O) tripodands **11–14** was confirmed, in addition to the FAB mass spectra, by the appearance in the ^{1}H NMR spectra of two signals belonging to the alkyl chain, *viz*. a multiplet of the methylene groups at ~1.2–1.3 ppm and a triplet of the methyl groups at ~0.8 ppm. The ^{1}H NMR spectrum of **15** exhibits a triplet at 3.39 ppm for the CH_2Cl group, while in the case of **16** this signal is hidden under the multiplet at 3.29–3.58 ppm.

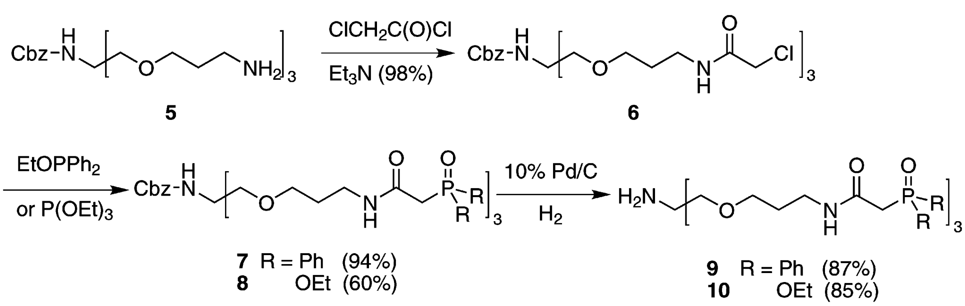
To study the possible influence of the spacer length between the oxygen and the amide atom on the complexation behavior, the tripodal derivatives **23** and **24** were prepared (Scheme 4). These compounds have one carbon atom shorter spacers compared to the corresponding CMP(O) tripodands **3** and **4**.

Using a modified literature procedure, trimethylolpropane **17**, was converted in two steps to methyl ester **19**[10] in 83% overall yield. Amidation of ester **19** with ammonia in methanol afforded tripodal amide **20** in 69% yield, which subsequently was reduced to tripodal amine **21** in 98% yield. Acylation of amine **21** followed by an Arbusov reaction resulted in the introduction of the desired CMP(O) moieties to give **23** and **24** in 38 and 56% yield, respectively.

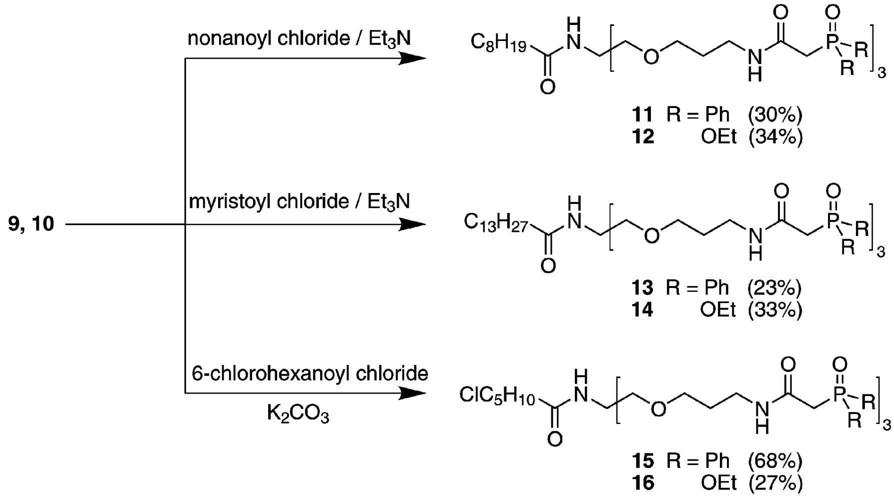
Potentiometric measurements

Recently, we reported potentiometric measurements with *N*-acyl(thio)urea- and picolin(thio)amide-functionalized tripodands.[8] Similar measurements, concerning complex formation within the polymeric membrane phase and the potentiometric selectivity of ion selective electrodes (ISEs), were performed with tripodands **3** and **4**. The studied cations (Eu^{3+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+} and Na^{+}) were selected for their presence in nuclear waste, as well as for their difference in charge and physical properties.

The complex formation constants were determined by means of the segmented sandwich method.[11] The values of the complex formation constants (expressed as $\log \beta_{ML}$) for ionophores **3** and **4** and selected cations are collected in Table 1. They show that CMPO tripodand **3** forms stronger complexes than CMP tripodand **4** with all the examined cations, following the expected trend of the complexation properties for P-containing compounds: phosphine oxide > phosphate > phosphonate.[12] The largest complex formation constant, $\log \beta_{ML}$, of CMPO tripodand **3** was found for Eu^{3+}, which was taken as a general representative for the trivalent actinides



Scheme 2



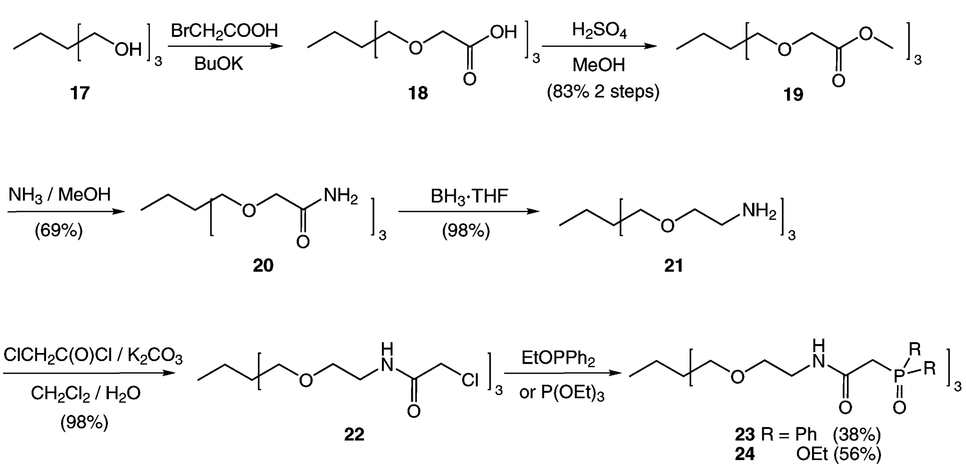
Scheme 3

(Am^{3+} and Cm^{3+}) and lanthanides. In contrary, the affinity of CMP **4** to Eu^{3+} is quite weak.

CMP(O) tripodands **3** and **4** were examined as ionophores in *o*-NPOE/PVC membranes also containing 30% mol of lipophilic anionic additives. The unbiased selectivity coefficients, $K^{pot}_{I,J}$, values were obtained in the same way as described earlier.[8] The logarithmic values of the selectivity coefficients, calculated for Pb^{2+} as the primary cation ($\log K^{pot}_{Pb,J}$) and Na^+, Cu^{2+}, Cd^{2+} and UO_2^{2+} as interfering ions, are presented in Fig. 1. It is well known that the ion-ionophore interactions, that can be expressed by the relative stability constants of complexes formed by an ionophore with primary and interfering ions within the membrane phase, are the main factor that is primarily responsible for the selectivity of polymeric membrane electrodes.[13] The obtained selectivity patterns: $UO_2^{2+} > Pb^{2+} > Cd^{2+} > Cu^{2+} \gg Na^+$ for CMPO tripodand **3** and $UO_2^{2+} > Pb^{2+} > Cu^{2+} > Cd^{2+} > Na^+$ for CMP tripodand **4** clearly reflect this statement. Comparison of the results obtained for membranes only doped with ion-exchanger (KTFPB) and those containing CMP(O) tripodands **3** or **4** as ionophore, reveals that the examined tripodands are able to induce selectivities that differ from the so-called Hofmeister series (based on the relative hydrophobicity of ions). This is especially seen for UO_2^{2+} and Na^+. The CMP(O) tripodands **3** and **4** exhibit the highest selectivity towards UO_2^{2+}, which is in agreement with the essentially greater stability constants for complexes with UO_2^{2+} than Pb^{2+} (see Table 1). The selectivity found for UO_2^{2+} over Pb^{2+} ions for membranes based on **3** and **4** is even better than that reported for CMP(O) tetrakis-functionalized cavitands.[14] The much weaker, compared to Pb^{2+}, interaction between Na^+ and tripodands **3** and **4** results in a significantly increased selectivity of the electrodes for Pb^{2+} over Na^+ compared to membranes without ionophore. The much less pronounced changes in $\log K^{pot}_{Pb,J}$ values in the case of Cu^{2+} and Cd^{2+}, observed for membranes doped with CMPO **3** or CMP **4**, can be explained by a similar stability of the complexes formed by these tripodands with Cu^{2+}, Cd^{2+} and Pb^{2+}.

Extraction experiments

Extraction of different types of cations. To obtain initial insight into the extraction properties of the CMP(O) tripodands **3** and **4**, the extraction of a number of cations (Na^+, K^+, Ag^+, Ca^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Eu^{3+} and Fe^{3+}) was investigated. In the extraction studies, Eu^{3+} was selected as a general representative for the trivalent actinides (*e.g.*



Scheme 4

Table 1 Formal complex formation constants, $\log \beta_{ML}$, obtained with ionophores **3** and **4** in PVC/*o*-NPOE (1 : 2) membranes, using the segmented sandwich method

	$\log \beta_{ML}$[a]	
Cation	CMPO (**3**)	CMP (**4**)
Na^{+}	8.4	4.8
Cu^{2+}	19.8	11.8
Cd^{2+}	19.1	9.3
Pb^{2+}	17.4	9.0
UO_2^{2+}	21.5	12.3
Eu^{3+}	28.3	7.9

[a] Standard deviations ≤0.3 (from at least three replicate measurements). The stoichiometries of the ion : ionophore was assumed to be 1 : 1.

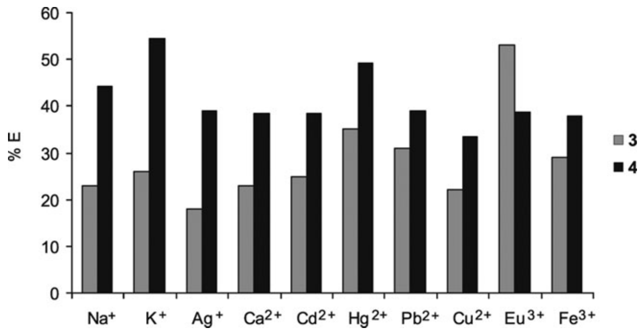


Fig. 2 Extraction results of CMP(O) tripodands **3** and **4**. Conditions: $[L]_{o,j}$ = 10^{-3} M in CH_2Cl_2; $[M^{n+}]_{w,j}$ = 10^{-3} M; $[LiPic]_w$ = 10^{-4} M; $[HNO_3]_w$ = 10^{-3} M; pH 3.

Am^{3+} and Cm^{3+}) and lanthanides, while the other cations were selected for their difference in charge and physical properties. The results of the picrate extractions[15] are summarized in Fig. 2.

The extraction percentages (%E values) reported in Fig. 2 show that CMP tripodand **4** has a very similar extraction behavior towards the different cations used. CMPO tripodand **3** has a higher affinity for Eu^{3+} than for the other cations, while it has the lowest affinity for Ag^{+}. The reason for this is that the CMPO ligating groups of **3** have hard donor atoms, while Ag^{+} is a soft donor cation (Pearson's principle).[16]

Extraction of americium and europium. Extraction experiments of Am^{3+} and Eu^{3+} were performed at first instance with *o*-nitrophenyl octyl ether (NPOE) as the organic phase at varying nitric acid concentrations, imposed by the need to simulate the strongly acidic conditions required in the reprocessing of nuclear waste. However, with NPOE as a solvent no reliable extraction data could be obtained due to the occurrence of precipitates. In a few cases precipitation was assumed based on the bad activity mass balances.

In order to avoid third phase formation, similar extractions were performed from 1 M HNO_3 into 1,1,2,2-tetrachloroethane (TCE) with CMP(O) tripodands **3**, **4** and **11–14**.

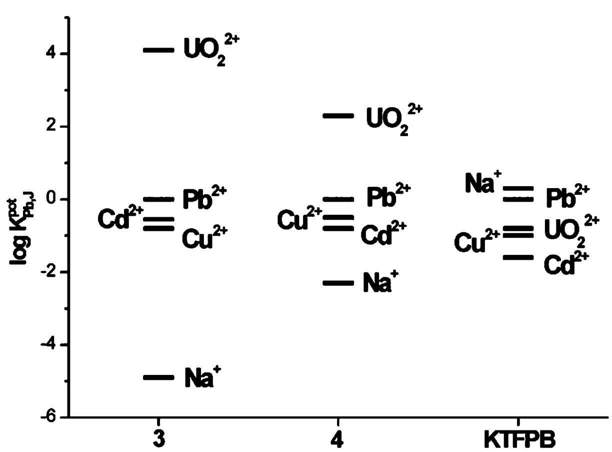


Fig. 1 Selectivity coefficients for electrodes prepared with PVC/*o*-NPOE (1 : 2 by weight) membranes containing CMP(O) tripodands **3**, **4** and lipophilic sites (KTFPB) as well as membranes with ion-exchanger only, with Pb^{2+} as the primary ion.

CMP(O) tripodands **11–14** have a long alkyl chain to enhance the solubility. However, CMP tripodands **4**, **12** and **14** form precipitates when dissolved in TCE and contacted with acidic aqueous solutions.

Table 2 shows the Eu^{3+} and Am^{3+} extraction data of the CMPO tripodands **3**, **11** and **13**. The data show that the introduction of a long alkyl chain does not enhance the extraction properties of CMPO tripodand **3** (**3** *vs.* **11** and **13**) due to a better complex solubility. The extraction properties are comparable to those of the malonamides used in the DIAMEX process (0.65 M *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-hexylethoxymalonamide (DMDOHEMA) in hydrogenated tetrapropene (TPH) at 1 M HNO_3), with D_{Am} = 0.2 and D_{Eu} = 0.1.

More diluted TCE solutions of the CMP tripodands **4**, **12** and **14** were also tested to prevent third phase formation. Even at a low concentration of 6.8×10^{-4} M CMP tripodand **4** could not be measured due to the appearance of a precipitate, when the organic layer is mixed with the HNO_3 solution. However, in the case of compound **12**, at a ligand concentration of 5.6×10^{-4} M in TCE, extraction of Am^{3+} and Eu^{3+} from 0.1–3 M HNO_3 was possible, although the distribution coefficients were very low (1.1×10^{-3}–3.9×10^{-3}). The extraction efficiency of CMP tripodand **14** could be measured at a somewhat higher concentration (1.9×10^{-3} M) to give distribution coefficients for Eu^{3+} and Am^{3+} of 2.1×10^{-3} and 3×10^{-3}, respectively, at 3 M HNO_3 (precipitation occurred at lower concentrations).

All ionophores are well-soluble in 1-octanol. However, from the extraction data collected in Table 3, it is clear that the

Table 2 Distribution coefficients and separation factors for the extraction of Eu^{3+} and Am^{3+} by CMPO tripodands **3**, **11** and **13** in TCE[a]

	Ionophore		
Cation	**3**	**11**	**13**
Eu^{3+}	0.26	0.33	0.27
Am^{3+}	0.51	0.64	0.52
$S_{Am/Eu}$	2.0	1.9	1.9

[a] Aqueous phase: ^{152}Eu and ^{241}Am trace level in 1 M $[HNO_3]$. Organic phase: ligand (1.4×10^{-2} M **3**, 1.7×10^{-2} M **11** and 1.2×10^{-2} M **13**) in TCE.

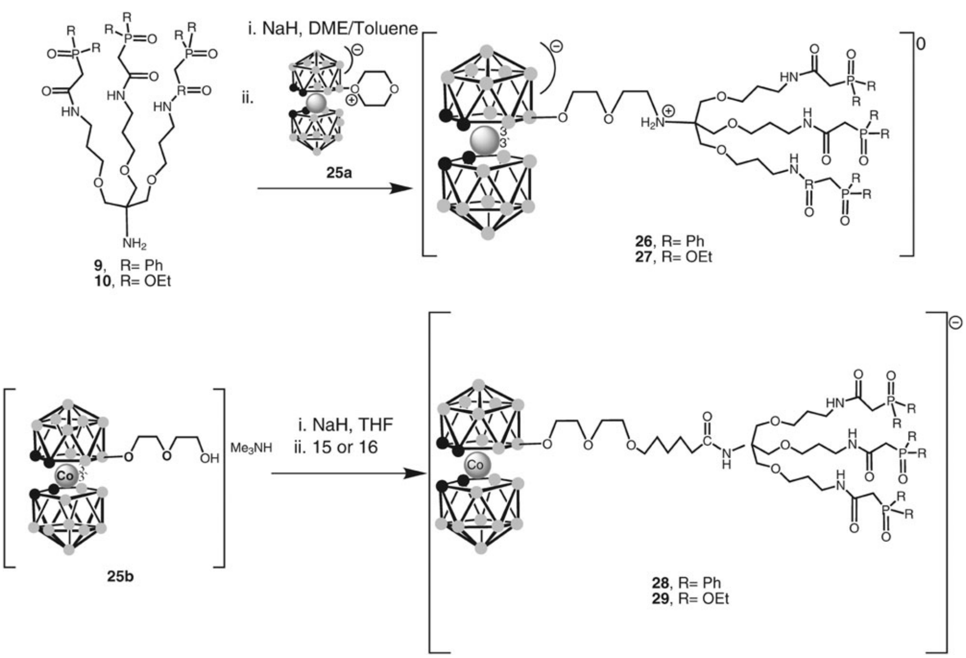
Table 3 Distribution coefficients and separation factors for the extraction of Eu^{3+} and Am^{3+} by CMP(O) tripodands **3**, **11–14**, **23** and **24** in 1-octanol[a]

		HNO_3/M				HNO_3/M	
Ionophore	Cation	1.37	2.70	Ionophore	Cation	0.98	3.07
3	Eu^{3+}	3.6×10^{-3}	1.3×10^{-3}	**4**	Eu^{3+}	$<10^{-3}$	9.9×10^{-2}
	Am^{3+}	6.9×10^{-3}	2.1×10^{-2}		Am^{3+}	$<10^{-3}$	1.0×10^{-2}
	$S_{Am/Eu}$	1.9	1.6		$S_{Am/Eu}$	—	1.0
11	Eu^{3+}	3.5×10^{-3}	1.1×10^{-2}	**12**	Eu^{3+}	$<10^{-3}$	2.6×10^{-3}
	Am^{3+}	6.8×10^{-3}	1.7×10^{-2}		Am^{3+}	$<10^{-3}$	3.0×10^{-3}
	$S_{Am/Eu}$	1.9	1.6		$S_{Am/Eu}$	—	1.1
13	Eu^{3+}	4.2×10^{-3}	1.1×10^{-2}	**14**	Eu^{3+}	$<10^{-3}$	1.6×10^{-3}
	Am^{3+}	8.9×10^{-3}	1.9×10^{-2}		Am^{3+}	$<10^{-3}$	1.5×10^{-3}
	$S_{Am/Eu}$	2.1	1.8		$S_{Am/Eu}$	—	0.9
23	Eu^{3+}	2.4×10^{-3}	6.7×10^{-3}	**24**	Eu^{3+}	$<10^{-3}$	$<10^{-3}$
	Am^{3+}	4.5×10^{-3}	1.1×10^{-2}		Am^{3+}	$<10^{-3}$	$<10^{-3}$
	$S_{Am/Eu}$	1.9	1.6		$S_{Am/Eu}$	—	—

[a] In all cases the ligand concentration is 10^{-3} M.

distribution coefficients (of **3**, **11** and **13**) are much lower in the polar 1-octanol than in TCE. Furthermore, gel formation occurred when using a higher concentration of CMPO tripodand **3** in 1-octanol (10^{-2} M).

COSAN moieties covalently linked to CMP(O) tripodands. In order to enhance the extraction ability of CMP(O) tripodands **3** and **4**, as well as the solubility in the case of **4**, the hydrophobic cobalt bis(dicarbollide) anion (COSAN) was covalently attached to amino terminated (**9**, **10**) and chloroalkyl-containing CMP(O) tripodands **15** and **16** to give **26**, **27** and **28**, **29**, respectively (Scheme 5). Compounds **26** and **27** were prepared by ring opening of the reactive COSAN-dioxane **25a**, which is known to serve as a versatile building block for many applications,[17] by the terminal amino group of the tripodands **9** and **10**. As can be expected, only uncharged zwitterionic compounds result, in which the tripodal part is separated from the COSAN anion by a protonated amino group and the effect of the anionic charge is shielded. Compounds **28** and **29** were prepared in moderate yields by alkylation of the terminal OH group of the diethyleneglycolyl-substituted COSAN **25b** (reacted as dry disodium salt generated from the corresponding Me_3NH^+ salt in THF by addition of two equivalents of NaH) with chloroalkyl group-containing tripodands **15** and **16**, respectively (Scheme 5). Due to the presence of the carboxamide group in the connecting arm, these compounds tend to be protonated to give the respective uncharged *enol*-forms. Nevertheless, it can be assumed that compounds **28** and **29** can act as real anions in extractions at low acidity. This can be concluded from the



Scheme 5

Table 4 Distribution coefficients for the extraction of Eu^{3+} and Am^{3+} by CMP(O) tripodands **3** and **4** and their synergistic mixtures with bromo-COSAN in nitrobenzene

Compound[a]		HNO$_3$/M			
		0.01	0.1	1.0	3.0
3	D_{Eu}	0.57	0.43	1.31	4.03
	D_{Am}	1.01	0.72	2.38	6.97
3 + HBBr	D_{Eu}	$>10^3$	$>10^3$	$>10^3$	222
	D_{Am}	$>10^3$	$>10^3$	$>10^3$	357
4	D_{Eu}	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	4.50×10^{-3}
	D_{Am}	1.36×10^{-3}	1.25×10^{-3}	1.08×10^{-3}	8.14×10^{-3}
4 + HBBr	D_{Eu}	$>10^3$	$>10^3$	14.3	1.04
	D_{Am}	$>10^3$	$>10^3$	16.0	1.82

[a] 1×10^{-3} M **3**, **4** and 3×10^{-3} M HBBr (bromo-COSAN).

Table 5 Distribution coefficients for the extraction of Eu^{3+} and Am^{3+} by COSAN-containing CMP(O) tripodands **28** and **29** in nitrobenzene

Ionophore[a]		HNO$_3$/M				
		0.001	0.01	0.1	1.0	3.0
28	D_{Eu}	$>10^3$	346	18.0	5.68×10^{-2}	2.05×10^{-2}
	D_{Am}	$>10^3$	414	25.8	9.78×10^{-2}	2.76×10^{-2}
29	D_{Eu}	$>10^3$	$>10^3$	3.55	2.48×10^{-2}	1.56×10^{-2}
	D_{Am}	$>10^3$	$>10^3$	4.80	6.52×10^{-2}	3.20×10^{-2}

[a] 1.27×10^{-3} M **28**, 1.43×10^{-3} M **29**.

increase of its extraction properties in the low acidity range, compared to those of the former couple of compounds **26** and **27**.

Extraction experiments of Am^{3+} and Eu^{3+} from HNO_3 solutions were performed with COSAN-containing CMP(O) tripodands **26** and **27**. CMPO derivative **26** gave low distribution coefficients, D_{Am} = 0.4 and D_{Eu} = 0.3 (5.6×10^{-3} M **26** in toluene, 0.1 M HNO_3). The distribution coefficients for Eu^{3+} with COSAN-containing CMP tripodand **27** in nitrobenzene (8.1×10^{-4} M) at 0.1 and 1 M HNO_3, are 311 and 4.55, respectively, indicating a good extraction ability. The extraction results of an equimolar synergistic mixture of **3** and **4** with bromo-COSAN are given in Table 4. CMP tripodand **4** itself does not extract Eu/Am at all over the range of acidities. In the synergistic mixture with bromo-COSAN, the distribution ratios are several orders of magnitude higher. CMPO tripodand **3** itself exhibits a modest Eu/Am extraction, while the presence of bromo-COSAN again leads to an enormous increase of the extraction ability. These results demonstrate the importance of the presence of COSAN, either in a synergistic mixture or covalently bound. The attachment of COSAN moieties to the CMP(O) tripodand derivatives, **26** and **27**, gives rise to modest extraction properties at higher pH. Due to effect of the COSAN acidity, the secondary amine is always protonated, and consequently compounds **26** and **27** are not negatively charged. This assumption is supported by the results obtained with synergistic mixtures (no amine group present). However, the linkage of COSAN to the CMP tripodand **27** makes it more soluble and no precipitation was formed during the Eu^{3+} extraction experiments. In the case of compounds **28** and **29**, good extraction properties can be observed for acidities up to 0.1 M. The consecutive increase of the acid concentration leads in both cases to a significant drop of the distribution ratio, as can be seen from the results presented in Table 5.

The decrease of the extraction effectivity at higher acidities may be due to the length of the linker between COSAN and the tripodand moieties or again to the presence of an amide group (possible protonation). The separation factors D_{Am}/D_{Eu} for **28** and **29** vary in the range 1–2.5.

CMP(O) tripodand-containing magnetic particles. Recently, a new separation technology was introduced for nuclear waste treatment, *viz*. magnetically assisted chemical separation with extractant coated particles.[18] It combines the selectivity of a ligand used for liquid–liquid extractions with improved phase separation due to the magnetic field, resulting in an effective system that provides only a small volume of high level waste. The magnetic particles can be directly vitrified or stripped, to enable their re-use in an automated process. Fundamental studies have been performed by Nuñez and Kaminski *et al.*[19–21] The better extraction properties (~12-fold)[22,23] obtained with calix[4]arenes bearing four CMPO groups covalently bound to the particle surface in comparison with particles with adsorbed CMPO moieties, inspired our alternative strategy of covalent attachment of CMP(O) tripodal ionophores on the surface of magnetic particles for Eu^{3+}/Am^{3+} separation from high activity liquid wastes.

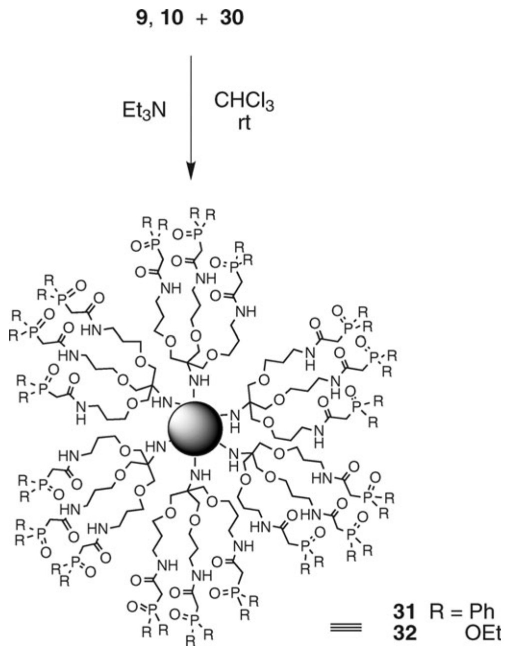
In order to achieve a further increase of the lanthanide and actinide extraction capacity of functionalized magnetic particles, starburst dendrimers have been introduced on the particle surface. These dendrimer coated magnetic particles have a high potential for immobilization of a large variety of selective chelators in a very high density on the particle surface.[24] The extraction studies for Eu^{3+} and Am^{3+} were carried out under highly acidic conditions with Eu^{3+} and Am^{3+} solutions found in real waste.

CMP(O) tripodand-containing magnetic particles were prepared by reaction of CMP(O) tripodands **9** and **10** with magnetic particles functionalized with third generation dendrimers **30** (Scheme 6).

The distribution coefficient K_D for solid/liquid extractions is defined as:

$$K_D = \frac{(C_{L,0} - C_L)}{C_L}\frac{V_L}{m_s}$$

Due to saturation phenomena, these K_D values are usually not constant and thus only values obtained under identical conditions (concentration in the liquid phase, amount of solid phase) can be compared. Therefore the distribution coefficients (K_D) for Eu^{3+} and Am^{3+} extraction with magnetic particles (m_s) with 10 mL (V_L) of Eu^{3+} or Am^{3+} containing test solution of known activity (C_L) were measured in the supernatant. The results of the extraction experiments with CMP(O) tripodand modified particles **31** and **32** towards Am^{3+} and Eu^{3+} are given in Table 6.



Scheme 6

The CMPO tripodand bearing particles **31** are very effective for Eu^{3+} and Am^{3+} at 0.01 M HNO_3 and have a selectivity factor of 3.7 at 0.1 M HNO_3. CMP tripodand bearing particles **32** are not so effective as **31**, but they have a higher separation factor at 0.01 M HNO_3 (2.5 *vs.* 1 for **31**). At HNO_3 concentrations higher than 0.01 M the distribution coefficients decrease to values lower than 1, abruptly in the case of CMP tripodand bearing particles **32**, and gradually for CMPO tripodand bearing particles **31**. The distribution coefficients for CMPO tripodand bearing particles **31** at 3 M HNO_3 are much lower than those reported for simple CMPO-bearing particles (K_D = 23 and 48 for Eu^{3+} and Am^{3+}, respectively).[25] However, the high distribution coefficients of the CMPO tripodand bearing particles at low HNO_3 concentrations constitute a system for potential future industrial development.

Conclusions

C_3-Symmetric tris-CMP(O) ligand systems **3**, **4**, **11–16**, **23** and **24** were developed. Liquid–liquid extractions and ISE data demonstrated that CMPO tripodand **3** has a higher affinity for actinides (UO_2^{2+}, Am^{3+}) and Eu^{3+} than CMP tripodand **4**, that has a very high complex formation constant for Eu^{3+} ($\log \beta_{ML}$ = 28.3).

Extractions of Am^{3+} and Eu^{3+} suffer from precipitate and third phase formation in NPOE as the organic phase. In the case of the CMP tripodands attachment of a long alkyl chain and going to TCE as an organic solvent does not improve. In the case of the CMPO tripodands **3**, **11** and **13** reasonable extraction data were obtained using TCE. However, with the more polar 1-octanol as the extraction solvent, all tripodands dissolved, but gave rise to poor extraction results. The distribution coefficients were considerably enhanced upon addition of bromo-COSAN as a synergistic agent. However, in the case the COSAN is covalently attached to the tripodand, the effect on the extraction is strongly dependent on the HNO_3 concentration.

Dendrimer-coated magnetic silica particles functionalized on the surface with CMPO tripodand **31** have high distribution coefficients for Am^{3+} and Eu^{3+} extraction at low HNO_3 concentration, which may make it a promising system for industrial development.

Table 6 Distribution coefficients for the extraction of Am^{3+} and Eu^{3+} by microparticles **31** and **32** bearing CMP(O) tripodands on the surface[a]

		HNO_3 concentration/M			
Particle type	Cation	0.01	0.1	1	3
31	Eu^{3+}	1215	221	1.5	<1
	Am^{3+}	1359	59	2.1	<1
32	Eu^{3+}	102	<1	<1	<1
	Am^{3+}	256	<1	<1	<1

[a] Extraction conditions: Aqueous phase: 10 mL of HNO_3 + ^{152}Eu + ^{241}Am; mass of particles 300 mg; stirring time: 1 h.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) and a Varian Unity 400 WB NMR spectrometer, respectively. All spectra were recorded in $CDCl_3$ unless otherwise stated. ^{11}B NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer in deuterioacetone. Residual solvent protons were used as an internal standard and chemical shifts are given in ppm relative to tetramethylsilane (TMS). Fast atom bombardment (FAB) mass spectra were measured on a Finnigan MAT 90 spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. Matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectra were recorded using a Perkin Elmer/PerSpective Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer. Elemental analyses were carried out using a 1106 Carlo-Erba Strumentazione element analyser. All solvents were purified by standard procedures. All other chemicals were analytically pure and were used without further purification. All reactions were carried out under an inert argon atmosphere. Melting points (uncorrected) of all compounds were obtained on a Reichert melting point apparatus.

Compounds **1**[26] and **5**[9] were prepared following a literature procedure. The COSAN derivatives **25a**[27] and **25b**[28] were prepared as reported previously.

Syntheses

1,1,1-Tris[(chloroacetamidopropoxy)methyl]propane (2). To a solution of 1,1,1-tris[(aminopropoxy)methyl]propane **1** (865 mg, 2.84 mmol) and Et_3N (6.4 mL, 45.6 mmol) in CH_2Cl_2 (50 mL) was added chloroacetyl chloride (2.75 mL, 34.6 mmol), and the reaction mixture was heated at reflux overnight. The solution was washed with 1 M HCl (2 × 25 mL), H_2O (2 × 25 mL), 2 M NaOH (3 × 25 mL) and 1 M HCl (2 × 25 mL) and dried over $MgSO_4$. Evaporation of the solvent afforded **2** as a pale yellow oil. Yield 813 mg (54%); FAB-MS: m/z 535.4 ($[M + H]^+$, calc. 535.1); ^1H NMR δ: 6.96–6.98 (m, 3H, NH), 4.06 (s, 6H, CH_2Cl), 3.50 (t, 6H, J = 6.0 Hz, OCH_2), 3.43 (q, 6H, J = 6.0 Hz, CH_2NH), 3.34 (s, 6H, CCH_2O), 1.82 (q, 6H, J = 6.0 Hz, CH_2), 1.46 (q, 2H, J = 7.7 Hz, CH_2), 0.85 (t, 3H, J = 7.7 Hz, CH_3); ^{13}C NMR δ: 165.8, 71.8, 70.0, 42.7, 38.2, 37.9, 29.1, 23.2, 7.7.

1,1,1-Tris[(diphenylcarbamoylmethylphosphine oxide *N*-propoxy)methyl]propane (3). In an open flask compound **2** (933 mg, 1.25 mmol) was dissolved in a small amount of ethyl diphenylphosphinite (1 mL, 4.125 mmol), while the temperature was gradually increased from 100 to 150 °C. Subsequently, the mixture was stirred for 1 h at 150 °C. After cooling of the reaction mixture, diisopropyl ether was added till a precipitate was formed. The precipitate was filtered off and dissolved in CH_2Cl_2 (50 mL) in order to take all the compound from the filter. The organic solvent was removed in vacuo yielding **3** as a light brown solid. Yield 1.07 g (83%); mp 130–132 °C; FAB-MS: m/z 1032.7 ($[M + H]^+$, calc. 1032.4); ^1H NMR δ: 7.70–7.82 and 7.45–7.51 (2m, 12 + 18H, P-phenyl), 3.40 (d, 6H, J = 13.2 Hz, CH_2P), 3.21–3.31 (m, 12H, OCH_2 + CH_2NH), 3.15 (s, 6H, CCH_2O), 1.62 (q, 6H, J = 6.6 Hz, CH_2), 1.33 (q, 2H, J = 7.3 Hz, CH_2), 0.79 (t, 3H, J = 7.3 Hz, CH_3); ^{13}C NMR δ: 162.0, 132.0, 131.0, 130.0, 128.0, 71.0, 68.0, 42.0, 39.0, 38.0, 37.5, 36.0, 22.5, 7.0. Anal. Calc. for $C_{57}H_{68}N_3O_9P_3 \cdot 1/2CH_2Cl_2$: C, 64.27; H, 6.47; N, 3.91. Found: C, 64.76; H, 6.17; N, 3.82%.

1,1,1-Tris[(diethylcarbamoylmethylphosphonate *N*-propoxy)-methyl]propane (4). In an open flask compound **2** (813 mg, 1.52 mmol) was dissolved in a small amount of triethyl phosphite (0.86 mL, 5.01 mmol), while the temperature was gradually increased from 100 to 150 °C. Subsequently, the mixture was stirred for 1 h at 150 °C. After cooling of the reaction mixture, diisopropyl ether was added and the mixture left stirring overnight. The organic solution was decanted remaining **4** as a brown oil. Yield 1.13 g (89%). FAB-MS: m/z 839.4 ($[M + H]^+$, calc. 839.0); ^1H NMR δ: 4.16 (q, 12H, J = 7.1 Hz, OCH_2), 3.46 (t, 6H, J = 6.0 Hz, OCH_2), 3.35 (q, 6H, J = 6.0 Hz, CH_2NH), 3.27 (s, 6H, CCH_2O), 2.85 (d, 6H, J = 20.8 Hz, CH_2P), 1.78 (q, 6H, J = 6.0 Hz, CH_2), 1.20–1.36 (m, 18 + 2H, CH_3 + CH_2), 0.84 (t, 3H, J = 7.1 Hz, CH_3); ^{13}C NMR δ: 163.0, 71.0, 68.0, 62.0, 42.5, 37.0, 36.0, 34.0, 28.5, 22.5, 18.0, 7.5.

Cbz-chloroacetamido-tripodand 6. To a solution of carbamate **5** (526 mg, 1.23 mmol) and Et_3N (2.2 mL, 16 mmol) in CH_2Cl_2 (35 mL) was added chloroacetyl chloride (1.27 mL, 12.3 mmol), and the reaction mixture was refluxed overnight. The solution was washed with 1 M HCl (2 × 20 mL), H_2O (2 × 20 mL), 2 M NaOH (3 × 20 mL), and 1 M HCl (2 × 20 mL) and dried over $MgSO_4$. Evaporation of the solvent afforded **6** as a pale yellow oil. Yield 795 mg (98%); FAB-MS: m/z 657.5 ($[M + H]^+$, calc. 657.3); ^1H NMR δ: 7.33 (s, 5H, ArH), 6.97–6.99 (m, 3H, NH), 5.03 (s, 2H, CH_2), 4.06 (s, 6H, CH_2Cl), 3.69 (s, 6H, CCH_2O), 3.51 (t, 6H, J = 5.8 Hz, OCH_2), 3.37 (q, 6H, J = 5.8 Hz, CH_2NH), 1.77 (q, 6H, J = 5.8 Hz, CH_2); ^{13}C NMR δ: 165.6, 154.6, 135.1, 127.9, 127.51, 69.4, 65.8, 58.1, 42.1, 37.4, 28.4.

Cbz-CMPO-tripodand 7. In an open flask compound **6** (300 mg, 0.76 mmol) was dissolved in a small amount of ethyl diphenylphosphinite (0.6 mL, 5.0 mmol), while the temperature was gradually increased from 100 to 150 °C. Subsequently, the mixture was stirred for 1 h at 150 °C. After cooling of the reaction mixture, diisopropyl ether was added till a precipitate was formed. The precipitate was filtered off and dissolved in CH_2Cl_2 in order to collect all product from the filter. The organic solvent was evaporated to give **7** as a light brown solid. Yield 703 mg (94%); mp 58–60 °C; FAB-MS: m/z 1153.5 ($[M + H]^+$, calc. 1153.0); ^1H NMR δ: 7.70–7.80 and 7.42–7.54 (2m, 12 + 18H, P-phenyl), 7.28 (s, 5H, ArH), 5.32 (s, 2H, OCH_2Ar), 3.65 (s, 6H, CCH_2O), 3.35 (t, 6H, J = 6.0 Hz, OCH_2), 3.30 (d, 6H, J = 13.2 Hz, CH_2P), 3.25 (q, 6H, J = 6.0 Hz, CH_2NH), 1.62 (q, 6H, J = 6.0 Hz, CH_2); ^{13}C NMR δ: 164.6, 155.5, 136.8, 132.2, 131.0, 130.8, 128.8, 128.7, 128.5, 128.4, 69.6, 69.3, 65.3, 46.2, 38.6, 37.5, 29.2. Anal. Calc. for $C_{63}H_{71}N_4O_{11}P_3 \cdot 1/2CH_2Cl_2$: C, 63.79; H, 6.07; N, 4.69. Found: C, 63.30; H, 5.93; N, 4.23%.

Cbz-CMP-tripodand 8. In an open flask compound **8** (500 mg, 0.76 mmol) was dissolved in a small amount of triethyl phosphite (0.86 mL, 5.01 mmol), while the temperature was gradually increased from 100 to 150 °C. Subsequently, the mixture was stirred for 1 h at 150 °C. After cooling of the reaction mixture diisopropyl ether was added and left stirring overnight. The organic solution was decanted to give compound **8** as a brown oil. Yield 438 mg (60%). FAB-MS: m/z 962.3 ($[M + H]^+$, calc. 962.4); ^1H NMR δ: 7.31 (s, 5H, ArH), 5.29 (s, 2H, OCH_2Ar), 4.10 (q, 12H, J = 7.1 Hz, OCH_2), 3.66 (s, 6H, CCH_2O), 3.49 (t, 6H, J = 5.5 Hz, OCH_2), 3.31 (q, 6H, J = 5.5 Hz, CH_2NH), 2.79 (d, 6H, J = 20.8 Hz, CH_2P), 1.74 (q, 6H, J = 5.5 Hz, CH_2), 1.29 (t, 18H, J = 7.1 Hz, CH_3); ^{13}C NMR δ: 163.5, 154.9, 135.9, 127.8, 127.4, 69.2, 68.8, 65.6, 61.9, 58.3, 36.9, 33.6, 28.4, 15.7.

Amino-CMPO-tripodand 9. A suspension of compound **7** (632 mg, 0.64 mmol) and 10% Pd/C (98 mg) in MeOH (25 mL) was stirred under a hydrogen atmosphere overnight. The reaction mixture was filtered over Celite and washed thoroughly with small portions of MeOH. Removal of the solvent gave a solid, which was redissolved in CH_2Cl_2. Evaporation of CH_2Cl_2 afforded **9** as a light yellow solid. Yield 500 mg (87%); mp 70–72 °C; MALDI-MS: m/z 1019.4 ($[M + H]^+$, calc. 1019.0); ^1H NMR δ: 7.70–7.80 and 7.42–7.54 (2m, 12 + 18H, P-phenyl), 3.64 (s, 6H, CCH_2O), 3.36–3.39 (m, 6H, OCH_2), 3.30 (d, 6H, J = 13.2 Hz, CH_2P), 3.24–3.28 (m, 6H, CH_2NH), 1.62 (q, 6H, J = 5.7 Hz, CH_2); ^{13}C NMR δ: 164.2, 131.2, 130.8, 128.8, 128.0, 69.9, 62.8, 59.0, 37.7, 37.2, 29.1, 28.4. Anal. Calc. for $C_{55}H_{65}N_4O_9P_3 \cdot 3/4CH_2Cl_2$: C, 61.84; H, 6.19; N, 5.17. Found: C, 62.15; H, 5.82; N, 5.43%.

Amino-CMP-tripodand 10. A suspension of compound **8** (185 mg, 0.19 mmol) and 10% Pd/C (98 mg) in MeOH (20 mL) was stirred under a hydrogen atmosphere overnight. The reaction mixture was filtered over Celite and washed thoroughly with small portions of MeOH. Removal of the solvent gave **10** as a brown oil. Yield 135 mg (85%); MALDI-MS: m/z 827.2 ($[M + H]^+$, calc. 827.0); ^1H NMR δ: 4.16 (q, 12H, J = 7.1 Hz, OCH_2), 3.65 (s, 6H, CCH_2O), 3.58 (t, 6H, J = 5.5 Hz,

OCH_2), 3.42 (q, 6H, J = 5.5 Hz, CH_2NH), 3.05 (d, 6H, J = 21.2 Hz, CH_2P), 1.74 (q, 6H, J = 5.5 Hz, CH_2), 1.35 (t, 18H, J = 7.1 Hz, CH_3); ^{13}C NMR δ: 164.2, 70.4, 63.0, 62.7, 37.9, 34.3, 28.4, 16.3.

General procedure for the synthesis of tripodands 11–14. A solution of compounds **9** or **10**, nonanoyl chloride or myristoyl chloride and Et_3N (1.1 equiv.) in CH_2Cl_2 (25 mL) was refluxed for 24 h. Upon cooling the solution was sequentially washed with a saturated solution of NH_4Cl (2 × 25 mL), H_2O (2 × 25 mL), 2 M NaOH (3 × 25 mL) and a saturated solution of NH_4Cl (2 × 25 mL), and dried over $MgSO_4$. Evaporation of the solvent afforded the crude compounds. Final purification was performed by preparative TLC (SiO_2, EtOAc–MeOH = 95 : 5; the target compounds remain at the bottom of the plate). The compounds were removed from the silica with CH_2Cl_2. Evaporation of the solvent gave the pure compounds **11**–**14**.

Nonanoyl-CMPO-tripodand 11. The general procedure was applied to **9** (145 mg, 0.14 mmol), nonanoyl chloride (0.03 mL, 0.15 mmol) and Et_3N (0.02 mL, 0.15 mmol) to give compound **11** as a light brown solid. Yield 49 mg (30%); mp 64–66 °C; FAB-MS: m/z 1181.0 ([M + Na]$^+$, calc. 1181.5); ^{1}H NMR δ: 7.62–7.72 and 7.31–7.46 (2m, 12 + 18H, P-phenyl), 3.55 (s, 6H, CCH_2O), 3.15–3.31 (m, 18H, OCH_2, CH_2P, CH_2NH), 2.05–2.10 (m, 2H, CH_2), 1.53 (q, 6H, J = 5.8 Hz, CH_2), 1.13–1.20 (m, 12H, CH_2), 0.80 (t, 3H, J = 6.6 Hz, CH_3); ^{13}C NMR δ: 164.0, 130.8, 129.4, 129.3, 127.1, 126.9, 69.6, 69.3, 68.7, 39.2, 38.6, 37.0, 30.0, 27.8, 21.7, 14.1. Anal. Calc. for $C_{64}H_{81}N_4O_{10}P_3 \cdot 2CH_2Cl_2$: C, 59.64; H, 6.45; N, 4.22. Found: C, 59.35; H, 6.35; N, 3.92%.

Nonanoyl-CMP-tripodand 12. The general procedure was applied to **10** (183 mg, 0.22 mmol), nonanoyl chloride (0.044 mL, 0.24 mmol) and Et_3N (0.03 mL, 0.24 mmol) to give compound **12** as a brown oil. Yield 73 mg (34%); FAB-MS: m/z 989.6 ([M + Na]$^+$, calc. 989.0); ^{1}H NMR δ: 4.07 (q, 12H, J = 7.1 Hz, OCH_2), 3.63 (s, 6H, CCH_2O), 3.43 (t, 6H, J = 5.9 Hz, OCH_2), 3.28 (q, 6H, J = 5.9 Hz, 6H, CH_2NH), 2.80 (d, 6H, J = 20.8 Hz, CH_2P), 2.1 (t, 2H, J = 6.9 Hz, CH_2), 1.68 (q, 6H, J = 5.9 Hz, CH_2), 1.27 (t, 18H, J = 7.1 Hz, CH_3), 1.18–1.19 (m, 12H, CH_2), 0.80 (t, 3H, J = 6.9 Hz, CH_3); ^{13}C NMR δ: 164.2, 69.8, 69.2, 62.6, 59.7, 37.4, 35.8, 34.5, 31.8, 29.4, 29.2, 25.8, 22.6, 16.4, 14.0.

Myristoyl-CMPO-tripodand 13. The general procedure was applied to **9** (147 mg, 0.14 mmol), myristoyl chloride (0.04 mL, 0.16 mmol) and Et_3N (0.02 mL, 0.16 mmol) to give compound **13** as a light brown solid. Yield 40 mg (23%); mp 60–62 °C; FAB-MS: m/z 1229.8 ([M + H]$^+$, calc. 1229.6); ^{1}H NMR δ: 7.61–7.68 and 7.35–7.42 (2m, 12 + 18H, P-phenyl), 3.55 (s, 6H, CCH_2O), 3.31 (t, 6H, J = 6.2 Hz, OCH_2), 3.22 (d, 6H, J = 13.6 Hz, CH_2P), 3.16 (q, 6H, J = 6.2 Hz, CH_2NH), 1.82–2.00 (m, 2H, CH_2), 1.53 (q, 6H, J = 6.2 Hz, CH_2), 1.13–1.18 (m, 22H, CH_2), 0.80 (t, 3H, J = 6.5 Hz, CH_3); ^{13}C NMR δ: 164.6, 132.3, 130.9, 130.8, 128.8, 128.7, 69.6, 69.3, 68.7, 39.2, 38.6, 37.0, 31.8, 29.2, 22.6, 14.1. Anal. Calc. for $C_{69}H_{91}N_4O_{10}P_3 \cdot 5/4CH_2Cl_2$: C, 63.18; H, 7.06; N, 4.91. Found: C, 63.20; H, 6.85; N, 4.73%.

Myristoyl-CMP-tripodand 14. The general procedure was applied to **10** (135 mg, 0.16 mmol), myristoyl chloride (0.045 mL, 0.18 mmol) and Et_3N (0.025 mL, 0.18 mmol) to give compound **14** as a brownish oil. Yield 56 mg (33%); FAB-MS: m/z 1024.6 ([M + Na]$^+$, calc. 1024.0); ^{1}H NMR δ: 4.16 (q, 12H, J = 6.9 Hz, OCH_2), 3.72 (s, 6H, CCH_2O), 3.50 (t, 6H, J = 5.8 Hz, OCH_2), 3.28 (q, 6H, J = 5.8 Hz, CH_2NH), 2.88 (d, 6H, J = 20.8 Hz, CH_2P), 2.16–2.19 (m, 2H, CH_2), 1.68 (q, 6H, J = 5.8 Hz, CH_2), 1.37 (t, 18H, J = 6.9 Hz, CH_3), 1.25–1.27 (m, 22H, CH_2), 0.89 (t, 3H, J = 6.2 Hz, CH_3); ^{13}C NMR δ: 164.1, 69.8, 69.0, 62.7, 50.8, 37.3, 36.0, 34.3, 31.9, 29.6, 29.3, 29.1, 22.6, 16.4, 14.1.

6-Chlorohexanoyl-CMPO-tripodand 15. To a cold (0 °C) CH_2Cl_2 solution (30 mL) of **9** (751 mg, 0.74 mmol) were added dry K_2CO_3 (1.02 g, 7.38 mmol), 6-chlorohexanoyl chloride (1.24 g, 7.38 mmol). Subsequently, H_2O (130 mg, 7.22 mmol) was added in a few small portions over 1 h. The reaction mixture was allowed to warm up to room temperature and left for 24 h. After filtration of the solid material and evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2–EtOH–hexane = 84 : 12 : 4) resulting in pure **15**. Yield 576 mg (68%); FAB-HRMS: m/z 1189.4118, ([M + H]$^+$, calc. 1189.3944); ^{1}H NMR δ: 7.65–7.72 (m, 12H, PC_6H_5), 7.54 (t, 3H, J = 5.5 Hz, CH_2NHC(O)C), 7.36–7.49 (m, 18H, PC_6H_5), 6.93 (s, 1H, CH_2CONHC), 3.58 (s, 6H, CCH_2OCH_2), 3.39 (t, 2H, J = 6.6 Hz, ClCH_2), 3.15–3.34 (m, 18H, C(O)CH_2PO, O$CH_2$$CH_2CH_2$N), 2.14 (t, 2H, J = 7.4 Hz, Cl$CH_2C_3H_6$CH_2CO), 1.46–1.69, 1.24–1.34 (m, 12H, OCH_2C$H_2$$CH_2N, ClCH_2C_3H_6$$CH_2$CO); ^{13}C NMR δ: 173.2, 164.84, 164.78, 132.6, 132.51, 132.49, 131.2, 131.1, 130.9, 129.1, 128.9, 69.8, 69.1, 60.1, 45.1, 39.5, 38.7, 37.4, 36.8, 32.5, 29.5, 26.6, 25.1.

6-Chlorohexanoyl-CMP-tripodand 16. To a cold (0 °C) CH_2Cl_2 solution (40 mL) of **9** (482 mg, 0.58 mmol) were added dry K_2CO_3 (805 mg, 5.82 mmol) and 6-chlorohexanoyl chloride (986 mg, 5.83 mmol). Subsequently, H_2O (100 mg, 5.55 mmol) was added in a few small portions over 1 h. The reaction mixture was allowed to warm up to room temperature and left for 24 h. After filtration of the solid material and evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2–EtOH–hexane = 84 : 12 : 4) resulting in pure **16**. Yield 152 mg (27%). FAB-HRMS: m/z 959.3953, ([M + H]$^+$, calc. 959.4080); ^{1}H NMR δ: 7.13 (br, 3H, J = 2.7 Hz, CH_2NHCO), 6.66 (s, 1H, CH_2CONHC), 4.15 (m, 12H, PO$CH_2$$CH_3$), 3.71 (s, 6H, C$CH_2OCH_2$), 3.29–3.58 (m, 14H, O$CH_2$$CH_2CH_2N, ClCH_2$), 2.87 (d, 6H, J = 21 Hz, COCH_2PO), 2.23 (t, 2H, J = 7.4 Hz, Cl$CH_2C_3H_6$CH_2CO), 1.44–1.83 (m, 12H, OCH_2C$H_2$$CH_2N, ClCH_2C_3H_6$$CH_2$CO), 1.34 (t, 18H, J = 7.1 Hz, POCH_2CH_3); ^{13}C NMR δ: 173.4, 164.6, 164.5, 70.1, 69.4, 63.0, 62.9, 60.1, 45.1, 37.6, 36.9, 36.2, 34.5, 32.5, 29.5, 26.6, 25.2, 16.6, 16.5.

1,1,1-Tris[(carboxymethoxy)methyl]propane (18). A mixture of trimethylopropane **17** (6.99 g, 52 mmol) and potassium *tert*-butoxide (70.0 g, 624 mmol) in *tert*-butanol (250 mL) was refluxed for 3 h. Subsequently, bromoacetic acid (43.3 g, 312 mmol) was added dropwise to the mixture over a period of 4 h, whereupon the mixture was refluxed for another 140 h. After solvent evaporation, CH_2Cl_2 (100 mL) was added to the residue and the mixture was acidified to pH 1 with conc. HCl. After filtration of the insoluble precipitate, the solvent was evaporated giving 37.5 g of crude **18**, which was used for the next step without further purification.

1,1,1-Tris[(methoxycarbonyl)methyl]propane (19). A solution of crude **18** and a catalytic amount of H_2SO_4 (0.05 mL) in methanol (250 mL) was refluxed for 48 h (reflux passed through a bed of molecular sieves 3A). After evaporation of the methanol, the residue was dissolved in CH_2Cl_2 (10 mL) and passed through a layer of silica gel. Evaporation of the solvent afforded crude ester **19** as a yellow oil, which was used in the next step without further purification. Yield 15.2 g (83% based on alcohol **17**).

1,1,1-Tris[(carbamoyl)methyl]propane (20). In an open flask ester **19** (5.73 g, 13 mmol) was dissolved in a cold mixture of MeOH (60 mL) and liquid ammonia (100 mL). The mixture was allowed to warm up to room temperature and left for 72 h. After solvent evaporation the crude product was purified by column chromatography (SiO_2, CH_2Cl_2–EtOH–NH_3 = 65 : 32 : 3) to give pure **20**. Yield 2.77 g (69%); mp 107 °C; FAB-MS: m/z 306.2 ($[M + H]^+$, calc. 306.2); ^{1}H NMR δ: 3.78 (s, 6H, OCH_2CO), 3.36 (s, 6H, CCH_2O), 1.40 (q, 2H, J = 7.6 Hz, CH_3CH_2), 0.81 (t, 3H, J = 7.6 Hz, CH_3CH_2); ^{13}C NMR δ: 174.4, 71.2, 70.2, 42.6, 22.4, 7.4.

1,1,1-Tris[(2-aminoethoxymethyl]propane (21). To a suspension of **20** (1.00 g, 3.27 mmol) in dry THF (100 mL) was added 1 M BH_3 (60 mL, 60 mmol) and the mixture was refluxed for 48 h. After acidification at room temperature with 32% HCl to pH 1, the solvent was evaporated with a rotavapor. The remaining solid was suspended in a 25% aqueous NH_3 solution and extracted with $CHCl_3$ (4 × 20 mL). The organic layer was dried with $MgSO_4$ and evaporation of the solvent gave crude **21**, which was used in the next step without further purification. Yield 840 mg (98%).

Chloroacetamido tripodand 22. To a cold (0 °C) CH_2Cl_2 solution (50 mL) of **21** (840 mg, 3.19 mmol) were added dry K_2CO_3 (4.41 g, 32 mmol) and 6-chlorohexanoyl chloride (5.41 g, 32 mmol). Subsequently, H_2O (0.58 g, 32 mmol) was added in a few small portions over 1 h. The reaction mixture was allowed to warm up to room temperature and left for 24 h. After filtration of solid material, evaporation of the solvent resulted in crude **22**, which was used in the next step without purification. Yield 1.53 g (98%). ^{1}H NMR δ: 4.07 (s, 6H, $COCH_2Cl$), 3.51 (m, 12H, OCH_2CH_2N), 3.35 (s, 6H, CCH_2O), 1.44 (q, 2H, J = 7.5 Hz, CH_3CH_2), 0.87 (t, 3H, J = 7.5 Hz, CH_3CH_2).

1,1,1-Tris[(diphenylcarbamoylmethylphosphine oxide *N*-ethoxy)methyl]propane (23). In an open flask compound **22** (296 mg, 0.60 mmol) was dissolved in a small amount of ethyl diphenylphosphinite (0.45 mL, 2.08 mmol), while the temperature was gradually increased from 100 to 150 °C. Subsequently, the mixture was stirred for 1 h at 150 °C. After cooling of the reaction mixture, diisopropyl ether was added and the mixture left stirring overnight. The organic solution was decanted to give **23** as a yellow oil, which was purified by column chromatography (SiO_2, CH_2Cl_2–MeOH = 10 : 1 → 10 : 2). Yield 229 mg (38%); mp 189–190 °C; ^{1}H NMR δ: 7.70–7.77 (m, 12H, PC_6H_5), 7.65 (br, CH_2NHCO), 7.43–7.56 (m, 18H, PC_6H_5), 3.87 (s, 12H, OCH_2CH_2N), 3.33 (d, 6H, J = 13.2 Hz, CH_2PO), 3.27 (s, 6H, CCH_2O), 1.34 (q, 2H, J = 7.5 Hz, CH_3CH_2), 0.81 (t, 3H, J = 7.5 Hz, CH_3CH_2); ^{13}C NMR δ: 165.0, 132.7, 132.5, 131.4, 131.2, 131.0, 129.1, 128.9, 71.3, 69.9, 43.5, 40.0, 38.7, 33.6, 26.6, 8.0. Anal. Calc. for $C_{54}H_{62}N_3O_9 \cdot 1/3\ CH_2Cl_2$: C, 64.10; H, 6.20; N, 4.13. Found: C, 64.23; H, 5.99; N, 3.98%.

1,1,1-Tris[(diethylcarbamoylmethylphosphonate *N*- ethoxy)-methyl]propane (24). In an open flask compound **22** (438 mg, 0.889 mmol) was dissolved in a small amount of triethyl phosphite (0.78 mL, 4.46 mmol), while the temperature was gradually increased from 100 to 150 °C. Subsequently, the mixture was stirred for 1 h at 150 °C. After cooling of the reaction mixture, diisopropyl ether was added and the mixture left stirring overnight. The organic solution was decanted remaining a yellow oil, which was purified by column chromatography (SiO_2, CH_2Cl_2–*i*-PrOH = 10 : 2). Yield 400 mg (56%). FAB-HRMS: m/z 798.3533, ($[M + H]^+$, calc. 798.3472); ^{1}H NMR δ: 7.14 (t, 3H, J = 4.8 Hz, CH_2NH), 4.14 (dq, 12H, J_q = 7.2 Hz, J_d = 8.1 Hz, $POCH_2CH_3$), 3.15–3.42 (m, 12H, OCH_2CH_2NH), 3.32 (s, 6H, CCH_2O), 2.86 (d, 6H, J = 20.7 Hz, CH_2PO), 1.39 (q, 2H, J = 7.5 Hz, CH_3CH_2), 1.36 (t, 18H, J = 7.2 Hz, $POCH_2CH_3$), 0.83 (t, 3H, J = 7.5 Hz, CH_3CH_2); ^{13}C NMR δ: 164.41, 164.37, 71.4, 70.0, 62.94, 62.87, 43.5, 40.0, 36.0, 34.7, 23.1, 16.36, 16.30, 7.8.

Cosan-containing CMPO tripodand 26. CMPO tripodand **9** (95 mg, 0.115 mmol) was dissolved under stirring in DME (5 mL) in a two necked 25 mL Schlenk flask, equipped with a nitrogen inlet and a rubber septum. Then solid NaH (12 mg, 0.5 mmol) was added in one portion and the content of the flask was stirred for 2 h. A solution of COSAN-dioxane **25a** (47 mg, 0.115 mmol) in toluene (4.5 mL) was dropwise added with a syringe through the septum, and the reaction mixture was stirred at ambient temperature for 7 days. 50% Aqueous ethanol (1 mL) was added to the reaction mixture followed by three drops of acetic acid (3 M), whereupon the solvents were evaporated. The residue was dissolved in diethyl ether and treated with 3 M HCl (3 × 10 mL). The organic phase was separated and the solvents evaporated. The crude product was purified by column chromatography (SiO_2, CH_3CN–CH_2Cl_2 = 1 : 3). The fraction corresponding to R_f 0.07 on TLC (Silufol®, CH_3CN–CH_2Cl_2 = 1 : 3) was collected to give **26** as an orange semi-solid material. Yield 30 mg (21%). ^{11}B NMR (128 MHz, acetone-d_6, 25 °C, $BF_3 \cdot Et_2O$) δ: 23.4 (s, 1B, B8), 4.4 (d, ^1J(B,H) = 125 Hz, 1B, B8′), 0.4 (d, ^1J(B,H) = 129 Hz, 1B, B10′), −2.5 (d, ^1J(B,H) = 142 Hz, 1B, B10), −4.1 (d, ^1J(B,H) = 153 Hz, 2B, B4′,7′), −7.5 (2d, overlap, 6B, B4,7,9,12, 9′,12′), −17.3 (d, ^1J(B,H) = 131 Hz, 2B, B5′,11′), −20.3 (d, ^1J(B,H) = 144 Hz, 2B, B5,11), −21.7 (d, overlap, 1B, B6′), −28.1 (d, ^1J(B,H) = 139 Hz, 1B, B6); ^{1}H NMR (acetone-d_6) δ: 7.87–7.91 and 7.28–7.59 (4m, 12 + 18H, PC_6H_5), 4.22–4.25 (m, 6H, OCH_2CH_2O, CH_2O), 3.79, 4.06 (2s, 4H, $CH_{carborane}$), 3.53–3.71 (m, 18H, CH_2O, CH_2P,

CH_2NH), 3.27–3.29 (m, 2H, CH_2NH), 1.27–1.30 (m, 6H, CH_2).

Cosan-containing CMP tripodand 27. Compound **27** was prepared analogously to the previous procedure, but without addition of NaH in the first step. A solution of CMP tripodand **10** (48 mg, 0.0471 mmol) in DME (5 mL) was reacted with a solution of COSAN-dioxane **25a** (23 mg, 0.506 mmol) in toluene at ambient temperature for 6 days. After evaporation of the solvent the resulting residue was purified by flash chromatography (SiO_2, $CH_3CN–CH_2Cl_2$ = 1 : 4). The fraction corresponding to R_F 0.24 on TLC (Silufol®, $CH_3CN–CH_2Cl_2$ = 1 : 6) was collected to give **27** as an orange semi-solid material. Yield 40 mg (58%). ^{11}B NMR (128 MHz, acetone-d_6, 25 °C, $BF_3 \cdot Et_2O$) δ: 23.8 (s, 1B, B8), 4.5 (d, ^1J(B,H) = 125 Hz, 1B, B8′), 0.4 (d, ^1J(B,H) = 129 Hz, 1B, B10′), −2.5 (d, ^1J(B,H) = 142 Hz, 1B, B10), −4.1 (d, ^1J(B,H) = 153 Hz, 2B, B4′,7′), −7.3 (2d, overlap, 6B, B4,7,9,12, 9′,12′), −17.3 (d, ^1J(B,H) = 131 Hz, 2B, B5′,11′), −20.3 (d, ^1J(B,H) = 144 Hz, 2B, B5,11), −21.7 (d, overlap, 1B, B6′), −28.1 (d, ^1J(B,H) = 139 Hz, 1B, B6); ^{1}H NMR (acetone-d_6) δ: 4.07–4.17 (m, 18H, OCH_2CH_2O, OCH_2), 3.86, 4.05 (4H, $CH_{carborane}$), 3.45–3.64 (m, 6H, OCH_2), 3.41–3.65 (m, 14H, CH_2NH, CCH_2O, CH_2NH), 2.95 (br d, 6H, CH_2P), 1.82–1.96 (m, 6H, CH_2), 1.29–1.31 (m, 18H, CH_3).

Cosan-containing CMPO tripodand 28. A stirred solution of [8-(HO(CH_2CH_2O)-COSAN]Me_3NH **25b** (22 mg, 0.045 mmol) in THF (5 mL) was treated with NaH (6 mg, 0.25 mmol). The slurry was stirred for 4 h and then the solvent and the trimethylamine were evaporated on a vacuum line almost to dryness. Subsequently, freshly distilled THF was injected (5 mL). A solution of **15** (52 mg, 0.045 mmol) in THF (5 mL) was dropwise added with a syringe through a septum during 2 h, and the reaction mixture was stirred at 50 °C for 24 h. NaH (6 mg, 0.25 mmol) was added and the reaction mixture was stirred at 50 °C for an additional 48 h. After cooling down, the reaction mixture was quenched by addition of 50% aqueous ethanol (1 mL) followed by three drops of acetic acid (3 M), whereupon the solvents were evaporated. The residue was dissolved in ethyl acetate and treated with 3 M HCl (3 × 10 mL), cold (0 °C) 5% Na_2CO_3 solutions (3 × 10 mL), and with brine (4 × 10 mL). After evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, $CH_3CN–CH_2Cl_2$ = 1 : 3 followed by CH_3CN–MeOH = 1 : 1). The fraction corresponding to R_F 0.03 on TLC (Silufol®, $CH_3CN–CH_2Cl_2$ = 1 : 3) was collected, the solvent evaporated, dried in vacuum, the residue redissolved in dry CH_3CN, filtered, and the solvent evaporated to give **28** as an orange semi-solid material. Yield 45 mg (63%). ^{11}B NMR (128 MHz, acetone-d_6, 25 °C, $BF_3 \cdot Et_2O$) δ: 23.3 (s, 1B, B8), 4.5 (d, ^1J(B,H) = 125 Hz, 1B, B8′), 0.4 (d, ^1J(B,H) = 129 Hz, 1B, B10′), −2.5 (d, ^1J(B,H) = 142 Hz, 1B, B10), −4.3 (d, ^1J(B,H) = 153 Hz, 2B, B4′,7′), −7.3 to −8.0 (2d, overlap, 6B, B4,7,9,12, 9′,12′), −17.2 (d, ^1J(B,H) = 131 Hz, 2B, B5′,11′), −20.4 (d, ^1J(B,H) = 144 Hz, 2B, B5,11), −21.7 (d, overlap, 1B, B6′), −28.4 (d, ^1J(B,H) = 139 Hz, 1B, B6); ^{1}H NMR δ: 7.71–7.85 (m, 12H, PC_6H_5), 7.48–7.54 (m, 6H, PC_6H_5), 7.21–7.28 (m, 12H, PC_6H_5), 7.03 (t, 3H, J = 5.5 Hz, CH_2NHC(O)C), 6.23 (s, 1H, CH_2CONHC), 4.08, 4.21 (2s, 4H, $CH_{carborane}$), 3.82–3.95 (m, 6H, CCH_2OCH_2, CH_2O), 3.71 (t, 4H, J = 5.6 Hz, OCH_2), 3.59 (t, 2H, J = 5.0 Hz, OCH_2), 3.44 (t, 4H, J = 5.1 Hz, OCH_2), 3.31–3.32 (m, 6H, OCH_2), 3.28 (m, 12H, C(O)CH_2PO, $OCH_2CH_2CH_2$N), 2.13 (t, 2H, J = 7.4 Hz, $OCH_2C_3H_6CH_2CO$), 1.79–1.91 (m, 8H, $OCH_2CH_2CH_2N$, $OCH_2C_3H_6CH_2CO$), 1.70–1.72, 1.46–1.50 (m, 6H, $OCH_2C_3H_6CH_2CO$).

Cosan-containing CMP tripodand 29. A stirred solution of [8-(HO(CH_2CH_2O)-COSAN]Me_3NH **25b** (39 mg, 0.08 mmol) in THF (5 mL) was treated with NaH (12 mg, 0.5 mmol). The slurry was stirred for 4 h and then evaporated on a vacuum line almost to dryness to remove the solvent and the trimethylamine. Then freshly distilled THF was injected (5 mL). A solution of **16** (78 mg, 0.08 mmol) in THF (5 mL) was dropwise added with a syringe through a septum during 2 h, and the reaction mixture was stirred at 60 °C for 72 h. After cooling down, the reaction was quenched by addition of 50% aqueous ethanol (1 mL), followed by three drops of acetic acid (3 M). Silica gel (2 g) was added and the solvents were evaporated. The silica gel containing crude product was poured on top of a chromatographic column and purified by column chromatography (SiO_2, $CH_3CN–CH_2Cl_2$ = 1 : 3 followed by CH_3CN–MeOH = 1 : 1). The fraction corresponding to R_F 0.01 on TLC (Silufol®, $CH_3CN–CH_2Cl_2$ = 1 : 3) was collected to give **29** as an orange semi-solid material. Yield 49 mg (44%). ^{11}B NMR (128 MHz, acetone-d_6, 25 °C, $BF_3 \cdot Et_2O$) δ: 23.3 (s, 1B, B8), 4.6 (d, ^1J(B,H) = 125 Hz, 1B, B8′), 0.5 (d, ^1J(B,H) = 129 Hz, 1B, B10′), −2.6 (d, ^1J(B,H) = 142 Hz, 1B, B10), −4.3 (d, ^1J(B,H) = 153 Hz, 2B, B4′,7′), −7.2 to −8.1 (2d, overlap, 6B, B4,7,9,12, 9′,12′), −17.3 (d, ^1J(B,H) = 131 Hz, 2B, B5′,11′), −20.3 (d, ^1J(B,H) = 144 Hz, 2B, B5,11), −21.7 (d, overlap, 1B, B6′), −28.4 (d, ^1J(B,H) = 139 Hz, 1B, B6); ^{1}H NMR δ: 7.61 (br s, 3H, CH_2NHCO), 7.90 (s, 1H, CH_2CONHC), 4.15 (m, 12H, $POCH_2CH_3$), 3.80, 3.89 (2s, 4H, $CH_{carborane}$), 3.74 (s, 6H, CCH_2OCH_2), 3.61–3.80 (m, 4H, OCH_2), 3.32–3.39 (m, 6H, $OCH_2CH_2CH_2N$), 3.32–3.39 (m, 4H, OCH_2), 3.02 (d, 6H, J = 18 Hz, $COCH_2PO$), 2.24 (t, 2H, J = 5.2 Hz, $OCH_2C_3H_6CH_2CO$), 1.45–1.82 (m, 12 H, $OCH_2CH_2CH_2N$, $OCH_2C_3H_6CH_2CO$), 1.31 (t, 18H, J = 7.2 Hz, $POCH_2CH_3$).

Picrate extractions

Solutions. The 10–4 M salt stock solutions were prepared by dissolving the required amounts of the appropriate metal nitrate $M^{n+}(NO_3^-)_n$ and LiPic in 10^{-3} M HNO_3 adjusting the total volume of the solution to 100 mL using volumetric glassware. The pH of the solutions was close to pH 3, and adjusted to pH 3 by adding small amounts of LiOH. The 10^{-3} M stock solutions of the ligands were prepared by dissolving the appropriate amount of ligands in 20 mL of CH_2Cl_2.

Procedure. Equal volumes (1.0 mL) of the organic and the aqueous solutions were transferred into a stoppered glass vial and stirred at ambient temperatures (about 23 °C) for 17 h. The two phases were separated by centrifugation (1600 rpm for 10 min). The concentration of picrate ion in the aqueous and organic phase was determined spectrophotometrically

(λ_{max} = 355 nm). Each measurement was repeated three times. Blank experiments showed that no picrate extraction occurred in the absence of ionophore. The percentage of the cation extracted into the organic phase ($\%E = E \times 100\%$), defined as the ratio of the activity in the organic phase (A_o) and the total activity in both the organic and the aqueous phase (A_w), is expressed by the following equation:

$$\%E = (A_o/(A_o + A_w)) \times 100\%$$

Potentiometric measurements

Reagents. The salts and membrane components potassium tetrakis[3,4-bis(trifluoromethyl)phenyl]borate (KTFPB), *o*-nitrophenyl octyl ether (*o*-NPOE), high molecular weight poly (vinyl chloride) (PVC) and tetrahydrofuran (THF, distilled prior to use) and all salts were purchased from Fluka (Ronkonkoma, NY). Aqueous solutions were obtained by dissolving the appropriate salts in Nanopure purified distilled water.

Membrane preparation. The polymeric membranes used for the determination of the stability constants contained ionophore (20 mmol/kg), KTFPB (2 mmol kg^{-1}) in PVC/*o*-NPOE (1 : 2 by weight) polymeric matrix (unless otherwise indicated in the text). The membrane components (total 140 mg) were dissolved in freshly distilled THF (1.4 mL). The solution was placed in a glass ring (22 mm i.d.) mounted over a glass plate and than covered with another glass plate to slow down the solvent evaporation. After 24 h, the resulting membrane was peeled from the glass plate and discs of 7 mm diameter were cut out. The procedure for the preparation of the polymeric membranes evaluated for the potentiometric ion response was similar to that described above. The total amount of membrane components was 200 mg and the membranes consisted of 1 wt% of ionophore, 30 mol% of KTFPB and PVC/*o*-NPOE (1 : 2 by weight).

Potentiometric response to cations and selectivity measurements. Membrane discs were mounted in conventional ISE electrode bodies (Type IS 561; Philips, Eindhoven, The Netherlands) for electromotive force (EMF) measurements. All measurements were made at ambient temperature (22 ± 1 °C) using a galvanic cell of the following type: Ag|$AgCl_{(s)}$|3 M KCl|bridge electrolyte|sample|ion-selective membrane|inner filling solution|$AgCl_{(s)}$/Ag. The bridge electrolyte consisted of 1 M lithium acetate. The inner filling solution of the ISEs was a 0.01 M NaCl solution. The EMF values were measured using a custom made 16-channel electrode monitor. Details of this equipment have been described previously.[29]

The performance of the electrodes was examined by measuring the EMF for solutions of the examined cations over the concentration range of 10^{-7}–10^{-1} M. Activity coefficients were calculated according to the Debye–Hückel approximation.[30] Potentiometric selectivity coefficients were determined by the separate solution method (SSM) according to the modification of the method described in literature.[13] Selectivity coefficient $K^{pot}_{I,J}$ values were obtained from adequate, unbiased E^0 measurements for each ion, according to the equation:

$$K^{pot}_{i,j} = \exp\left\{\frac{z_i F}{RT}(E^0_j - E^0_i)\right\}$$

where R, T and F are the gas constant, absolute temperature and the Faraday constant, respectively. The charge of the primary ion, i, is indicated as z_i and the measured potentials for primary and interfering ions are put as E^0_i and E^0_j, respectively.

Determination of the stability constants. Experiments were carried out according to the procedure described in literature.[11] Two sets of membranes were prepared: membranes with and without ionophore. A series of 7 mm i.d. membrane discs were cut from the parent membrane, and these disks were conditioned over 2–3 days in appropriate salt solutions (10^{-1} M NaCl, 10^{-2} M $CuCl_2$, 10^{-2} M $CdCl_2$, 5×10^{-3} M $PbCl_2$, 10^{-3} M $UO_2(NO_3)_2$/10^{-3} M NaCl (pH = 4)). After drying of the individual membranes, the sandwich membrane was made by attaching of the membrane with ionophore to the membrane without ionophore. The segmented membrane was than mounted into a Philips electrode body (membrane with ionophore faced the sample solution) and immediately immersed into an appropriate salt solution (identical as for conditioning of the membrane). The potential was recorded as the mean of the last minute of a 10 min measurement period in the appropriate salt solution. The potential of the electrodes with sandwich membranes remained free of diffusion-induced drifts for 20–50 min, depending on the ionophore incorporated within the membrane and the ion measured. Membrane potential values ΔEMF were calculated by subtracting the cell potential for a membrane without ionophore from that of the sandwich membrane. The formation constant, β_{IL_n}, was calculated from the following equation:

$$\beta_{IL_n} = \left(L_T - \frac{n}{z_i}R_T^-\right)^{-n} \exp\left(\frac{z_i F}{RT}\Delta EMF\right)$$

where: n is the complex stoichiometry, L_T and R_T are the concentrations of ionophore and ionic site additives in the membrane, respectively.

Extractions

Liquid–liquid extractions of europium and americium by CMP(O) tripodands 3, 4, 11–14, 23 and 24. 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 IKA device (Vibrax VXR). Tubes were centrifuged and 40 μL of each phase were diluted either in 560 μL of 1,1,2,2-tetrachloroethane or 1-octanol for the organic samples, or in 560 μL of 1 or 3 M nitric acid for the aqueous samples. 550 μL of each sample were used for radiometric (gamma) analyses. All extractions were performed in duplicate. The accuracy of the D values of Table 2 is about 20%. The D values (10^{-2} and lower) in Table 3, when 1-octanol is used as a solvent, were determined with a surprisingly high accuracy (about 10%). The reason is that the organic phase, although of low activity, cannot be contaminated when sampling it.

The acidity of the initial and final aqueous solutions was determined by potentiometric titration on 100 μL samples, using a METROHM 751 GPD Titrino device and a [NaOH] = 0.1 mol L^{-1} solution.

Liquid–liquid extractions of europium and americium by the COSAN-containing samples. All extraction experiments were executed in polypropylene test tubes at 25 ± 0.5 °C. The volume of both phases was 1 mL. The samples were shaken for 1 h on a rotating apparatus. The organic and aqueous phases were separated by centrifugation. All reagents and solvents used were of AR purity. ^{152}Eu and ^{241}Am tracers (radiochemical purity) were used for the measurement of the Eu/Am distribution. Their γ activity was measured by a single channel analyzer with a NaI-Tl well-type detector. All extractions were performed in duplicate. In the range of 0.1–10 the error in the D values is about 5%, while in the ranges of 0.01–0.1 and 10–100 the error is about 10%. For higher and lower D values the error may increase to 30–40%.

Extractions of Am^{3+} and Eu^{3+} with CMP(O) tripodand-containing magnetic particles. In aqueous phase was prepared at varying HNO_3 concentrations (0.01–3 M). Europium, as radioisotope ^{152}Eu, and americium, as radioisotope ^{241}Am, were added at an activity around 1500 kBq dm^{-3}, which corresponds approximately to a concentration of 5×10^{-8} M for Am^{3+} and 1.5×10^{-9} M for Eu^{3+}. 10 mL of the aqueous phase was shaken with particles (300 mg) for 1 h and than separated by magnetic techniques. The initial and final concentrations of the lanthanides and actinides in the aqueous phases were determined using a single-channel γ analyzer with a NaI (Tl) well detector. All experiments were carried out in duplicate. The error in the D values is about 10%.

Acknowledgements

We gratefully acknowledge the financial support from the EEC (contracts FIKW-CT-2000-00088 and F16W-CT-2003-508854). The part of this work related to the potentiometric studies was financially supported by the Warsaw University of Technology.

References

1 (*a*) E. P. Horwitz, K. A. Martin, H. Diamond and L. Kaplan, *Solvent Extr. Ion Exch.*, 1986, **4**, 449; (*b*) E. P. Horwitz, H. Diamond, K. A. Martin and R. Chiarizia, *Solvent Extr. Ion Exch.*, 1987, **5**, 419.
2 (*a*) F. Arnaud-Neu, V. Böhmer, J.-F. Dozol, C. Grüttner, R. A. Jakobi, D. Kraft, O. Mauprivez, H. Rouquette, M.-J. Schwing-Weill, N. Simon and W. Vogt, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1175; (*b*) S. E. Matthews, M. Saadioui, V. Böhmer, S. Barboso, F. Arnaud-Neu, M.-J. Schwing-Weill, A. Garcia Carrera and J.-F. Dozol, *J. Prakt. Chem.*, 1999, **341**, 341.
3 A. Arduini, V. Böhmer, L. Delmau, J.-F. Desreux, J.-F. Dozol, M. A. G. Carrera, B. Lambert, C. Musigmann, A. Pochini, A. Shivanyuk and F. Ugozzoli, *Chem. Eur. J.*, 2000, **6**, 2135.
4 (*a*) C. Schmidt, M. Saadioui, V. Böhmer, V. Host, M.-R. Spirlet, J.-F. Desreux, F. Brisach, F. Arnaud-Neu and J.-F. Dozol, *Org. Biomol. Chem.*, 2003, **1**, 4089; (*b*) P. Wang, M. Saadioui, C. Schmidt, V. Böhmer, V. Host, J.-F. Desreux and J.-F. Dozol, *Tetrahedron*, 2004, **60**, 2509.
5 (*a*) H. Boerrigter, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1997, **62**, 7148; (*b*) M. M. Reinoso-García, W. Verboom, D. N. Reinhoudt, F. Brisach, F. Arnaud-Neu and K. Liger, *Solvent Extr. Ion Exch.*, 2005, **23**, 425.
6 (*a*) M. W. Peters, E. J. Werner and M. J. Scott, *Inorg. Chem.*, 2002, **41**, 1707; (*b*) V. Rudzevich, D. Schollmeyer, D. Braekers, J.-F. Desreux, R. Diss, G. Wipff and V. Böhmer, *J. Org. Chem.*, 2005, **70**, 6027.
7 (*a*) R. Wietzke, M. Mazzanti, J.-M. Latour, J. Pécaut, P.-Y. Cordier and C. Madic, *Inorg. Chem.*, 1998, **37**, 6690; (*b*) J. L. Kiplinger, B. L. Scott and C. J. Burns, *Inorg. Chim. Acta*, 2005, **358**, 2813.
8 M. M. Reinoso-García, A. Dijkman, W. Verboom, D. N. Reinhoudt, E. Malinowska, D. Wojciechowska, M. Pietrzak and P. Selucky, *Eur. J. Org. Chem.*, 2005, 2131.
9 (*a*) S. Lebreton, N. Newcombe and M. Bradley, *Tetrahedron Lett.*, 2002, **43**, 2479; (*b*) S. Lebreton, S.-E. How, M. Buchholz, B.-E. Yingyongnarongkul and M. Bradley, *Tetrahedron*, 2003, **59**, 3945.
10 K. Kita, T. Kida, Y. Nakatsuji and I. Ikeda, *J. Org. Chem.*, 1997, **62**, 8076.
11 (*a*) Y. Mi and E. Bakker, *Anal. Chem.*, 1999, **71**, 5279; (*b*) Y. Qin, Y. Mi and E. Bakker, *Anal. Chim. Acta*, 2000, **421**, 207.
12 I. Goldberg and D. Meyerstein, *Anal. Chem.*, 1980, **52**, 2105.
13 (*a*) E. Bakker, E. Pretsch and P. Bühlman, *Anal. Chem.*, 2000, **72**, 1127; (*b*) E. Bakker, P. Bühlman and E. Pretsch, *Chem. Rev.*, 1997, **97**, 3083.
14 E. Malinowska, L. Górski, D. Wojciechowska, M. M. Reinoso-García, W. Verboom and D. N. Reinhoudt, *New J. Chem.*, 2003, **27**, 1440.
15 S. S. Moore, T. L. Tarnowski, M. Newcomb and D. J. Cram, *J. Am. Chem. Soc.*, 1997, **99**, 6398.
16 G. R. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 353.
17 B. Grüner, L. Mikulášek, J. Báča, I. Císařová, V. Böhmer, C. Danila, M. M. Reinoso-García, W. Verboom, D. N. Reinhoudt, A. Casnati and R. Ungaro, *Eur. J. Org. Chem.*, 2005, 2022.
18 B. A. Buchholz, H. E. Tuazon, M. D. Kaminski, S. B. Aase, L. Nuñez and G. F. Vandergift, *Sep. Purif. Technol.*, 1997, **11**, 211.
19 L. Nuñez, B. A. Buchholz and G. F. Vandergift, *Sep. Sci. Technol.*, 1995, **30**, 1455.
20 M. Kaminski, S. Landsberger, L. Nuñezj and G. F. Vandergift, *Sep. Sci. Technol.*, 1997, **32**, 115.
21 L. Nuñez and M. D. Kaminski, *J. Magn. Magn. Mater.*, 1999, **194**, 102.
22 S. E. Matthews, P. Parzuchowski, A. Garcia-Carrera, C. Grüttner, J.-F. Dozol and V. Böhmer, *Chem. Commun.*, 2001, 417.
23 V. Böhmer, J.-F. Dozol, C. Grüttner, K. Liger, S. E. Matthews, S. Rudershausen, M. Saadioui and P. Wang, *Org. Biomol. Chem.*, 2004, **2**, 2327.
24 R. Haag, *Chem. Eur. J.*, 2001, **7**, 327.
25 C. Grüttner, V. Böhmer, A. Casnati, J.-F. Dozol, D. N. Reinhoudt, M. M. Reinoso-García, S. Rudershausen, J. Teller, R. Ungaro, W. Verboom and P. Wang, *J. Magn. Magn. Mater.*, 2005, **293**, 559.
26 M. M. Meijler, R. Arad-Yellin, Z. I. Cabantchik and A. Shanzer, *J. Am. Chem. Soc.*, 2002, **124**, 12666.
27 J. Plešek, S. Heřmánek, A. Franken, I. Cásařová and C. Nachtigal, *Collect. Czech. Chem. Commun.*, 1997, **62**, 47.
28 I. B. Sivaev, Z. A. Starikova, S. Sjoberg and V. I. Bregadze, *J. Organomet. Chem.*, 2002, **649**, 1.
29 Z. Brzózka, *Pomiary Autom. Kontrola*, 1988, **9**, 197.
30 P. C. Meier, *Anal. Chim. Acta*, 1982, **136**, 363.

