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Adamantylcalixarenes with CMPO groups at the wide rim: synthesis and extraction of lanthanides and actinides

Alina Motornaya,[a] Ivan Vatsouro,[a] Elvira Shokova,[a] Véronique Hubscher-Bruder,[b] Mikhail Alyapyshev,[c] Vasily Babain,[c] Maria Karavan,[c] Françoise Arnaud-Neu,[b] Volker Böhmer[d] and Vladimir Kovalev[a,*]

[a]*Laboratory of Macrocyclic Receptors, Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russia*
[b]*Département des Sciences Analytiques, IPHC, ULP, CNRS, 67087 Strasbourg Cedex 2, France*
[c]*V. G. Khlopin Radium Institute, 194021 St. Petersburg, Russia*
[d]*Abteilung Lehramt Chemie, Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg Universität, D-55099 Mainz, Germany*

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Abstract—Starting from *p*-adamantylcalix[4]- and [6]arenes functionalized with carboxylic acid or ester groups at the adamantane nuclei, carbamoylmethylphosphine oxide (CMPO)-containing ligands of a novel type were synthesized. They were studied as extractants for a series of f-block elements including radioactive ^{152}Eu(III), ^{241}Am(III), ^{233}U(VI), and ^{239}Pu(IV). Tetrameric ligand **4b** in which CMPO residues are connected to adamantane nuclei through methylene groups gave the best extraction results for lanthanides and actinides. For all the ligands the extraction efficiency does not decrease at higher nitric acid concentration. Although the discrimination between trivalent actinides and lanthanides is not good, all ligands are highly selective for thorium(IV) with the best separation factor achieved in the case of hexameric ligand **5** ($D_{Th}/D_{Ln}>24$).

1. Introduction

Carbamoylmethylphosphine oxides (CMPO) **1** (Fig. 1) are well known for the extraction of Am^{3+} and Eu^{3+} from nuclear wastes.[1,2] The attachment of CMPO functions to the wide or narrow rim of a calixarene led to derivatives **2** and **3**, which are excellent extractants for actinides and lanthanides.[3,4] In addition, the wide rim tetra CMPO derivatives **2** show a pronounced selectivity for trivalent actinides and light lanthanides over heavy lanthanides.[5] In the case of narrow rim CMPO-substituted calixarenes **3**, the extraction efficiency and selectivity depend strongly on the lengths of the spacers between the calixarene unit and the CMPO groups. In general, these compounds are considerably better extractants for thorium in comparison with **2** and their efficiency toward all the cations does not decrease at higher nitric acid concentrations (>2 M).

Studies of CMPO-modified calixarenes and other multifunctional compounds[6,7] showed that the grafting of several ligating functions onto a polyvalent scaffold is important, but not the only factor that determines the complexation properties. A number of structural variations of ligands **2** and **3** were investigated to improve the extraction characteristics of these ligands. Thus, secondary amide functions were replaced with tertiary ones,[8] eight CMPO functions were introduced at the wide or narrow rim in a dendritic manner,[9] ligating groups were attached to the wide rim through the phosphorus site of CMPO,[10] and the substitution pattern at the narrow rim was varied in order to change the conformational properties of **2**.[11,12] The results obtained suggested that the extraction properties of ligands depend strongly on the mutual arrangement of acetamidophosphine oxide groups. In spite of the fact that some improvement of the extraction characteristics was achieved, the search for extractants with high efficiency and high actinide/lanthanide selectivity still remains active.

We have recently reported, in a preliminary paper, the highly effective extraction of ^{241}Am and ^{152}Eu from nitric acid solutions by the wide rim CMPO adamantylcalix[4]arene **4b**.[13] Here we describe the full synthesis of novel wide rim tetra- and hexameric CMPO ligands **4** and **5** and present a complete study of their extraction properties for lanthanides and actinides.

* Corresponding author. Tel.: +7 495 939 1302; fax: +7 495 932 8846; e-mail: kovalev@petrol.chem.msu.ru

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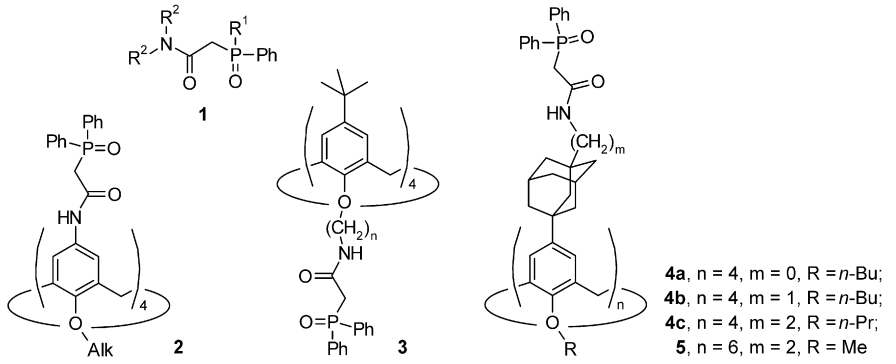


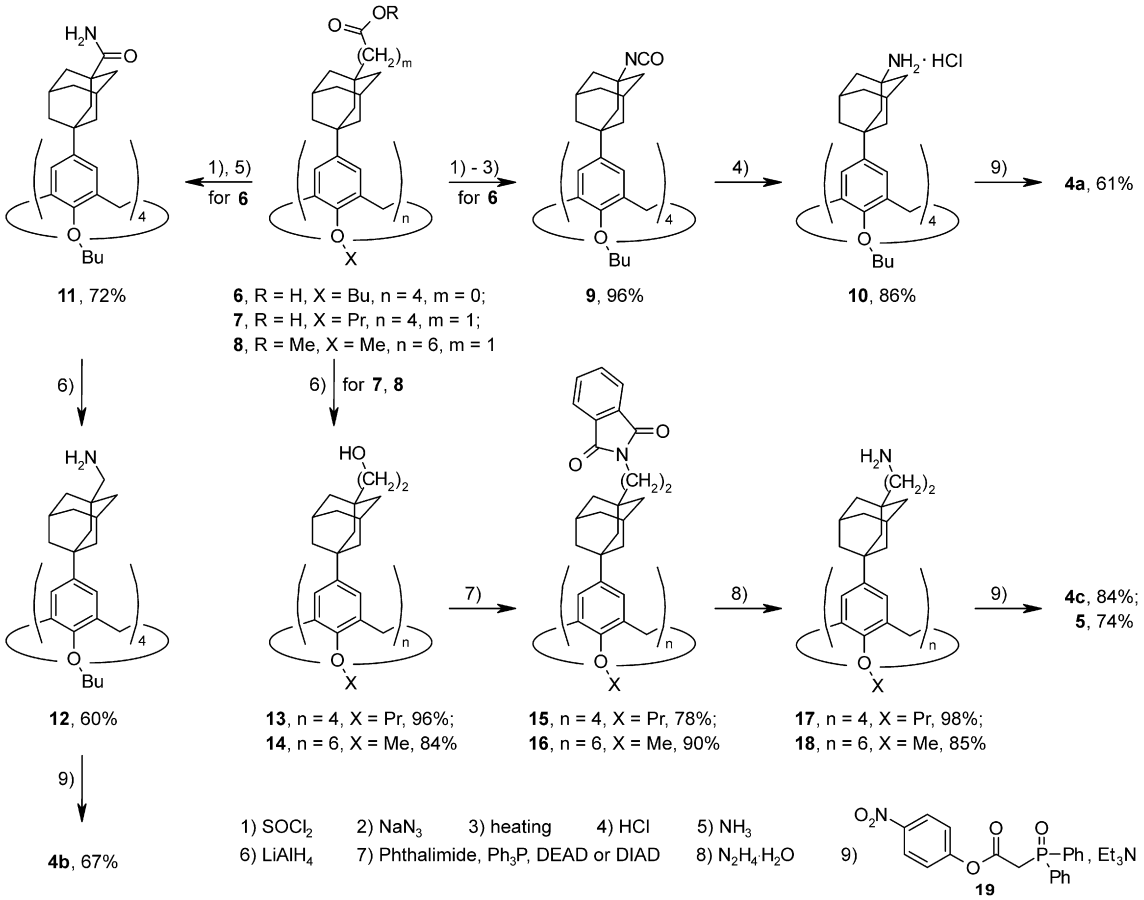
Figure 1. CMPO-like ligands.

2. Results and discussion

2.1. Synthesis

In recent years, we developed a high yielding synthesis for *p*-(3-functionalized-1-adamantyl)calixarenes. It allows, in particular, to synthesize calix[4]- and calix[6]arenes exhaustively modified with carboxylic acid functional groups at their wide rims by the reaction of de-*tert*-butylated precursors with the corresponding 1-adamantanols in trifluoroacetic acid.[14,15] In the present study, we used these *p*-adamantylcalix[4/6]arenes **6–8** with CO_2H or CH_2CO_2R (R=H, Me) groups in the 3-positions of the adamantyl residues as starting material to prepare a new type of CMPO ligands. To exclude undesired reactions of the phenolic hydroxyls and to fix calix[4]arenes in the *cone* conformation,[16] the narrow rims of **6** and **7** are substituted with propyl or butyl groups. In the case of **8**, where the *O*-alkylated derivatives have much more conformational flexibility,[17] we have selected methyl groups to impose no steric restrictions.

The key compounds in the synthesis of ligands **4** and **5** (see Scheme 1) are adamantylcalixarenes **10**, **12**, **17**, and **18** in which amino groups are directly connected to the adamantane framework or separated by methylene or ethylene



Scheme 1. Synthesis of CMPO derivatives of adamantylcalixarenes.

linkers. To prepare **10**, we reacted *p*-(3-carboxy-1-adamantyl)calix[4]arene tetrabutyl ether **6**[14] with thionyl chloride and then with NaN_3 to obtain the corresponding tetraazide. Subsequent Curtius rearrangement and hydrolysis of the isocyanate **9** in acidic medium[18] gave tetraamine **10** in excellent yield.

Initially we tried the same pathway to synthesize tetraamine **12** starting from acid **7** since such a conversion of 1-adamantylacetic acid to 1-adamantylmethylamine is published.[19] However, we got a mixture of compounds from which the desired amine could not be separated. The same problem was faced starting from the acid derived from calix[6]arene **8**.[15] Probably, this failure is due to the lower stability of adamantylmethyl isocyanate in comparison with 1-adamantyl isocyanate, which leads to various inseparable side products in the case of calixarenes. The target tetraamine **12** was finally obtained from **6** in two steps involving the formation of tetraamide **11** followed by reduction. Unfortunately, we could not obtain the corresponding hexaamines because the calix[6]arenes modified at the wide rim with 3-carboxy-1-adamantanes are not available.

To synthesize tetraamine **17** and hexamine **18** with CH_2CH_2 linkers we used the Mitsunobu reaction as a key step. The treatment of the tetraacid **7** or the hexamethyl ester **8** with $LiAlH_4$ gave the corresponding alcohols **13** and **14**, which were transformed to derivatives **15** and **16** by the reaction with phthalimide in the presence of Ph_3P and diethylazodicarboxylate (DEAD) or diisopropylazodicarboxylate (DIAD). Cleavage of the phthalimide functions by hydrazine hydrate gave amines **17** and **18**. CMPO ligands **4** and **5** were obtained in high yield by acylation with the active ester **19**.[3a]

All the newly obtained compounds were characterized by their NMR and mass spectra. The ^1H NMR data confirm the *cone* conformation for the calix[4]arenes (one pair of doublets for the ArCH_2Ar protons), while the calix[6]arene derivatives are conformationally flexible in solution (one singlet for ArCH_2Ar).

2.2. Extraction of f-block elements

The liquid–liquid extraction of non-radioactive f-block elements was studied using the spectrophotometric determination of the metal ion concentration in the aqueous source phase before and after extractions as described earlier for ligands **2** and **3**.[3a,4] The extraction results for lanthanides (La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Yb^{3+}) and Th^{4+} (as a model for plutonium) by the novel ligands **4** and **5** from 1 M HNO_3 solutions into dichloromethane are summarized in Table 1. For comparison, data for **1** (R^1=Oct, R^2=*i*-Bu) and for the best known calixarene ligands **2** (Alk=C_5H_{11}) and **3** (*n*=3, 4) are also included.

All new CMPO-modified calixarenes **4** and **5** are thorium selective, similar to the narrow rim CMPO derivatives **3**.[4] Meaningful extraction values for this ion could be obtained only when the ligand concentration was lowered from 10^{-3} M (optimal for lanthanides) to 10^{-4} M. The hexamer **5** with an estimated $D_{Th}/D_{Ln}>24$ is most effective and selective for thorium, while the lanthanides are best extracted by tetramer **4b**. The co-operative effect of several CMPO groups attached to the calixarene platform may be characterized by the ratio between the distribution coefficients observed for a calixarene ligand and for **1** at equal concentration of ligating group [c(**1**)=4×c(**4**)=6×c(**5**)]. These ratios are greater than 1 for all new calixarenes and reach a maximum in the case of **4b** with D_{Eu}(**4b**)/D_{Eu}(**1**)>10. Apparently, without spacers (compound **4a**) the ligating CMPO functions are 'shielded' by the adamantane groups, while the ethylene spacers in **4c** are too long and lower the pre-organization of the CMPO groups. In the case of **4b**, the methylene spacers provide the best balance between flexibility and accessibility of the complexation site. There is no serious difference between the lanthanide extraction by tetrameric and hexameric ligands **4c** and **5**. Although **4** and **5** are formally wide rim CMPO calixarenes, they are superior to **2** in ytterbium extraction and the pronounced intra-series selectivity provided by **2**[4] is not observed for the CMPO-modified adamantylcalixarenes.

Table 1. Distribution coefficients [D=%E/(100−%E)] for the extraction of lanthanides and thorium by CMPO-substituted calixarenes[a] and **1** (R^1=Oct, R^2=*i*-Bu) from an aqueous phase (c_M=10^{-4} M, 1 M HNO_3) into dichloromethane at 20 °C

Ligand	La^{3+}	Pr^{3+}	Nd^{3+}	Eu^{3+}	Yb^{3+}	Th^{4+}
4a	0.28	0.25	0.23	0.25	0.49	
4b	0.72	1.50	1.70	1.17	0.43	1.22
4c	0.14	0.15	0.11	0.18	0.10	1.04
5	0.15	0.12	0.15	0.15	0.12	3.55
2[b]	49[c]			1.38	0.03	1.56
3 (*n*=3)[b]	0.15			0.14	<0.02	4.26
3 (*n*=4)[b]	2.33			2.12	0.59	24[c]
1, 4×10^{-3} M				0.11		0.18
1, 6×10^{-3} M				0.11		0.35

[a] For all calixarenes $c_L=10^{-3}$ M for Ln^{3+} extraction and $c_L=10^{-4}$ M for Th^{4+} extraction.
[b] Values from Ref. 4.
[c] Unreliable D value derived from a very high extraction close to 100%.

The differences in the extraction behavior of **4** and **2** may be explained by the different structures of the extracted complexes. By the UV-spectrophotometric titration of **4b** with La^{3+} ($0\le c_M/c_L\le4$) in methanol[20] we observed the presence of 1:2 (M:L) species with a stability constant $\log\beta_{1:2}=8.9\pm0.1$ (25 °C, I=0.01 M, NEt_4NO_3). This result correlates with the slope analysis given below, but is in contrast to the results for **2** where 1:1 and 2:1 (M:L) complexes with $\log\beta_{1:1}\sim6$ and $\log\beta_{2:1}\sim11$ were detected under similar conditions.[8a]

The extraction of active ^{152}Eu(III) and ^{241}Am(III) was also studied by γ-radiometry at different concentrations of **1**, **4**, and **5**; here the distribution coefficients were directly calculated from the activities of aqueous and organic phases after extraction. The results are represented in Figure 2. Under these conditions all the novel CMPO ligands extract these cations efficiently, surpassing **1** (R^1=Ph, R^2=Bu), and **4b** gives the highest extraction values. The distribution coefficients of americium D_{Am} were 0.27, 32, and 0.48 for **4a–c** (dichloromethane, $c_L=5\times10^{-3}$ M, 3 M HNO_3); the same tendency was observed for europium (D_{Eu}=0.19, 26, and 0.56). Again, the behavior of hexamer **5** is similar to tetramer **4c**. No notable selectivity toward americium was found for **5** as well as for **4**. The separation factors D_{Am}/D_{Eu} are in the range of 0.8–1.9 for all the adamantylcalixarene ligands,

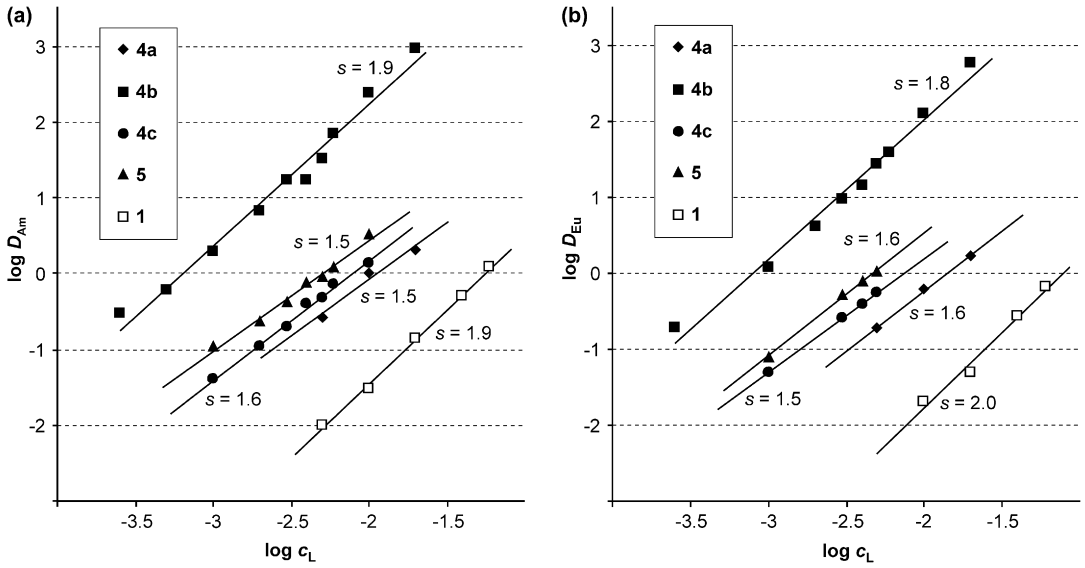


Figure 2. Plots of log D versus log c_L for the extraction of ^{241}Am (a) and ^{152}Eu (b) by **4**, **5**, and **1** (R^1=Ph, R^2=Bu) from an aqueous phase (3 M HNO_3, c_M=10^{-5} M $Eu(NO_3)_3$ spiked with ^{152}Eu or ^{241}Am at trace level to the activity of ~5 kBq/ml) into dichloromethane at 20 °C (s=slopes of the linear plots).

while for the known wide rim CMPO derivative **2** (Alk=C_5H_{11}) it reaches 4.9 in 3 M HNO_3 and even more under different conditions.[4] On the other hand, a low selectivity (D_{Am}/D_{Eu}=1.3) is known for narrow rim CMPO-substituted calix[4]arene **3** (n=4).[4] The behavior (high extraction efficiency but low selectivity, except for thorium) of ligands **4** and **5** in which CMPO residues are connected to the *wide* rim through adamantane units is similar to that for *narrow* rim CMPO ligands **3**.

Plots of log D versus log c_L are linear (Fig. 2) with slopes between 1.5 and 1.9. This shows that the extraction occurs in a complicated manner with the formation of at least ML and ML_2 complexes with close stabilities. Similar data available for the europium extraction show that wide rim CMPO calixarenes **2** form ML_2 complexes under extraction conditions (in the presence of an excess of ligand),[3a,11] while the narrow rim ligands **3** (n=3, 4) prefer ML species.[4]

We also checked the influence of the nitric acid concentration on extraction. The results are close to those observed for narrow rim CMPO calixarenes **3**;[4] an increase in the distribution coefficients was found at higher acidities. For instance, D_{Am} for **4b** (c_L=10^{-2} M) changed from 88 to 240 on increasing the acidity from 1 to 3 M HNO_3; D_{Am} values for **5** (c_L=10^{-3} M) are 0.02, 0.04, 0.08, and 0.11 for 0.5, 1, 2, and 3 M HNO_3 solutions, respectively.

The most efficient ligand (CMPO-like adamantylcalixarene **4b**) was tested in the extraction of ^{233}U(VI) and ^{239}Pu(IV) from acidic solutions (α-radiometry). As shown in Figure 3, the uranium extraction occurs with the highest efficiency in 5–6 M HNO_3 and the complex composition is as complicated as for Am and Eu extractions. The data for the plutonium extraction are too preliminary yet to be presented in a figure, but **4b** behaves as a good extractant also in this case with, for instance, D_{Pu}=5.2 and 20.2 for the extraction into dichloromethane and *m*-nitrotrifluoromethylbenzene, respectively (3 M HNO_3, c_L=10^{-3} M, traces of ^{239}Pu).

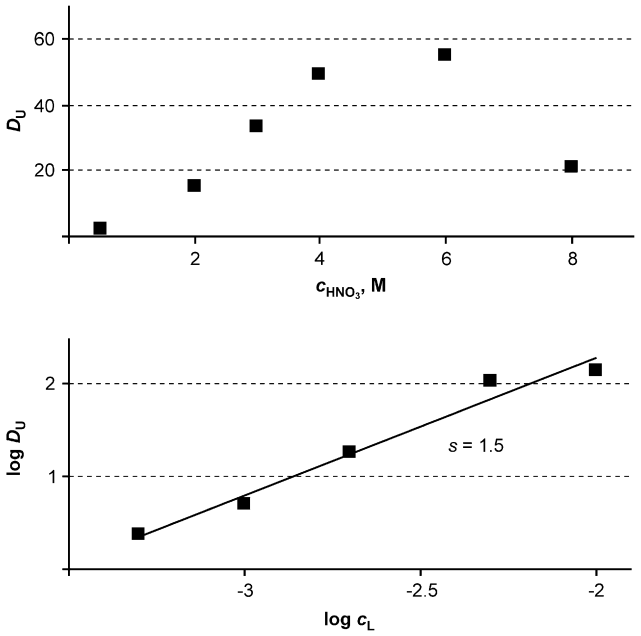


Figure 3. Extraction of ^{233}U (D) (c_M=10^{-5} M) by calixarene **4b** at different nitric acid concentrations (c_L=10^{-3} M) (top) and at different ligand concentrations (1 M HNO_3) (bottom) into dichloromethane at 20 °C (s=slope of the linear plot).

3. Conclusions

The wide rim CMPO-substituted adamantylcalixarenes **4** and **5** represent a new type of active extractants for lanthanides, thorium, and americium. In some senses, they combine features of wide rim CMPO ligands of type **2** with those of narrow rim ligands of type **3** and significantly surpass the industrial ligand **1**. Still we do not know much about the extraction details (complex composition, etc.), but two points are clear: for the extraction purposes the optimum spacers separating adamantylcalixarene platform and CMPO sites are methylene groups (compound **4b**), and the

transfer of ligating groups from the calix[4]- to the calix[6]-arene framework (at least to a flexible one) does not lead to any drastic changes of the complexation properties, except for thorium extraction, for which **5** seems to be very selective.

4. Experimental

4.1. Synthesis

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker Avance 400 spectrometer with solvent signals as internal reference (85% H_3PO_4 as external standard for ^{31}P NMR). Signals labeled with an asterisk (*) are close to one another and could not be attributed more definitely without additional experiments. ESI mass spectra were recorded on an Agilent 1100 LC/MS instrument. Melting points are uncorrected. Chemicals were of commercial grade and used without further purification. ^{152}Eu, ^{241}Am, ^{233}U, and ^{239}Pu nitrates were obtained from ISOTOPE company (St. Petersburg). Solvents were purified and dried according to standard procedures. *p*-(3-Carboxy-1-adamantyl)calix[4]arene tetrabutyl ether **6**,[14] *p*-(methoxycarbonylmethyl-1-adamantyl)calix[6]arene hexamethyl ether **8**,[15] and *p*-nitrophenyl(diphenyl)phosphorylacetate **19**[3a] were prepared according to the published procedures. Synthetic details (for the last step only) and full spectral data for CMPO derivatives **4a** and **4b** were published earlier.[13]

4.1.1. *p*-(3-Carboxymethyl-1-adamantyl)calix[4]arene tetrapropyl ether 7. 1-Iodopropane (3.9 ml, 40 mmol) and NaH (60%, 1.60 g, 40 mmol) were added under nitrogen to a stirred solution of *p*-(3-carboxymethyl-1-adamantyl)calix[4]arene[14] (1.19 g, 1 mmol) in DMF (20 ml). The reaction mixture was stirred at room temperature for 24 h and then quenched by the addition of 1 M HCl (40 ml). The products were extracted into dichloromethane (2×40 ml), washed with sodium thiosulphate solution (5%, 40 ml) and with water (2×40 ml). After evaporation, the remaining oil was dissolved in an ethanol solution of potassium hydroxide (0.25 M, 60 ml). The mixture was refluxed for 12 h, cooled, filtered, and the filtrate was concentrated to an oil. The precipitate formed upon addition of 1 M HCl was collected, washed with water, dried, and then re-crystallized from dichloromethane. Yield 0.91 g (67%), light yellow powder, mp 281–283 °C. δ_H (400 MHz, $CDCl_3$): 6.75 (8H, s, ArH), 4.42 (4H, d, *J* 12.5 Hz, $ArCH_2Ar$), 3.80 (8H, t, *J* 7.7 Hz, $OCH_2CH_2CH_3$), 3.14 (4H, d, *J* 12.5 Hz, $ArCH_2Ar$), 2.15 (8H, s, CH_2CO), 2.05 (8H, br s, CH_{Ad}), 1.90–1.20 (56H, m, $CH_{2,Ad}$+$OCH_2CH_2CH_3$), 0.99 (12H, t, *J* 7.5 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 178.31 (C═O), 153.70, 143.34, 133.83 (C_{Ar}), 124.25 (CH_{Ar}), 77.20 ($OCH_2CH_2CH_3$), 48.76 (C_{Ad}), 46.52 (CH_2CO), 43.03, 41.83, 36.08, 35.80, 33.64 (C_{Ad}), 30.88 ($ArCH_2Ar$), 29.20 (CH_{Ad}), 23.18 ($OCH_2CH_2CH_3$), 10.21 (CH_3). ESI-MS *m*/*z*=1379.0 $[M+H_2O]^+$. Anal. Calcd for $C_{88}H_{112}O_{12}$ (1361.8): C 77.61, H 8.29. Found: C 77.08, H 8.23.

4.1.2. Isocyanate 9. A solution of calixarene **6** (1.36 g, 1 mmol) in thionyl chloride (7 ml, 96 mmol) was stirred at reflux for 1.5 h. The excess of thionyl chloride was removed by co-evaporation with benzene (2×10 ml). The acid chloride was dissolved in acetone (30 ml), sodium azide (1.3 g, 20 mmol) in water (5 ml) was added, and the reaction mixture was stirred at room temperature for 2 h. Water (40 ml) was added, and the products were extracted with dichloromethane. The organic phase was washed with water, dried over $MgSO_4$, and evaporated. The crude azide was stirred in benzene (10 ml) at reflux for 1 h (*Caution: evolution of N_2*), and the solvent evaporated. Yield 1.29 g (96%), yellow solid. δ_H (400 MHz, $CDCl_3$): 6.76 (8H, s, ArH), 4.45 (4H, d, *J* 12.3 Hz, $ArCH_2Ar$), 3.84 (8H, t, *J* 7.7 Hz, $OCH_2CH_2CH_2CH_3$), 3.14 (4H, d, *J* 12.3 Hz, $ArCH_2Ar$), 2.22–1.56 (64H, m, H_{Ad}+$OCH_2CH_2CH_2CH_3$), 1.53 (8H, m, $OCH_2CH_2CH_2CH_3$), 1.03 (12H, t, *J* 7.2 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 154.11, 142.09, 134.18 (C_{Ar}), 124.24 (CH_{Ar}), 77.10 ($OCH_2CH_2CH_2CH_3$), 56.53, 50.53, 44.53, 42.00, 38.01, 34.97 (C_{Ad}), 33.51 ($OCH_2CH_2CH_2CH_3$), 30.96 ($ArCH_2Ar$), 30.13 (CH_{Ad}), 20.30 ($OCH_2CH_2CH_2CH_3$), 14.75 (CH_3).

4.1.3. Tetraamine tetrachlorohydrate salt 10. A solution of compound **9** (1.29 g, 0.96 mmol) in dioxane (15 ml) and 2 M HCl (20 ml) was refluxed for 12 h. The solid formed was separated, dried, and washed with diethyl ether. Yield 1.14 g (86%), white solid, mp 275–277 °C. δ_H (400 MHz, CD_3OD): 6.85 (8H, s, ArH), 4.45 (4H, d, *J* 12.3 Hz, $ArCH_2Ar$), 3.86 (8H, t, *J* 7.5 Hz, $OCH_2CH_2CH_2CH_3$), 3.18 (4H, d, *J* 12.3 Hz, $ArCH_2Ar$), 2.25–1.60 (64H, m, H_{Ad}+$OCH_2CH_2CH_2CH_3$), 1.53 (8H, m, $OCH_2CH_2CH_2CH_3$), 1.05 (12H, t, *J* 7.4 Hz, CH_3). δ_C (100 MHz, CD_3OD): 155.27, 142.78, 135.26 (C_{Ar}), 125.30 (CH_{Ar}), 76.12 ($OCH_2CH_2CH_2CH_3$), 53.94, 46.15, 42.84, 40.49, 38.56, 35.65 (C_{Ad}), 33.40 ($OCH_2CH_2CH_2CH_3$), 31.77 ($ArCH_2Ar$), 30.63 (CH_{Ad}), 20.35 ($OCH_2CH_2CH_2CH_3$), 14.62 (CH_3). ESI-MS *m*/*z*=1245.9 $[M]^+$ for $C_{84}H_{116}N_4O_4$ (1245.9).

4.1.4. Tetraamide 11. To a THF solution (30 ml) of the acid chloride obtained from **6** (2.04 g, 1.5 mmol) as described for **9** an aqueous solution of ammonia (25%, 8 ml) was added. The emulsion was stirred at room temperature for 1 h, concentrated in vacuo, and diluted with water (20 ml). The solid formed was filtered off, washed with water, dried, and re-crystallized from ethanol. Yield 1.47 g (72%), white solid, mp 237–239 °C. δ_H (400 MHz, $CDCl_3$): 6.77 (8H, s, ArH), 6.12 (8H, br s, NH_2), 4.43 (4H, d, *J* 12.3 Hz, $ArCH_2Ar$), 3.86 (8H, t, *J* 7.5 Hz, $OCH_2CH_2CH_2CH_3$), 3.13 (4H, d, *J* 12.3 Hz, $ArCH_2Ar$), 2.20–1.45 (64H, m, H_{Ad}+$OCH_2CH_2CH_2CH_3$), 1.40–1.30 (8H, m, $OCH_2CH_2CH_2CH_3$), 1.05 (12H, t, *J* 7.5 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 180.92 (C═O), 153.89, 142.98, 133.94 (C_{Ar}), 124.19 (CH_{Ar}), 75.09 ($OCH_2CH_2CH_2CH_3$), 44.44, 42.65, 41.53, 38.31, 35.80, 35.66 (C_{Ad}), 32.27 ($OCH_2CH_2CH_2CH_3$), 30.88 ($ArCH_2Ar$), 28.83 (CH_{Ad}), 19.25 ($OCH_2CH_2CH_2CH_3$), 14.02 (CH_3). ESI-MS *m*/*z*=1358.0 $[M]^+$. Anal. Calcd for $C_{88}H_{116}N_4O_8$ (1357.9): C 77.84, H 8.61, N 4.13. Found: C 77.71, H 8.63, N 4.11.

4.1.5. Tetraamine tetrachlorohydrate salt 12. A solution of **11** (0.54 g, 0.4 mmol) in anhydrous THF (20 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (0.55 g, 14.5 mmol) in THF (20 ml). The reaction mixture was stirred at 55 °C for 4 h, cooled to −5 °C, and quenched with care by the addition of water (0.5 ml), 3 M NaOH (0.5 ml), and water again (1.5 ml). The precipitate was

filtered off, washed with THF, and the filtrate evaporated in vacuo to dryness. The crude amine was dissolved in anhydrous THF (7 ml) and converted to the tetrachlorohydrate by bubbling gaseous HCl. The solid was separated, washed with diethyl ether, and dried. Yield 0.35 g (60%), light gray solid, mp 272–274 °C. For free amine: δ_H (400 MHz, $CDCl_3$): 6.82 (8H, s, ArH), 4.45 (4H, d, *J* 12.4 Hz, $ArCH_2Ar$), 3.88 (8H, t, *J* 7.8 Hz, $OCH_2CH_2CH_2CH_3$), 3.16 (4H, d, *J* 12.4 Hz, $ArCH_2Ar$), 2.39 (8H, br s, CH_2NH_2), 2.20–1.40 (72H, m, H_{Ad}+$OCH_2CH_2CH_2CH_3$+ $OCH_2CH_2CH_2CH_3$), 1.06 (12H, t, *J* 7.3 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 153.60, 143.53, 133.80 (C_{Ar}), 124.15 (CH_{Ar}), 75.06 ($OCH_2CH_2CH_2CH_3$), 54.76 (CH_2NH_2), 45.81, 43.01, 38.96, 36.23, 35.82, 34.71 (C_{Ad}), 32.23 ($OCH_2CH_2CH_2CH_3$), 30.67 ($ArCH_2Ar$), 28.95 (CH_{Ad}), 19.19 ($OCH_2CH_2CH_2CH_3$), 14.02 (CH_3). ESI-MS *m*/*z*= 1302.9 $[M+H]^+$ for $C_{88}H_{124}N_4O_4 \cdot H$ (1303.0).

4.1.6. Tetraalcohol 13. It was obtained from acid **7** (0.54 g, 0.4 mmol) by reduction with $LiAlH_4$ (0.4 g, 10.6 mmol) in THF (30 ml) as described for **12**. The product collected after evaporation of the solvent was pure enough for further reactions. Yield 0.49 g (96%), white solid, mp 227–228 °C. δ_H (400 MHz, $CDCl_3$): 6.75 (8H, s, ArH), 4.41 (4H, d, *J* 12.1 Hz, $ArCH_2Ar$), 3.80 (8H, t, *J* 7.7 Hz, $OCH_2CH_2CH_3$)*, 3.69 (8H, t, *J* 7.6 Hz, CH_2OH)*, 3.11 (4H, d, *J* 12.1 Hz, $ArCH_2Ar$), 2.34 (4H, br s, OH), 2.05–1.95 (16H, m, CH_{Ad}+ $OCH_2CH_2CH_3$), 1.65–1.35 (56H, m, $CH_{2,Ad}$+CH_2CH_2OH), 0.99 (12H, t, *J* 7.5 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 153.74, 143.75, 133.87 (C_{Ar}), 124.28 (C H_{Ar}), 76.96 ($OCH_2CH_2CH_3$), 58.44 (CH_2OH), 48.64 (C_{Ad}), 47.12 (CH_2CH_2OH), 43.22, 41.62, 36.24, 36.14, 32.77 (C_{Ad}), 30.99 ($ArCH_2Ar$), 29.33 (CH_{Ad}), 23.25 ($OCH_2CH_2CH_3$), 10.27 (CH_3). ESI-MS *m*/*z*=1329.1 $[M+Na]^+$. Anal. Calcd for $C_{88}H_{120}O_8$ (1305.9): C 80.94, H 9.26. Found: C 80.68, H 9.30.

4.1.7. Hexaalcohol 14. It was obtained from ester **8** (0.20 g, 0.1 mmol) by reduction with $LiAlH_4$ (0.10 g, 2.63 mmol) in THF (15 ml) as described for **13**. The crude product was washed with methanol and dried. Yield 0.15 g (84%), white solid, mp 193–195 °C (decomp.). δ_H (400 MHz, DMSO-d_6): 6.98 (12H, br s, ArH), 4.27 (6H, br s, OH), 3.84 (12H, br s, $ArCH_2Ar$), 3.48 (12H, br s, CH_2OH), 2.83 (18H, br s, OCH_3), 2.02 (12H, br s, CH_{Ad}), 1.70–1.40 (72H, m, $CH_{2,Ad}$), 1.29 (12H, br s, CH_2CH_2OH). δ_C (100 MHz, DMSO-d_6): 153.53, 144.95, 132.90 (C_{Ar}), 125.30 (CH_{Ar}), 59.36 (OCH_3), 56.33 (CH_2OH), 48.54 (C_{Ad}), 46.73 (CH_2CH_2OH), 42.52, 40.13, 35.80, 35.75, 32.37 (C_{Ad}), 28.83 (CH_{Ad}). ESI-MS *m*/*z*=1813.0 $[M+Na]^+$. Anal. Calcd for $C_{120}H_{156}O_{12}$ (1790.5): C 80.50, H 8.78. Found: C 79.83, H 8.71.

4.1.8. Tetraphthalimide 15. Diethylazodicarboxylate (DEAD) (40% solution in toluene, 1.55 ml, 3.4 mmol) was added dropwise with stirring under argon to a cooled (0 °C) solution of Ph_3P (0.89 g, 3.4 mmol) in anhydrous THF (10 ml). After 30 min, phthalimide (0.51 g, 3.4 mmol) was added, and stirring was continued for additional 30 min. A solution of alcohol **13** (0.45 g, 0.34 mmol) in THF (20 ml) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h and then kept overnight at room temperature. The solvent was evaporated in vacuo, and the resultant solid was treated with ethanol (10 ml). The precipitate formed was collected, washed with ethanol and dried. Yield 0.48 g (78%), pale yellow powder, mp 152–154 °C. δ_H (400 MHz, $CDCl_3$): 7.79 (8H, m, ArH_{Pht}), 7.66 (8H, m, ArH_{Pht}), 6.77 (8H, s, ArH), 4.40 (4H, d, *J* 12.1 Hz, $ArCH_2Ar$), 3.80 (8H, t, *J* 7.6 Hz, $OCH_2CH_2CH_3$), 3.66 (8H, m, CH_2N), 3.12 (4H, d, *J* 12.1 Hz, $ArCH_2Ar$), 2.06–1.98 (16H, m, CH_{Ad}+$OCH_2CH_2CH_3$), 1.60–1.35 (56H, m $CH_{2,Ad}$+ CH_2CH_2N), 1.00 (12H, t, *J* 7.5 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 168.07 (C=O), 153.69, 143.61, 133.89 (C_{Ar}), 133.64 ($CH_{Ar,Pht}$), 132.30 ($C_{Ar,Pht}$), 124.34 (CH_{Ar}), 122.96 ($CH_{Ar,Pht}$), 76.97 ($OCH_2CH_2CH_3$), 48.41, 42.83 (C_{Ad}), 42.16 (CH_2N), 40.90, 36.09, 36.07, 33.15 (C_{Ad}), 32.83 (CH_2CH_2N), 30.83 ($ArCH_2Ar$), 29.21 (CH_{Ad}), 23.26 ($OCH_2CH_2CH_3$), 10.28 (CH_3). ESI-MS *m*/*z*=1845.1 $[M+Na]^+$. Anal. Calcd for $C_{120}H_{132}N_4O_{12}$ (1822.4): C 79.09, H 7.30, N 3.07. Found: C 78.56, H 7.29, N 3.04.

4.1.9. Hexaphthalimide 16. It was obtained from calixarene **14** (1.02 g, 0.57 mmol), Ph_3P (1.79 g, 6.84 mmol), phthalimide (1.01 g, 6.84 mmol), and diisopropylazodicarboxylate (DIAD) (1.35 ml, 6.84 mmol) in THF (100 ml) as described for **15**. The crude product after evaporation of the solvent was washed with methanol, dried, and purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol, 20:1). Yield 1.32 g (90%), pale yellow powder, mp 193–195 °C. δ_H (400 MHz, $CDCl_3$): 7.79 (12H, m, ArH_{Pht}), 7.66 (12H, m, ArH_{Pht}), 6.98 (12H, s, ArH), 3.90 (12H, s, $ArCH_2Ar$), 3.66 (12H, m, CH_2N), 2.98 (18H, s, OCH_3), 2.05 (12H, s, CH_{Ad}), 1.75–1.40 (84H, m, CH_2CH_2N+$CH_{2,Ad}$). δ_C (100 MHz, $CDCl_3$): 168.02 (C=O), 154.23, 144.99 (C_{Ar}), 133.61 ($CH_{Ar,Pht}$), 133.50 (C_{Ar}), 132.19 ($C_{Ar,Pht}$), 125.49 (CH_{Ar}), 122.93 ($CH_{Ar,Pht}$), 59.86 (OCH_3), 48.12, 42.72, 42.00 (C_{Ad}), 40.83 (CH_2N), 36.31, 35.97 (C_{Ad}), 33.08 (CH_2CH_2N), 32.83 (C_{Ad}), 31.18 ($ArCH_2Ar$), 29.09 (CH_{Ad}). ESI-MS *m*/*z*=2583.0 $[M+NH_4]^+$. Anal. Calcd for $C_{168}H_{174}N_6O_{18}$ (2565.2): C 78.66, H 6.84, N 3.28. Found: C 78.14, H 6.86, N 3.24.

4.1.10. Tetraamine 17. A mixture of calixarene **15** (0.48 g, 0.26 mmol), hydrazine hydrate (0.5 ml, 10 mmol), ethanol (20 ml), and THF (20 ml) was stirred at reflux for 8 h. After cooling the reaction mixture was concentrated in vacuo and diluted with water (20 ml). The product was extracted with chloroform (75 ml), washed with water, and the solvent evaporated. Yield 0.33 g (98%), white solid, mp 268–270 °C (decomp.). δ_H (400 MHz, $CDCl_3$): 6.75 (8H, s, ArH), 4.40 (4H, d, *J* 12.1 Hz, $ArCH_2Ar$), 3.79 (8H, t, *J* 7.6 Hz, $OCH_2CH_2CH_3$), 3.10 (4H, d, *J* 12.1 Hz, $ArCH_2Ar$), 2.70 (8H, m, CH_2N), 2.12–1.92 (16H, m, CH_{Ad}+$OCH_2CH_2CH_3$), 1.65–1.25 (56H, m, $CH_{2,Ad}$+CH_2CH_2N), 0.98 (12H, t, *J* 7.4 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 153.71, 143.83, 133.91 (C_{Ar}), 124.34 (CH_{Ar}), 77.01 ($OCH_2CH_2CH_3$), 48.83 (C_{Ad})*, 48.46 (CH_2N)*, 43.14, 41.75, 36.62*, 36.35* (C_{Ad}), 36.16 (CH_2CH_2N)*, 33.00 (C_{Ad}), 30.92 ($ArCH_2Ar$), 29.42 (CH_{Ad}), 23.30 ($OCH_2CH_2CH_3$), 10.30 (CH_3). ESI-MS *m*/*z*= 1303.0 $[M+H]^+$ for $C_{88}H_{124}N_4O_4 \cdot H$ (1303.0).

4.1.11. Hexaamine 18. It was obtained from calixarene **16** (1.32 g, 0.52 mmol) and hydrazine hydrate (3.03 ml, 62.4 mmol) in ethanol (20 ml) and THF (20 ml) as described for **17**. The solid formed after diluting with water was separated, washed with water, and dried. Yield 0.78 g (85%), white solid, mp 138–140 °C. δ_H (400 MHz, $CDCl_3$): 6.97

(12H, s, ArH), 3.90 (12H, br s, $ArCH_2Ar$), 2.93 (18H, s, OCH_3), 2.69 (12H, br s, CH_2N), 2.10–1.15 (96H, m, H_{Ad}+CH_2CH_2N). δ_C (100 MHz, $CDCl_3$): 154.16, 145.23, 133.45 (C_{Ar}), 125.48 (CH_{Ar}), 59.85 (OCH_3), 48.72 (CH_2N), 48.29, 42.76, 41.58 (C_{Ad}), 36.38 (CH_2CH_2N)*, 36.34*, 36.11, 32.93 (C_{Ad}), 31.19 ($ArCH_2Ar$), 29.22 (CH_{Ad}). ESI-MS m/z=1823.4 $[M+K]^+$ for $C_{120}H_{162}KN_6O_6$ (1823.7).

4.1.12. CMPO ligand 4c. A solution of amine **17** (0.28 g, 0.22 mmol), active ester **19** (0.46 g, 1.2 mmol), and triethylamine (0.30 ml, 2.1 mmol) in toluene (20 ml) was stirred at 65 °C for 7 h. The solvent was evaporated, and the remaining oil was taken up in chloroform. The solution was washed repeatedly with 5% Na_2CO_3 and subsequently with water, dried over $MgSO_4$, and the solvent was evaporated. The product was purified by re-precipitation from chloroform/hexane. Yield 0.40 g (84%), light gray powder, mp 155–157 °C (decomp.). δ_H (400 MHz, $CDCl_3$): 7.74 (16H, m, ArH_{Ph}), 7.60–7.40 (28H, m, ArH_{Ph}+NH), 6.72 (8H, s, ArH), 4.39 (4H, d, J 12.4 Hz, $ArCH_2Ar$), 3.78 (8H, t, J 7.3 Hz, $OCH_2CH_2CH_3$), 3.35 (8H, d, J 13.1 Hz, CH_2P), 3.18 (8H, m, CH_2N), 3.11 (4H, d, J 12.4 Hz, $ArCH_2Ar$), 2.15–1.95 (16H, m, CH_{Ad}+$OCH_2CH_2CH_3$), 1.60–1.35 (56H, m, $CH_{2,Ad}$+CH_2CH_2N), 0.98 (12H, t, J 7.3 Hz, CH_3). δ_C (100 MHz, $CDCl_3$): 164.38 (d, J 5.1 Hz, C=O), 153.60, 143.61, 133.81 (C_{Ar}), 132.17 (br s, CH_{Ph}), 130.77 (d, J 101.8 Hz, C_{Ph}), 130.76 (d, J 10.2 Hz, CH_{Ph}), 128.68 (d, J 11.6 Hz, CH_{Ph}), 124.29 (CH_{Ar}), 75.12 ($OCH_2CH_2CH_3$), 47.83 (C_{Ad}), 43.25 (CH_2N), 43.03, 41.30 (C_{Ad}), 38.78 (d, J 60.4 Hz, CH_2P), 36.15, 36.02 (C_{Ad}), 34.97 (CH_2CH_2N), 32.71 (C_{Ad}), 30.78 ($ArCH_2Ar$), 29.19 (CH_{Ad}), 23.22 ($OCH_2CH_2CH_3$), 10.23 (CH_3). δ_P (162 MHz, $CDCl_3$) 29.57 (P=O). ESI-MS m/z=2272.4 $[M+H]^+$. Anal. Calcd for $C_{144}H_{168}N_4O_{12}P_4$ (2270.8): C 76.16, H 7.46, N 2.47. Found: C 76.35, H 7.68, N 2.41.

4.1.13. CMPO ligand 5. It was obtained from calixarene **18** (0.53 g, 0.3 mmol), active ester **19** (0.86 g, 2.25 mmol), and triethylamine (0.50 ml, 3.6 mmol) in toluene (25 ml) at 50 °C for 8 h as described for **4c**. Yield 0.71 g (74%), light gray powder, mp 172–174 °C. δ_H (400 MHz, $CDCl_3$): 7.71 (24H, m, ArH_{Ph}), 7.55–7.35 (36H, m, ArH_{Ph}), 6.92 (8H, s, ArH), 3.88 (12H, br s, $ArCH_2Ar$), 3.35 (12H, d, J 12.9 Hz, CH_2P), 3.17 (12H, br s, CH_2N), 2.94 (18H, br s, OCH_3), 2.10–1.10 (96H, m, H_{Ad}+CH_2CH_2N). δ_C (100 MHz, $CDCl_3$): 164.30 (d, J 3.8 Hz, C=O), 154.18, 145.05, 133.51 (C_{Ar}), 133.50 (br s, CH_{Ph}), 131.74 (d, J 102.5 Hz, C_{Ph}), 130.75 (d, J 9.5 Hz, CH_{Ph}), 128.70 (d, J 12.4 Hz, CH_{Ph}), 125.46 (CH_{Ar}), 59.86 (OCH_3), 48.28 (C_{Ad}), 43.07 (CH_2N), 42.57, 41.30 (C_{Ad}), 38.82 (d, J 60.0 Hz, CH_2P), 36.27, 36.03, 34.92 (C_{Ad}), 32.75 (CH_2CH_2N), 31.16 ($ArCH_2Ar$), 29.10 (C_{Ad}). δ_P (162 MHz, $CDCl_3$) 29.71 (P=O). ESI-MS m/z=3238.4 $[M+H]^+$. Anal. Calcd for $C_{204}H_{228}N_6O_{18}P_6$ (3237.9): C 75.67, H 7.10, N 2.60. Found: C 75.69, H 7.24, N 2.55.

4.2. Extraction studies

4.2.1. Extraction of non-active lanthanides and thorium into dichloromethane. The aqueous phase consisted of a solution of lanthanide(III) or thorium(IV) nitrate and HNO_3 in bidistilled water; the organic phase was a solution of the ligand in dichloromethane, at a concentration, suited for an extraction percentage ranging between 10 and 90%. A 1 ml aliquot of each phase was stirred in a stoppered tube immersed in a thermostated bath at 20 °C for 12 h. After separation of the two phases, the concentration of the cation remaining in the aqueous phase was monitored spectrophotometrically using arsenazo(III) (3,6-bis(*o*-arsonophenyl)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid) as reagent. The arsenazo solution (5 ml, c=6.4×10^{-4} M) was added to a 0.65 ml aliquot of the aqueous phase. The volume of this sample was then adjusted to 50 ml with a sodium formiate/formic acid buffer (pH 2.8) for the determination of lanthanides and with HNO_3 (4 M) for the determination of thorium. The absorbances (A) were measured at 665 nm for thorium and at 655 nm for lanthanides. Since the concentration of arsenazo is at least 30 times higher than the concentration of the cation, complete complexation of the cation can be assumed. The extraction percentages were derived as $\%E=100\times[A^1-A/(A^1-A^0)]$, where A^0 is the absorbance of the arsenazo solution without cation and A^1 the absorbance of the arsenazo solution containing a known concentration of the cation before extraction.

4.2.2. Extraction of ^{152}Eu and ^{241}Am into dichloromethane. The aqueous phase consisted of a solution of europium(III) nitrate (c_{Eu}=10^{-5} M) spiked with ^{152}Eu or ^{241}Am (activity of ~5 kBq/ml in both cases) and HNO_3 in bidistilled water; the organic phase was a solution of the ligand in dichloromethane. A 1 ml aliquot of each phase was mechanically shaken in a stoppered flask immersed in a thermostated bath at 20 °C for 1 h (the extraction equilibrium was usually achieved in few minutes). The liquid phases were separated by centrifugation. The activities of both phases (0.4 ml) were determined by radiometry using a scintillation γ-spectrometer. Distribution coefficients were derived as activity of the organic phase divided by the activity of aqueous phase after extraction.

4.2.3. Extraction of ^{233}U and ^{239}Pu into dichloromethane or NTFB. The aqueous phase for the uranium extraction consisted of a solution of ^{233}U(VI) nitrate (containing an admixture of ^{238}U) at the activity of ~5 kBq/ml corresponding to an overall uranium concentration of ca. 10^{-5} M and HNO_3 in bidistilled water. In case of plutonium extraction, the aqueous phase consisted of HNO_3 in bidistilled water spiked with ^{239}Pu to the activity of ~5 kBq/ml. The organic phase was a solution of the ligand in dichloromethane or NTFB. The extraction experiments were performed as described above for Eu and Am extractions using an α-spectrometer for the determination of the activities.

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