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# Dendritic octa-CMPO derivatives of calix[4]arenes

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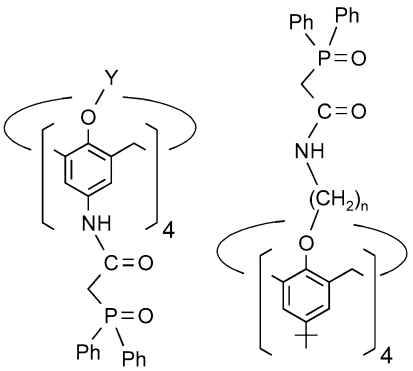
**Abstract**—Calix[4]arenes substituted at the narrow or wide rim by eight carbamoylmethyl-phosphine oxide (=CMPO) functions in a dendritic manner were synthesised and studied in extraction of $Eu^{3+}$ and $Am^{3+}$ from aqueous nitric acid into *o*-nitrophenylhexyl ether. $^1H$ NMR relaxivity titrations for a wide rim octa-CMPO reveal the clear formation of a solvent-free 1:2 ligand/metal complex, while the wide rim tetra-CMPO formed oligomeric complexes under similar conditions.


## 1. Introduction

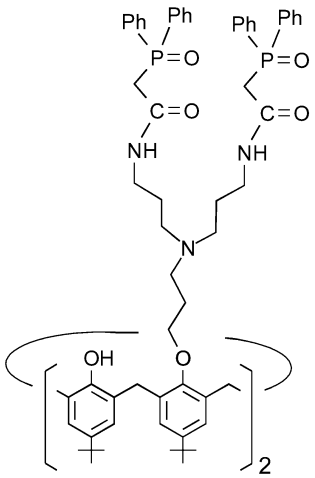
Calix[4]arenes bearing at their wide[1] or at their narrow rim[2] four CMPO functions (general formulas **1** and **2**) are much better extractants for lanthanides and actinides than *N*,*N*-diisobutyl carbamoylmethyl-(octyl)phenyl phosphine oxide, the extractant technically used in the so-called TRUEX process.[3] Distribution coefficients higher by several orders of magnitude (depending on the conditions and on the cation[4] to be extracted) are convincing evidence that it is advantageous to preorganise several CMPO-functions by covalent attachment to a basic platform.[5]




**1** **2**

## 2. Syntheses

Since it could well be that merely a high local concentration of CMPO-functions is responsible for the beneficial extraction properties of **1** and **2**, we decided to increase the number of CMPO functions attached to the calix[4]arene skeleton, using structural principles well-known from dendrimers.[6] Compounds **6a**,**b** with eight CMPO groups at the narrow rim were prepared from the known aminoalkoxy calix[4]arenes **3** by Michael addition of acrylonitrile, followed by reduction and acylation with the active *p*-nitrophenyl ester **7** (Scheme 1). The tetra-CMPO derivative **8** in which the two remaining phenolic hydroxyl groups could be used in principle for the attachment of additional




**8**

*Keywords*: Calix[4]arenes; Dendrimers; CMPO; Extraction; NMR relaxation.
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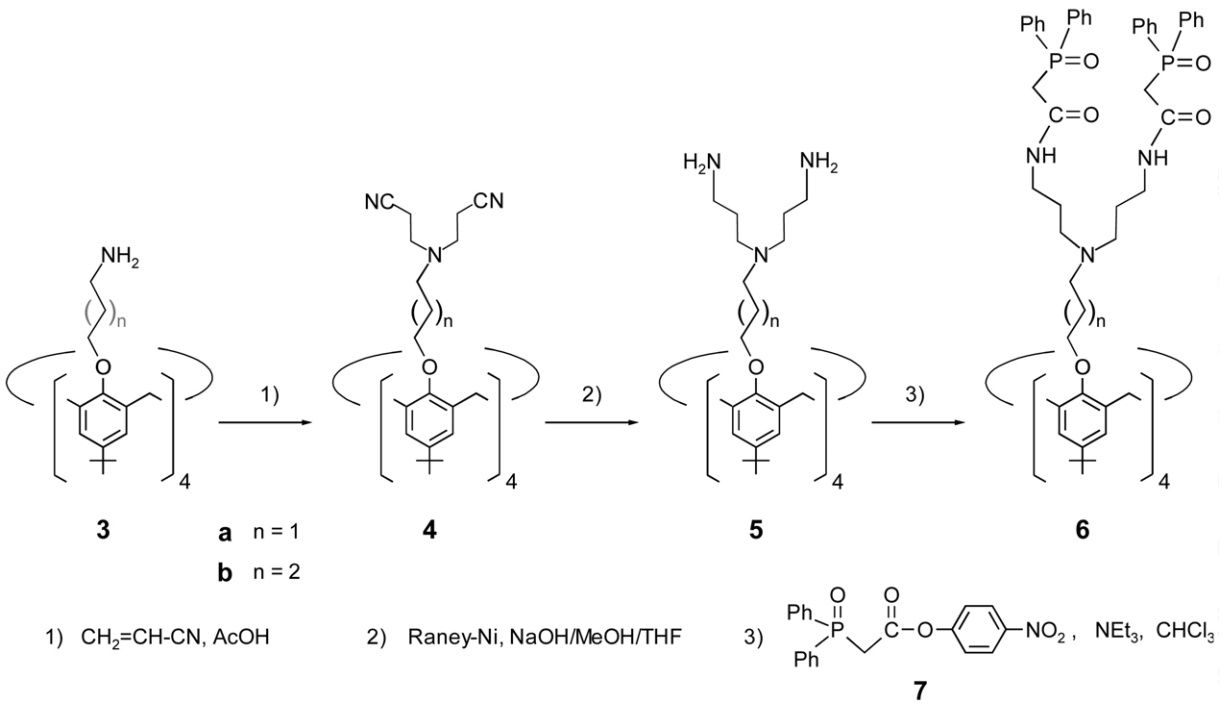



**Scheme 1.**

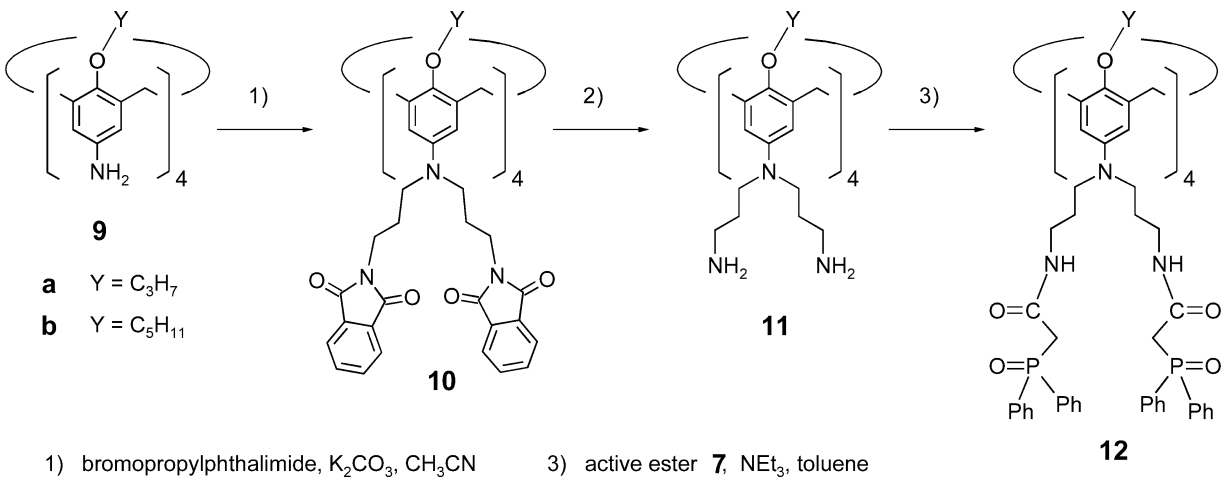
functional groups was prepared analogously starting with the respective 1,3-diamine.

Addition of acrylonitrile was not successful with wide rim tetraamine **9** due to the lower nucleophilicity of the amino groups. Mixtures of compounds containing less than one nitrile residue per amino group were formed. However, an exhaustive alkylation with bromopropylphthalimide led to the tertiary amine **10**. Cleavage of the phthalimide groups by hydrazine and subsequent acylation with **7** furnished the octa-CMPO derivative **12**; see Scheme 2.

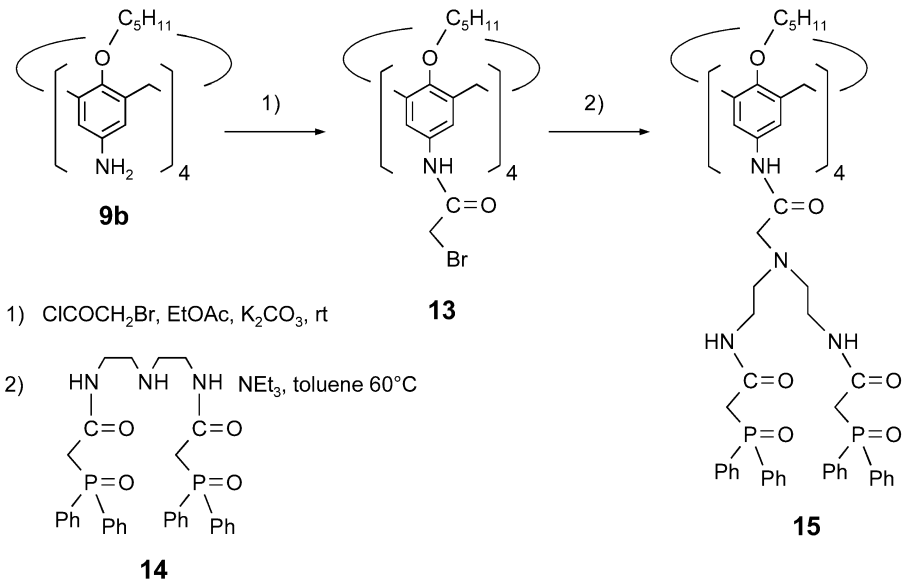
Yet another strategy was used for the synthesis of **15** (Scheme 3): wide rim tetra-amine **9** was acylated with bromoacetyl chloride to prepare **13** that was subsequently reacted with the di-CMPO-derivative **14**. The latter was obtained by mild acylation of diethylene triamine with the active ester **7**.

## 3. Liquid–liquid extraction and complexation studies

The separation of trivalent actinides from lanthanides remains a challenging problem because of the close similarity of these ions. This is especially true if $Am^{3+}$ has to be separated from $Eu^{3+}$ by extraction from strongly acidic media as it is required in the reprocessing of nuclear fuels.[3] Calixarenes **1** and **2** proved to be efficient extracting agents and the extraction properties of their dendritic analogues **6**, **8** and **12** were analyzed under the conditions




**Scheme 2.**




**Scheme 3.**

used previously (concentrated nitric acid as aqueous phase, *o*-nitrophenylhexylether, NPHE, as organic solvent). In addition, nuclear magnetic relaxation studies were performed on **12b**, the dendritic analogue of **1** which is the most promising calixarene extracting agent found so far.[1,2] As reported earlier,[7] NMR relaxation studies require only very small amounts of material and yield information that are not easily obtained by other methods.

As shown by the values collected in Table 1, the extraction efficiency of the dendritic CMPO calixarenes is distinctly lower in comparison with **1** and **2**. This phenomenon is observed whether the CMPO units are located on the wide or on the narrow rim of the calixarene units. In addition, the $Am^{3+}/Eu^{3+}$ separation coefficients are lower and complications arise due to precipitation and to the formation of a third liquid phase during the extractions. The solubility problem could probably be alleviated by the introduction of more lipophilic residues (e.g. the ether group Y in **12**). However, the extraction results suggest that the simple accumulation of CMPO functions is not an appropriate way of improving the extraction properties.

**Table 1**. Distribution coefficients $D$ for the extraction of $Eu^{3+}$ and $Am^{3+}$ for various calix[4]arenes bearing CMPO units ([L]=$10^{-3}$ M in NPHE) as a function of the nitric acid concentration in the aqueous phase

| Ligand | | [$HNO_3$] (M) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.01 | 0.1 | 1 | 2 | 3 | 4 |
| **1**[a] (Y=$C_5H_{11}$) | $D_{Am}$ | | 19 | 195 | 275 | 150 | 100 |
| | $D_{Eu}$ | | 2.3 | 30 | 52 | 37 | 19 |
| **12b** | $D_{Am}$ | 0.001 | 0.12 | [b] | [b] | [b] | [b] |
| | $D_{Eu}$ | 0.001 | 0.07 | [b] | [b] | [b] | [b] |
| **2**[c] (n=4) | $D_{Am}$ | | 48 | 51 | 61 | 63 | |
| | $D_{Eu}$ | | 28 | 33 | 44 | 48 | |
| **6b**[d] | $D_{Am}$ | 0.05 | 0.14 | 2.1 | 4.8 | 7.5 | 8.4 |
| | $D_{Eu}$ | 0.02 | 0.11 | 0.7 | 1.9 | 2.4 | 2.8 |
| **8** | $D_{Am}$ | $11\times10^{-3}$ | 0.02 | 0.57 | 1.45 | 0.88 | |
| | $D_{Eu}$ | $6\times10^{-3}$ | $7\times10^{-3}$ | 0.22 | 0.59 | 0.38 | |

[a] Compare Ref. 7b.
[b] Precipitation.
[c] Compare Ref. 2.
[d] Partly third phase formation.

NMR relaxation studies shed some light on the origin of the striking differences between the extraction properties of the simple and the dendritic CMPO calixarenes. This technique takes advantage of the relaxation properties of the $Gd^{3+}$ ion to establish the stoichiometry of lanthanide complexes as well as their solvation and dynamic behaviour. It has already been showed that calix[4]arenes substituted on the narrow rim such as **2** exclusively form monomeric 1:1 $Gd^{3+}$ perchlorate complexes in anhydrous acetonitrile while their analogues substituted on the wide rim such as **1** occur as oligomeric species in a large range of [ligand]/[$Gd^{3+}$] concentration ratios.[7] As shown in Figure 1(a), the progressive complexation of the metal ions by **2** brings about the removal of solvent molecules from the paramagnetic centres and thus a decrease of $1/T_1$ as the relaxation of solvent protons takes place in the bulk of the solution rather than close to the unpaired electronic spins. A relaxivity plateau is reached for a ~1 [ligand]/[metal] ratio when the $Gd^{3+}$ complex is fully formed. By contrast, aggregation phenomena at low [ligand **1**]/[$Gd^{3+}$] ratios cause an increase in relaxation rates because of the decreased rotational mobility of the oligomeric species[7,8] and a range of complexes of different stoichiometries are formed in solution. Contrary to all expectations, ligand **12b** forms a monomeric $Gd^{3+}$ complex of well-defined 2:1 metal/ligand stoichiometry even though this calixarene is substituted by CMPO groups on the wide rim.

The differences between calix[4]arenes **1**, **2** and **12b** are also shown in Figure 1(b) that shows the dispersion of the nuclear magnetic relaxation with the resonance frequency. A relaxivity maximum is observed at 40 MHz for the complex with ligand **1** because it forms oligomers.[7] By contrast, the relaxivity of the $(Gd^{3+})_2$·**12b** complex is much lower than that of uncomplexed $Gd^{3+}$ and of the complex

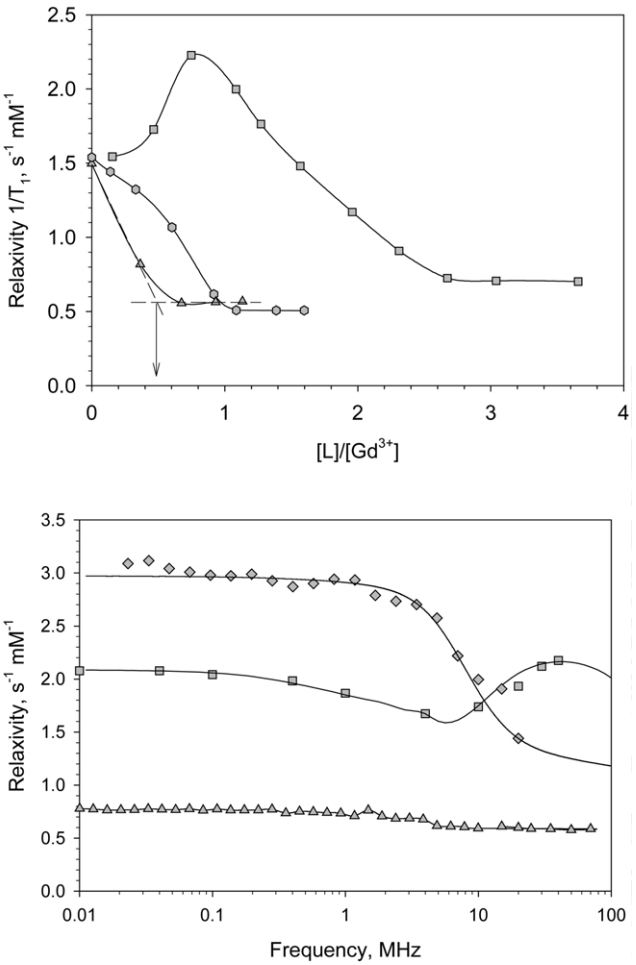



**Figure 1.** (a) (Top) Relaxivity titration curves of $Gd^{3+}$ by calix[4]arenes **1** (■), **2** (●) and **12b** (▲) in anhydrous acetonitrile. (b) (Bottom) Nuclear magnetic relaxation dispersion curves of anhydrous acetonitrile solutions of uncomplexed $Gd^{3+}$ (◆), $Gd^{3+}$·**1** (■, concentration ratio [**1**]/[$Gd^{3+}$]=1) and $Gd^{3+}$·**12b** (▲, concentration ratio [**12b**]/[$Gd^{3+}$]=1.3).

with **1** at all frequencies. This low relaxivity is ascribed to essentially outer-sphere effects due to solvent molecules in the second co-ordination sphere of the metal complexes (note: the relaxation rate of pure acetonitrile[9] is $6.2\times10^{-2}$ $s^{-1}$). It thus seems that **12b** forms exclusively a monomeric 2:1 metal/ligand complex in which the two $Gd^{3+}$ ions are totally encapsulated by the CMPO and amino coordinating groups and are essentially unsolvated. The extraction of trivalent lanthanides and actinides would thus proceed as

$$2\mathrm{Me}(\mathrm{H_2O})n^{3+} + 6\mathrm{NO_3^{3-}} + \overline{\mathbf{12b}} \rightarrow \overline{\mathrm{Me_2}(\mathbf{12b})(\mathrm{NO_3})_6} + n\mathrm{H_2O}$$

where $n$=8 or 9[8] and where a bar over a symbol designates the organic phase species.

The dendritic calixarenes appear to be a class of ligands in their own right because of the unusual stoichiometry of their complexes and because of their monomeric behaviour in solution. Their poor extraction efficacy could be related to these unusual features. However, the correct preorganisation needed to achieve high extraction coefficients and a high selectivity is not yet understood in details and remains a crucial factor to be controlled.

## 4. Experimental

### 4.1. Reagents and methods

Tetraamino calix[4]arenes **3**,[2] **9**,[10] **13**,[7b] and *p*-nitrophenyl (diphenyl-phosphoryl)-acetate **7**[10] were prepared according to known procedures. Melting points, determined with a MEL TEMP 2 capillary melting point apparatus, are uncorrected. $^1$H NMR spectra were monitored on Bruker 200 and 400 MHz spectrometers. FD and ESI mass spectra were recorded in a positive mode with a Finnigan MAT 90 (5 kV/10 mA/min) and a QTof ULTIMA3 (Micromass), respectively.

NMRD measurements were conducted as reported previously[7] at 20 MHz on a Minispec 120 (Bruker Optics) and between 0.01 and 80 MHz on a Stelar relaxometer equipped with a 1.88 T electromagnet. Samples of $Gd^{3+}$ complexes were prepared as reported earlier.[7]

### 4.2. Narrow Rim CMPO-derivatives

**4.2.1. Octanitrile 4a.** A solution of tetraamine **3a** (1.2 g) and acetic acid (328 mg) in acrylonitrile (25 ml) was refluxed for 2.5 days. The excess of acrylonitrile was removed by distillation under vacuum and the residue was dissolved in chloroform. After filtration the solution was washed three times with conc. ammonia, then water, dried over $MgSO_4$ and evaporated. The oily residue was purified by column chromatography (chloroform/methanol 20/1). Colourless oil, yield 87%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.79 (s, 8H, Ar*H*), 4.41 (d, $J$=12.3 Hz, 4H, ArC$H_2$Ar), 4.07 (t, $J$=7.1 Hz, 8H, OC$H_2$), 3.21 (d, $J$=12.5 Hz, 4H, ArC$H_2$Ar), 2.86 (t, $J$=6.5 Hz, 16H, CNC$H_2$), 2.65 (t, $J$=7.5 Hz, 8H, NC$H_2$), 2.40 (t, $J$=6.8 Hz, 16H, NC$H_2$), 2.17–2.10 (m, 8H, C$H_2$), 1.09 (s, 36H, *t*-Bu); FD-MS $m/z$=1301.2 ($M^+$, 100%). Anal. calcd for $C_{80}H_{108}N_{12}O_4$ (1301.8) C 73.81, H 8.36, N 12.91. Found C 73.38, H 8.12, N 12.39.

**4.2.2. Octanitrile 4b.** The title compound was prepared as described for **4a**. Colourless oil, yield 54%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.75 (s, 8H, Ar*H*), 4.35 (d, $J$=12.5 Hz, 4H, ArC$H_2$Ar), 3.89 (t, $J$=7.8 Hz, 8H, OC$H_2$), 3.10 (d, $J$=12.5 Hz, 4H, ArC$H_2$Ar), 2.85 (t, $J$=6.7 Hz, 16H, CNC$H_2$), 2.62 (t, $J$=7.5 Hz, 8H, NC$H_2$), 2.44 (t, $J$=6.7 Hz, 16H, NC$H_2$), 2.01–1.94 (m, 8H, C$H_2$), 1.60–1.52 (m, 8H, C$H_2$), 1.05 (s, 36H, *t*-Bu); FD-MS $m/z$=1357.8 ($M^+$, 100%). Anal. calcd for $C_{84}H_{116}N_{12}O_4$ (1357.9) C 74.30, H 8.61, N 12.38. Found C 75.88, H 8.42, N 12.19.

**4.2.3. Octaamine 5a.** NaOH (0.33 g in 3 ml water) was added to a suspension of octanitrile **4a** (0.5 g) in a mixture of methanol (20 ml) and THF (10 ml) and the solution was stirred at room temperature for 1 h. Raney-nickel (0.8 g) was added and the reaction mixture was stirred under hydrogen at room temperature overnight. The catalyst was filtered off, the solvents were removed in vacuum and the obtained residue was dissolved in a mixture of $CH_2Cl_2$ and water. The aqueous layer was washed three times with $CH_2Cl_2$ and the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to give a colourless oil, yield 55%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.72 (s, 8H,

ArH), 4.31 (d, J=12.5 Hz, 4H, ArC$H_2$Ar), 3.90 (t, J=7.1 Hz, 8H, OC$H_2$), 3.38 (br s, 16H, N$H_2$), 3.08 (d, J=12.2 Hz, 4H, ArC$H_2$Ar), 2.65 (t, J=6.2 Hz, 16H, $NH_2CH_2$), 2.56 (t, J=7.5 Hz, 8H, NC$H_2$), 2.43 (t, J=6.8 Hz, 16H, NC$H_2$), 1.94–2.11 (m, 8H, C$H_2$), 1.58 (br, 16H, C$H_2$), 1.03 (s, 36H, *t*-Bu).

**4.2.4. Octaamine 5.** The title compound was prepared as described for **5a**. Colourless oil, yield 51%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.79 (s, 8H, ArH), 4.39 (d, J=12.7 Hz, 4H, ArC$H_2$Ar), 3.91 (t, J=7.5 Hz, 8H, OC$H_2$), 3.36 (br. s, 16H, N$H_2$), 3.16 (d, J=12.4 Hz, 4H, ArC$H_2$Ar), 2.89 (t, J=7.2 Hz, 16H, $NH_2CH_2$), 2.66 (t, J=7.1 Hz, 8H, NC$H_2$), 2.50 (t, J=6.8 Hz, 16H, NC$H_2$), 2.02–1.94 (m, 8H, C$H_2$), 1.59–1.51 (m, 8H, C$H_2$), 1.34 (br, 16H, C$H_2$), 1.09 (s, 36H, *t*-Bu).

**4.2.5. Octa-CMPO 6a.** Active ester **7** (0.531 g) was added to a solution of octaamine **5a** (0.2 g) and triethylamine (0.1 g) in chloroform (30 ml) and the mixture was stirred at room temperature overnight. Additional chloroform (20 ml) was added and the solution was washed repeatedly with 5% aq. NaOH, then water, and dried ($MgSO_4$). Evaporation of the solvent afforded a residue which was reprecipitated from chloroform/hexane to give the desired compound as a pale yellow powder, yield 80%; mp 255–259 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.01 (br s, 8H, ArNH), 7.83–7.66 (m, 32H, $PPh_2$), 7.55–7.36 (m, 48H, $PPh_2$), 6.78 (s, 8H, ArH), 4.37 (d, 4H, ArC$H_2$Ar), 3.96 (br t, 8H, OC$H_2$), 3.42–3.16 (m, 20H, ArC$H_2$Ar+POC$H_2$CO), 3.04–2.98 (m, 16H, CONHC$H_2$), 2.58–2.53 (m, 8H, NC$H_2$), 2.33 (br, 16H, C$H_2$N), 2.02–1.96 (m, 8H, C$H_2$), 1.35–1.29 (m, 16H, C$H_2$), 0.99 (s, 36H, *t*-Bu); ESI-MS *m*/*z*=3271.5 ($MH^+$, 42%).

**4.2.6. Octa-CMPO 6b.** The title compound was prepared as described for **6a**. Colourless powder, yield 51%; mp 237–239 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.93 (s, 8H, NH), 7.73–7.69 (m, 32H, $PPh_2$), 7.42–7.36 (m, 48H, $PPh_2$), 6.71 (s, 8H, ArH), 4.3 (d, 4H, ArC$H_2$Ar), 3.80 (t, 8H, OC$H_2$), 3.57 (d, 16H, POC$H_2$CO), 3.20 (br, 16H, CONHC$H_2$), 3.09 (d, 4H, ArC$H_2$Ar), 2.97–2.90 (m, 8H, C$H_2$N), 2.32 (br, 16H, NC$H_2$), 1.86–1.82 (m, 8H, C$H_2$), 1.50 (br, 8H, C$H_2$), 1.45–1.39 (br, 16H, C$H_2$), 0.99 (s, 36H, *t*-Bu); ESI-MS *m*/*z*=3327.8 ($MH^+$, 22%).

**4.2.7. 1,3-Tetra-CMPO calix[4]arene 8.** *Addition of acrylonitrile*. A solution of the 1,3-di(aminopropyl)calix[4]-arene (500 mg) in acrylonitrile (10 ml) was heated to reflux, acetic acid (140 mg) was added, and refluxing was continued for 12 h. The excess of acrylonitrile was removed by distillation and the residue dissolved in chloroform. Some insoluble material was filtered off and the solution was washed three times with conc. ammonia. The organic layer was dried over $MgSO_4$ and the solvent evaporated. Addition of hexane gave the desired tetranitrile as a white powder, yield 70%; mp 120–121 °C. Found C 76.48, H 8.62, N 8.39, $C_{62}H_{82}N_6O_4$ (975.4) requires C 76.35, H 8.47, N 8.62; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.19 (s, 2H, ArOH), 7.06 (s, 4H, ArH), 6.75 (s, 4H, ArH), 4.21 (d, J=13.2 Hz, 4H, ArC$H_2$Ar), 4.05 (t, J=5.9 Hz, 4H, OC$H_2$), 3.32 (d, J=13.2 Hz, 4H, ArC$H_2$Ar), 2.95 (m, 12H, NC$H_2$), 2.55 (t, J=6.8 Hz, 8H, C$H_2$), 2.12 (t, J=5.9 Hz, 4H, C$H_2$), 1.28 (s, 18H, *t*-Bu), 0.91 (s, 18H, *t*-Bu).

*Reduction of the nitrile groups*. To a stirred suspension of the tetranitrile (400 mg) and $CoCl_2$ (800 mg) in methanol (40 ml) was added sodium-borohydride (2.4 g) in small portions over 1 h. After 5 h conc. HCl (40 ml) was added cautiously and the methanol was evaporated. The remaining aqueous solution was mixed with conc. ammonia (100 ml) and extracted with chloroform (3×50 ml). The organic phase was dried ($MgSO_4$), concentrated and the tetraamine was precipitated by the addition of hexane as a white powder, yield 32%; mp 231–233 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.03 (s, 4H, ArH), 6.73 (s, 4H, ArH), 4.24 (d, J=13.2 Hz, 4H, ArC$H_2$Ar), 3.99 (s, 4H, OC$H_2$), 3.5 (br s, 8H, N$H_2$), 3.27 (d, J=13.2 Hz, 4H, ArC$H_2$Ar), 2.77 (br t, 12H, C$H_2$), 2.53 (br, 8H, C$H_2$), 2.10 (br, 4H, C$H_2$), 1.66 (br, 8H, C$H_2$), 1.27 (s, 18H, *t*-Bu), 0.91 (s, 18H, *t*-Bu).

*N-Acylation*. To a solution of the tetraamino calix[4]arene (130 mg) and triethylamine (1 ml) in chloroform (10 ml) was added the active ester **7** (300 mg). The mixture was stirred at room temperature for 24 h. Usual work up gave **8** as white powder, mp 210–211 °C, yield 83%; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.80–7.60 (m, 16H, $PPh_2$), 7.50–7.30 (m, 24H, $PPh_2$), 7.00 (s, 4H, ArH), 6.17 (s, 4H, ArH), 4.19 (d, J=12.2 Hz, 4H, ArC$H_2$Ar), 3.90 (br s, 4H, OC$H_2$), 3.4–3.1 (m, 20H, ArC$H_2$Ar, PC$H_2$ and NC$H_2$), 2.56 (br, 4H, C$H_2$), 2.35–1.90 (br m, 20H, C$H_2$), 1.50 (br, 8H, C$H_2$) 1.24 (s, 18H, *t*-Bu), 0.90 (s, 18H, *t*-Bu); FD-MS *m*/*z*=1960.8 (22%), ESI-MS *m*/*z*=1961.9 ($MH^+$, 73%).

### 4.3. Wide rim CMPO-derivatives

**4.3.1. N-Alkylation by *N*-(3-bromopropyl)phthalimide.** *Compound* **10a**. A suspension of tetraamine **9a** (0.37 g, 0.48 mmol) and $K_2CO_3$ (0.67 g, 4.8 mmol) in acetonitrile (40 ml) was refluxed for 1 h. *N*-(3-bromopropyl)phthalimide (1.30 g, 4.8 mmol) was added and the reaction mixture was stirred for 1.5 days. After cooling to room temperature, the solid was filtered and the solvent was evaporated. The remaining oil was extracted with chloroform/water and washed with brine. The organic layer was dried ($MgSO_4$). Column chromatography (chloroform) and reprecipitation from chloroform/hexane gave the octaphthalimido derivative **10a** as a pale yellow powder, yield 75%; mp 143–145 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.63–7.60 (m, 32H, Pht), 6.14 (s, 8H, ArH), 4.31 (d, J=13.2 Hz, 4H, ArC$H_2$Ar), 3.73 (t, J=6.2 Hz, 8H, OC$H_2$), 3.62 (t, J=6.4 Hz, 16H, PhtC$H_2$), 3.07 (t, J=6.2 Hz, 16H, NC$H_2$), 2.92 (d, J= 13.3 Hz, 4H, ArC$H_2$Ar), 1.93 (m, 8H, C$H_2$), 1.77 (m, 16H, C$H_2$), 0.94 (t, J=6.3 Hz, 12H, C$H_3$). Anal. calcd for $C_{128}H_{124}N_{12}O_{20}$ (2150.5) C 71.49, H 5.81, N 7.82. Found C 71.24, H 5.65, N 7.54.

*Compound* **10b** was prepared as described for **10a**, yield 86%; pale yellow powder, mp 156–157 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.60 (m, 32H, Pht), 6.14 (s, 8H, ArH), 4.31 (d, J=13.1 Hz, 4H, ArC$H_2$Ar), 3.76 (t, J=6.1 Hz, 8H, OC$H_2$), 3.61 (t, J=6.4 Hz, 16H, Pht-C$H_2$), 3.07 (t, J=6.2 Hz, 16H, NC$H_2$), 2.92 (d, J=13.4 Hz, 4H, ArC$H_2$Ar), 1.90 (m, 8H, C$H_2$), 1.77 (m, 16H, C$H_2$), 1.36 (m, 16H, C$H_2$), 0.93 (t, J=6.1 Hz, 12H, C$H_3$). Anal. calcd for $C_{136}H_{140}N_{12}O_{20}$ (2262.7) C 72.19, H 6.24, N 7.43. Found C 70.94, H 6.55, N 7.34.

*Octaamine* **11a**. Hydrazine hydrate (8 ml) was added to a solution of octaphthalimido-calix[4]arene **10a** (0.9 g, mmol) in ethanol (25 ml). After 2 h of reflux, the solvent was evaporated and the obtained residue was dissolved in a mixture of $CH_2Cl_2$ and water. The aqueous layer was washed three times with $CH_2Cl_2$, the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to give a yellow oil, yield 65%; $^1$H NMR (200 MHz, DMSO-$d_6$) $\delta$ 6.09 (s, 8H, Ar*H*), 4.26 (d, $J$=13.4 Hz, 4H, ArC$H_2$Ar), 3.65 (t, $J$=6.5 Hz, 8H, OC$H_2$), 3.00 (m, 16H, NC$H_2$), 2.85 (m, 20H, $NH_2CH_2$ and ArC$H_2$Ar), 2.54 (t, $J$=6.6 Hz, 16H, N$H_2$), 1.90 (m, 8H, C$H_2$), 1.46 (m, 16H, C$H_2$), 0.93 (t, $J$=6.4 Hz, 12H, C$H_3$).

*Octaamine* **11b** was prepared as described for **11a**. Pale yellow oil, yield 90%; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.13 (s, 8H, Ar*H*), 4.38 (br d, $J$=13.4 Hz, 4H, ArC$H_2$Ar), 3.76 (m, 8H, OC$H_2$), 3.01 (m, 20H, NC$H_2$ and ArC$H_2$Ar), 2.63 (br, 16H, $NH_2CH_2$), 2.19 (b, 16H, N$H_2$), 1.90 (br, 8H, C$H_2$), 1.53 (b, 16H, C$H_2$), 1.36 (br, 16H, C$H_2$), 0.92 (t, $J$=6.6 Hz, 12H, C$H_3$).

*Octa-CMPO* **12a**. Active ester **7** (0.6 g, 1.15 mmol) was added to a stirred solution of octaamine **11a** (0.2 g,) and triethylamine (0.1 g) in chloroform (25 ml). The mixture was stirred at room temperature overnight and the solution was washed repeatedly with 10% aq. NaOH and dried ($MgSO_4$). Evaporation of the solvent afforded a residue which was passed through a chromatography column (chloroform/methanol 9/1) and reprecipitated from chloroform/hexane to give the desired octa-CMPO derivative **12a** as a pale yellow powder, yield 80%; mp 220–222 °C; $^1$H NMR (400 MHz, DMSO-$d_6$, 120 °C) $\delta$ 8.16 (s, 8H, CO*NH*), 7.73 (m, 32H, $PPh_2$), 7.44 (m, 48H, $PPh_2$), 6.03 (s, 8H, Ar*H*), 4.22 (d, 4H, ArC$H_2$Ar), 3.64 (br, 24H, $POCH_2CO$+OC$H_2$), 2.92 (m, 36H, $NHCH_2$, NC$H_2$ and ArC$H_2$Ar), 1.84 (br, 8H, C$H_2$), 1.38–1.32 (m, 16H, C$H_2$), 0.92 (t, 12H, C$H_3$); FD-MS $m/z$=3044.5 ($M^+$, 35%).

*Octa-CMPO* **12b** was prepared as described for **12a**. Pale yellow powder, yield 82%; mp 239–242 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.08 (s, 8H, CO*NH*), 7.71–7.66 (m, 32H, $PPh_2$), 7.44–7.33 (m, 48H, $PPh_2$), 5.98 (s, 8H, Ar*H*), 4.14 (d, $J$=13.4 Hz, 4H, ArC$H_2$Ar), 3.61 (t, 8H, OC$H_2$), 3.49 (d, $J$=14.3 Hz, 16H, $POCH_2CO$), 3.20–2.88 (m, 36H, $NHCH_2$, NC$H_2$ and ArC$H_2$Ar), 1.88 (br, 8H, C$H_2$), 1.33 (br, 32H, C$H_2$), 0.89 (t, $J$=6.5 Hz, 12H, C$H_3$). FD-MS $m/z$=3158.7 ($M^+$, 100%).

*Di-CMPO-diethylenetriamine* **14**. To a solution of diethylenetriamine (27 mg) and triethylamine (0.2 ml) in chloroform (20 ml) was added dropwise a solution of active ester **7** (200 mg) in chloroform (20 ml). The mixture was stirred at room temperature overnight. The solution was washed repeatedly with 10% aq. NaOH and dried ($MgSO_4$). Evaporation of the solvent afforded a residue which was reprecipitated from chloroform/hexane to give the desired compound as a white powder, yield 58%; mp 157–158 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 8.52 (br s, 2H, N*H*), 7.7–7.3 (m, 20H, Ar*H*), 3.45 (d, $J$=13.6 Hz, 4H, $PCH_2$), 3.30 (m, 4H, NC$H_2$), 2.62 (t, $J$=5.4 Hz, 4H, NC$H_2$); FD-MS $m/z$=588.6 ($MH^+$, 100%).

*5,11,17,23-Octa-CMPO-25,26,27,28-tetrapentyloxycalix-[4]-arene* **15**. To a stirred solution of tetra-bromoacetamide **13** (1.0 g) and triethylamine (1 ml) in toluene (30 ml) was added dropwise a solution of **14** (2.5 g) in toluene (10 ml). The mixture was kept at 60 °C for 2 days and worked up as usual. Reprecipitation from chloroform/hexane afforded the desired compound as a white powder, yield 58%; mp 212–213 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.26 (s, 4H, CON*H*), 7.78–7.44 (m, 80H, $PPh_2$), 6.35 (s, 8H, Ar*H*), 4.22 (d, $J$=12.5 Hz, 4H, ArC$H_2$Ar), 3.83 (m, 16H, $COCH_2$ and OC$H_2$), 3.60 (d, $J$=13.5 Hz, 16H, $PCH_2$), 3.11 (m, 20H, NC$H_2$ and ArC$H_2$Ar), 2.62 (t, $J$=5.6 Hz, 16H, $NCH_2CH_2$), 1.84 (m, 8H, C$H_2$), 1.36 (m, 16H, C$H_2$), 0.91 (m, 12H, C$H_3$). ESI-MS $m/z$=3274.2 ($MH^+$, 65%).

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