Synthesis and Metal-Ion Extraction Properties of *para*-*tert*-Butylcalixareneglycine Ester Acetamides

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Dedicated to Professor Dirk Walther (Jena) on the occasion of his 60th birthday

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Calixareneglycine ester acetamides **4a–c** have been synthesized from calixareneacetyl chlorides **5a–c** and glycine ethyl ester (**6**). Their ion-binding properties have been investigated by liquid-liquid extraction with radiotracer techniques. The experiments reveal a moderate affinity towards silver(I) ions, which increases with calixarene ring size.

Introduction

Calixarenes are most suitable precursors for the synthesis of selective ionophores.[1] As illustrated by many examples their unique molecular structure allows the arrangement of functional groups in space for the coordination of metal cations.[2] Receptor molecules with remarkable selectivities in cation binding have been developed, e.g. from calix[4]arene, which was anchored in a particular conformation of the macrocycle by suitable derivatization[1] and functionalized with crown ethers.[3] But even the introduction of much simpler functional groups, such as ethers, esters, amides or ketones has a profound effect on the binding ability of calixarenes. It has been well established that the phenolic functions of calixarenes can be alkylated with alkyl bromoacetates to form alkyl calixarene acetates **1** with significant ion-binding potential for mainly alkali metal cations.[4] The series has been extended to calixarene ketones **2**,[5] amides **3**,[6] thioamides and carboxylic acids,[7] and their alkali and alkaline earth cation binding properties have been determined. The principal findings of these studies were that calix[4]arene esters **1a**, ketones **2a** and *tert*-amides **3a**[8] show a clear preference for Na^+ ions, the pentamer series (**1d**, **2d**, **3d**), reflecting the larger receptor volume than the tetramers, favors the larger cations K^+, Rb^+ and Cs^+ over Na^+, and calix[6]arene (**1b**, **2b**, **3b**) and calix[8]arene derivatives (**1c**, **2c**, **3c**) are characterized by lower extraction ability and low levels of discrimination among the alkali cations. The *tert*-amides **3a** and **3b** also bind the alkaline earth metal ions Ca^{2+}, Sr^{2+} and Ba^{2+} with high efficiency, but without clear size preference. This was confirmed by stability-constant measurements and solvent-extraction studies.[2a] In contrast to the behavior of tertiary amides ($R = R' =$ alkyl) the related secondary amides **3a**, **3b**, **3c** ($R =$ H; $R' = n$Bu) extract alkali metal ions only very weakly.[9] With the alkaline earth metals the same compounds give size-dependent extractabilities, which are furthermore graduated in the order **3b** > **3c** > **3a**. Less data have been reported on the complexation of transition-metal cations in solution, with the exception of Ag^+, for which a broad range of stability constants in methanol is available.[2a,2b] With *para*-*tert*-butylcalixarene tetra- (**1a**), penta- (**1d**) and hexaesters (**1b**) log β values range between 3.1 and 4.3, and no size selectivity is observed. The stability of complexes is slightly higher for the tetraketone **2a** and much higher for the tetraamide **3a**. In the amide series there is a size effect: Compound **3d** shows a higher log β value than **3a** or **3b**.[2a,8] The calix[4]arene-*tert*-amide **3a** is a useful extractant for Ag^I from strongly acidic medium.[10]

In order to investigate the effect of functional groups simultaneously present in each arene moiety,[11] we have synthesized a series of new calixareneglycine ester acetamides **4**, which represent examples of simple calixarenes that bear both secondary amide *and* ester groups as potential coordination sites for metal ion binding. Their binding properties have been investigated by liquid-liquid extraction of aqueous solutions of metal picrates. A first example of this type, calix[4]areneglycine tetra-*tert*-butyl ester acetamide, was recently reported by Reinhoudt et al.[12]

Results and Discussion

Synthesis

The synthesis of the *para*-*tert*-butylcalixareneglycine ester acetamides **4a–c** was achieved analogously to previously reported procedures for the synthesis of calixarene acetamides. The reaction of the *para*-*tert*-butylcalixareneacetyl chlorides **5a–c**[13] with glycine ethyl ester (**6**)[14] under standard conditions enabled the isolation of the glycine es-

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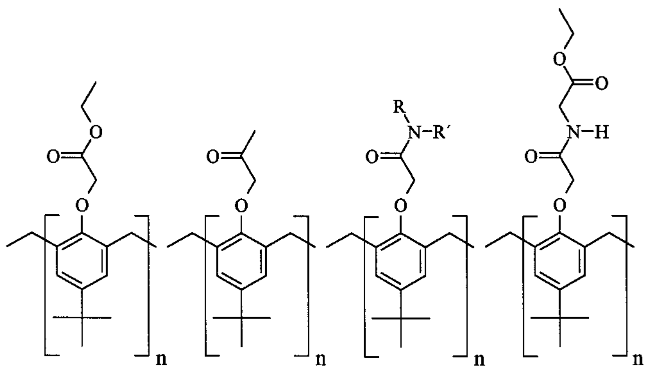


1 a n = 4
b n = 6
c n = 8
d n = 5

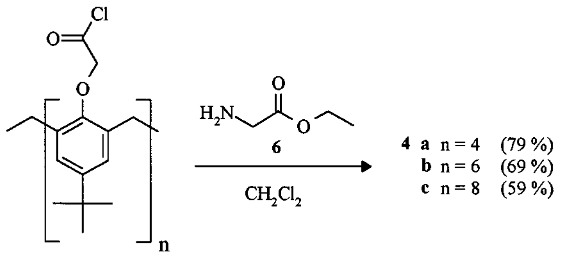
2 a n = 4
b n = 6
c n = 8
d n = 5

3 a n = 4
b n = 6
c n = 8
d n = 5

4 a n = 4
b n = 6
c n = 8

Scheme 1. Calixarene ionophores

ter acetamides **4a**–**c** in 59–79% yields. As indicated by the broad resonance signals in the NMR spectra of **4b**, the compound has a restricted conformational mobility on the NMR time scale. Obviously, compound **4a** is, like **5a**, fixed in the cone conformation, whereas the macrocyclic ring of **4c** is large enough to allow rotation of the substituted arene units. The reaction of **5a** with heterocyclic amino acid esters, such as **7** and **8**, proceeds analogously, but is much less efficient for **8**.[15] Surprisingly, amides **9** and **10** show significant decomposition in chloroform solution at room temperature, which renders them unsuitable for extraction studies. *N*-Benzylamide **11** and compound **14** were synthesized from **5a** and benzylamine, and alkylation of **12** with **13**,[16] respectively, for comparison of their extraction properties with compound **4a**.



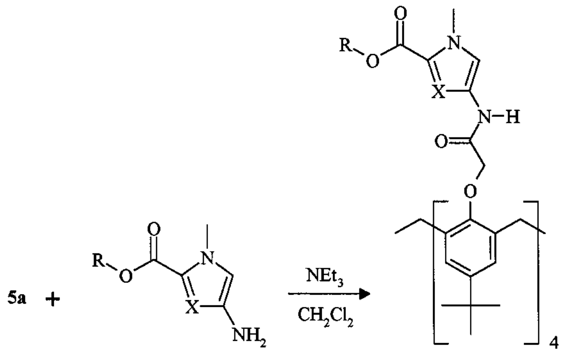
4 a n = 4 (79 %)
b n = 6 (69 %)
c n = 8 (59 %)

5 a n = 4
b n = 6
c n = 8

Scheme 2. Synthesis of *para-tert*-butylcalixareneglycine ester acetamides

Metal-Ion Extraction Properties

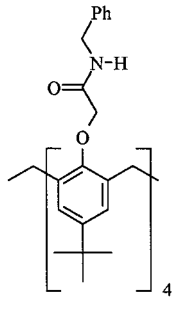
The binding properties of the new compounds were investigated by liquid-liquid extraction experiments. Aqueous solutions of the metal salts ($c = 1 \cdot 10^{-4}$ mol/l) and picric acid ($5 \cdot 10^{-3}$ mol/l), buffered to pH = 5.2 by NaOAc/HCl,[17] were extracted with chloroform solutions of the calixarene derivatives ($c = 1 \cdot 10^{-3}$ mol/l). The determination of the metal concentrations in both phases was carried out by measurement of the radiation of the corresponding radionuclides.[18] As metal ions Na^+, Ba^{2+}, Tl^+, Pd^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Eu^{3+} and Ag^+ were employed to obtain information about extraction properties towards alkali, alkaline earth and transition metal ions. Figure 1 summarizes the results. All glycine ester acetamides extract Ag^+, and the efficiency increases drastically from **4a** (1.8%) to **4b** (15%) and **4c** (57%).[19] For the large glycine ester acetamide **4c** some extraction of Cu^{2+} (7.1%), Hg^{2+} (5.5%), Eu^{3+} (3%) and Ba^{2+} (1.8%) was noted. Compound **4b** shows, besides Ag^+ binding, some uptake of Tl^+ (3.5%) but very low Hg^{2+}, Cu^{2+}, Eu^{3+} and Ba^{2+} extraction (< 2%). Extraction of Na^+ or Zn^{2+} was not observed in any case. The importance of the ester groups for extraction is illustrated by comparison with the *N*-benzylamide-substituted calix[4]arene **11**: None of the tested metal salts were ex-



7 X = CH, R = Me
8 X = N, R = Et

9 X = CH, R = Me 89 %
10 X = N, R = Et 9 %

Scheme 3. Reaction of **5a** with heterocyclic amino acid esters



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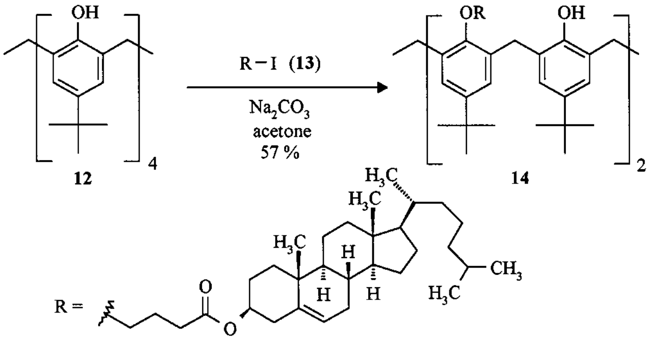
Scheme 4. *para-tert*-Butylcalix[4]arene *N*-benzylacetamide (**11**)



Scheme 5. Twofold alkylation of *para-tert*-butylcalix[4]arene

tracted under the selected experimental conditions and only a small affinity towards Pd^{2+} could be detected.[20] Compound **14**, lacking ester and amide groups, did not show any extraction of metal salts within the error of the experiment.

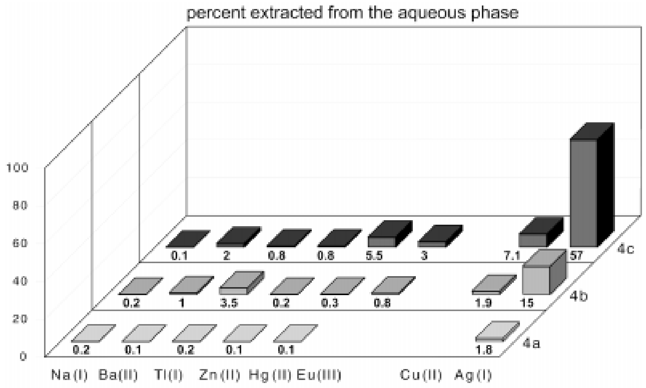


Figure 1. Extraction of metal picrates with compounds **4a**, **4b** and **4c**; $c_M = 1 \cdot 10^{-4}$ M; $c_{HPic} = 5 \cdot 10^{-3}$ M; pH = 5.2; $c_L = 1 \cdot 10^{-3}$ M/$CHCl_3$ a stoichometry of 1:1 for Hg^{2+}, Tl^+, Eu^+ complexes, and 1:1, 1:2 stoichometries for Ag^+ and Ba^{2+} complexes

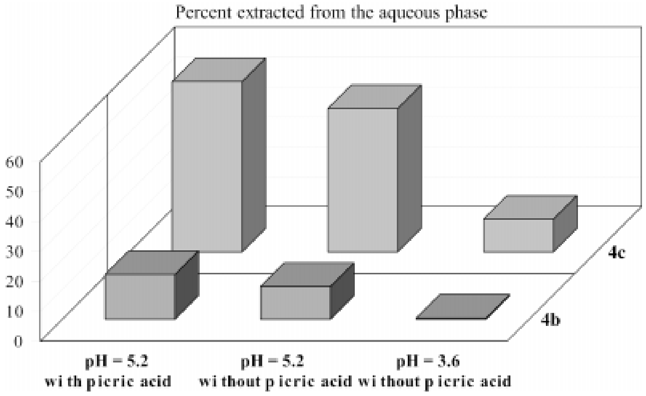


Figure 2. Influence of the pH value on the extraction of Ag^+ with **4b** and **4c**; $c_{Ag} = 1 \cdot 10^{-4}$ M; $c_L = 1 \cdot 10^{-3}$ M/$CHCl_3$

The extractability of Ag^+ with **4b** and **4c** strongly depends on the pH value of the aqueous phase. As it is shown in Figure 2 a decreasing pH value (from 5.2 to 3.6) led to a significant lower extraction (from 57% to 11% for **4c**; from 15% to 0.4% for **4b**). In contrast to this, amazingly, the influence of the picrate anion on the Ag^+ extraction is weak (see Figure 2). The extractability for **4c** in the absence of picrate is only 9%, and for **4b** 4% lower than with picrate present.

Some additional information about the stoichiometry of the calixarene metal complexes in the organic phase was derived from double log plots of distribution ratios of the metals versus ligand concentrations (Figure 3). The analysis suggests that **4b** and **4c** form 1:1 complexes with Hg^{2+}. The same composition is also obtained from **4b** with Tl^+ and Eu^{3+}; 1:1 and 1:2 complexes (M/L) are identified for Ag^+[21] with the calixarenes **4a** and **4b** and for Ba^{2+} with **4b**. The calculated extraction constants are summarized in Table 1. Preliminary molecular modeling studies give some evidence for the binding of the metal ion by ether and carbonyl oxygen donor atoms inside the cavity, similar to the known structures with tertiary amides.[2e] The limited extraction power of the novel compounds in comparison with *tert*-amides might be rationalized by a specific hydrogen-bonding pattern between the secondary amide and carbonyl oxygen functions in the molecule, as it is observed for compounds with related structure.[22] The interaction of the secondary amide with the solvent chloroform might also be taken into account.

Conclusion

In summary, calixarene derivatives that bear a secondary amide moiety and an ester group on each arene unit were obtained by reaction of calixareneacetyl chlorides **5** with glycine ethyl ester (**6**). The investigation of the binding

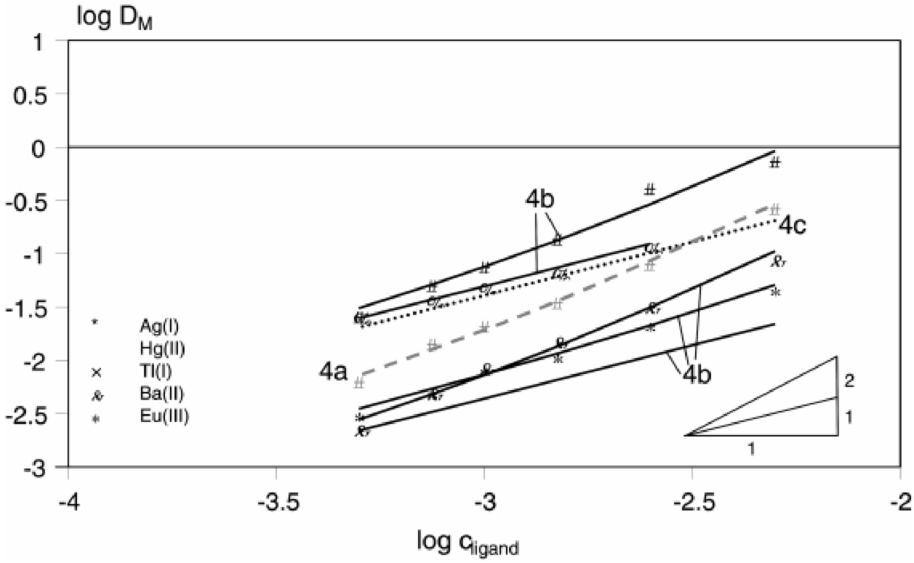


Figure 3. The double logarithmic plot suggests a stoichiometry of 1:1 for Hg^{2+} complexes in the organic phase, and 1:1, 1:2 or higher stoichiometries for Ag^+ complexes; $c_M = 1 \cdot 10^{-4}$ M; $c_{HPic} = 5 \cdot 10^{-3}$ M; pH = 5.2; $c_L = 5 \cdot 10^{-4} - 5 \cdot 10^{-3}$ M/$CHCl_3$

Table 1. Selected extraction constants for the calixarenes **4a−c**

Compound	**4a**	**4b**	**4c**
Ag^+	$\log K_{ex1} = 3.31$ $\log K_{ex2} = 6.29$	$\log K_{ex1} = 3.98$ $\log K_{ex2} = 6.76$	/
Hg^{2+}	/	$\log K_{ex1} = 2.94$	$\log K_{ex1} = 3.95$
Ba^{2+}	/	$\log K_{ex1} = 2.88$ $\log K_{ex2} = 5.84$	/
Tl^+	/	$\log K_{ex1} = 3.99$	/
Eu^{3+}	/	$\log K_{ex1} = 3.13$ $\log K_{ex2} = 5.15$	

properties of the new potential ionophores by liquid-liquid extraction of picrate salts revealed poor to moderate extraction of mainly silver(I) salts, in which the calix[8]arene derivative **4c** shows the largest extraction ability. For calixarenes bearing secondary amides on the lower rim efficient extraction of alkaline earth cations has been reported, and a little of this characteristic remains in compounds **4b** and **4c**. However, the affinity of calixareneacetates towards alkali cations[2a,8] is completely lost in **4**, where the ester is placed further away from the calixarene core and separated from it by an amide group. The ability of *para*-*tert*-butylcalixareneglycine ester acetamides **4** to bind Ag^+ ions is clearly surpassed by calixarene-*tert*-amides,[8] and in particular, -*tert*-thioamides.[23] In conclusion, calix[6]- and calix[8]areneglycine acetamides **4b** and **4c** show some affinity in metal ion extraction, but their efficiency and selectivity is inferior to other known calixarene ionophores.

Experimental Section

General Remarks: Melting points were taken with a hot-plate microscope apparatus and are not corrected. − NMR spectra were recorded at 400 MHz (^1H) and 100 MHz (^{13}C) in [D]chloroform solutions unless otherwise stated. The multiplicity of the ^{13}C signals was determined with the DEPT technique and quoted as: (+) for CH_3 or CH, (−) for CH_2 and (C_{quat}) for quaternary carbon atoms. CC means column chromatography on silica gel unless otherwise stated. PE means petroleum ether with a boiling range of 60−70°C, EA means ethyl acetate.

Determination of Metal-Ion Binding Properties by Liquid-Liquid Extraction: All extractions were performed at 25°C in agitated microreactors (2 cm^3). To reach the equilibrium of distribution the organic and aqueous phase of equal volumes were shaken for 30 min for all investigated metal ions. Only in the case of palladium was 2 h of shaking necessary to reach the equilibrium. The phases were separated, centrifuged and the concentration of metal ions in both phases was determined by the emission of the radionuclides which were used. The γ-radiation (^{203}Hg, ^{133}Ba, ^{110m}Ag, ^{109}Pd, ^{65}Zn, ^{64}Cu, ^{22}Na) was measured with an NaI(Tl) scintillation counter (Cobra II, Canberra Packard) and β-emission (^{204}Tl) was determined with a liquid scintillation counter (Tricarb 2500, Canberra Packard).

Calix[4]arene 4a: To a solution of the acyl chloride **5a** (0.24 g, 0.25 mmol) in 10 mL of CH_2Cl_2 was added glycine ethyl ester (**6**; 0.31 g, 3.0 mmol) in 10 mL of CH_2Cl_2 at 0°C, the reaction mixture was stirred at room temp. for 16 h, washed with saturated aqueous NH_4Cl solution, dried with $MgSO_4$ and the solvent was removed in vacuo. CC (Et_2O/EA, 5:1; $R_f = 0.49$) of the crude product gave 0.24 g (79%) of **4a** as a white solid, m.p. 230°C. − IR (KBr): $\tilde{\nu} = 3380\ cm^{-1}$, 1750, 1680, 1190. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (5.046), 216 (4.796). − ^1H NMR: δ = 7.92 (t, ^3J = 5.7 Hz, 4 H), 6.83 (s, 8 H), 4.58 (s, 8 H), 4.56 (d, ^2J = 13.9 Hz, 4 H), 4.19 (q, ^3J = 7.1 Hz, 8 H), 4.12 (s, 8 H), 3.31 (d, ^2J = 13.0 Hz, 4 H), 1.28 (t, ^3J = 7.1 Hz, 12 H), 1.09 (s, 36 H). − ^{13}C NMR: δ = 170.3 (C_{quat}), 170.1 (C_{quat}), 152.5 (C_{quat}), 146.1 (C_{quat}), 132.6 (C_{quat}), 125.9 (+), 74.1 (−), 61.2 (−), 41.0 (−), 33.9 (C_{quat}), 31.3 (+), 31.1 (−), 14.1 (+). − MS (MALDI-TOF); *m/z* (%): 1244.4 (100) $[M + Na]^+$. − C68H92N4O16·H2O (1239.5): calcd. C 65.89, H 7.64, N 4.52; found C 66.25, H 7.78, N 4.20.

Calix[6]arene 4b: To a solution of the acyl chloride **5b** (1.4 g, 1.0 mmol) in 30 mL of CH_2Cl_2 was added at 0°C glycine ethyl ester (**6**; 1.9 g, 18 mmol) in 30 mL of CH_2Cl_2; the mixture was stirred for 16 h at room temp. and was worked up as described for compound **4a**. The crude product was recrystallized from ethyl acetate (5 mL) and petroleum ether (30 mL) at −20°C overnight to yield 1.26 g (69%) of **4b** (R_f = 0.38 in Et_2O/EA, 5:1) as a white solid, m.p. 116−118°C. − IR (KBr): $\tilde{\nu} = 3410\ cm^{-1}$, 1750, 1680, 1190. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (5.264), 218 (4.995). − MS (MALDI-TOF); *m/z* (%): 1854.0 (100) $[M + Na]^+$. − $C_{102}H_{138}N_6O_{24}$ (1832.2): calcd. C 66.85, H 7.60, N 4.59; found C 66.53, H 7.66, N 4.29.

Calix[8]arene 4c: To a solution of the acyl chloride **5c** (1.4 g, 0.73 mmol) in 30 mL of CH_2Cl_2 was added at 0°C glycine ethyl ester (**6**; 1.9 g, 18 mmol), dissolved in 30 mL of CH_2Cl_2; the reaction mixture was stirred for 16 h at room temp. and worked up as described for **4c**. The crude product was recrystallized from CH_2Cl_2 (5 mL) and *n*-heptane (30 mL) at −20°C overnight to give 1.06 g (59%) of **4c** (R_f = 0.27 in Et_2O/EA, 5:1) as a white solid, m.p. 224−226°C. − IR (KBr): $\tilde{\nu} = 3430\ cm^{-1}$, 1750, 1690, 1200. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (5.366), 222 (5.075). − ^1H NMR: δ = 7.92 (t, ^3J = 5.7 Hz, 4 H), 6.83 (s, 8 H), 4.58 (s, 8 H), 4.56 (d, ^2J = 13.9 Hz, 4 H), 4.19 (q, ^3J = 7.1 Hz, 8 H), 4.12 (s, 8 H), 3.31 (d, ^2J = 13.0 Hz, 4 H), 1.28 (t, ^3J = 7.1 Hz, 12 H), 1.09 (s, 36 H). − ^{13}C NMR: δ = 169.9 (C_{quat}), 169.0 (C_{quat}), 151.9 (C_{quat}), 147.0 (C_{quat}), 132.0 (C_{quat}), 125.9 (+), 71.4 (−), 61.2 (−), 40.7 (−), 34.2 (C_{quat}), 31.3 (+), 31.2 (−), 14.0 (+). − MS (MALDI-TOF); *m/z* (%): 2466.1 (100) $[M + Na]^+$. − $C_{136}H_{184}N_8O_{32}\cdot H_2O$ (2461.0): calcd. C 66.38, H 7.62, N 4.55; found C 66.19, H 7.73, N 4.35.

Calix[4]arene 9: A mixture of methyl 1-methyl-4-nitropyrrole-2-carboxylate (0.5 g, 2.7 mmol) and Pd/C (0.15 g) in 200 mL of ethyl acetate and 100 mL of methanol was hydrogenated at an H_2 pressure of 4 bar for 16 h at room temp., the catalyst was removed by filtration and the solvent was removed in vacuo. The resulting amino acid **7** was dissolved in 30 mL of CH_2Cl_2, triethyl amine (2 mL, 14 mmol) and the acyl chloride **5a** (0.5 g, 0.52 mmol) were added at 0°C, the reaction mixture was stirred for 16 h at room temp., washed with saturated aqueous NH_4Cl solution, dried with Na_2SO_4 and the solvent was removed in vacuo. CC (CH_2Cl_2/MeOH, 97:3, R_f = 0.33) of the crude product gave 0.66 g (89%) of **9** as a white solid. − IR (KBr): $\tilde{\nu} = 3310\ cm^{-1}$, 1710, 1690, 1450, 1200. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 204 nm (5.016), 228 (4.978), 284 (4.525). − ^1H NMR: δ = 9.56 (s, 4 H), 7.32 (d, ^4J = 1.9 Hz, 4 H), 6.85 (d, ^4J = 1.9 Hz, 4 H), 6.79 (s, 8 H), 4.57 (s, 8 H), 4.52 (d, ^2J = 12.9 Hz, 4 H), 3.75 (s, 12 H), 3.71 (s, 12 H), 3.23 (d, ^2J = 13.1 Hz, 4 H), 1.07 (s, 36 H). − ^{13}C NMR: δ = 167.4 (C_{quat}), 161.4 (C_{quat}), 153.4 (C_{quat}), 145.7 (C_{quat}), 132.8 (C_{quat}), 125.8 (+), 121.7 (+), 121.1 (C_{quat}), 119.8 (C_{quat}), 109.0 (+), 74.8 (−), 50.9 (+), 36.5 (+), 33.8 (C_{quart}), 31.4 (−), 31.3 (+). − MS (ESI); *m/z* (%): 1448.4 (90) $[M + Na]^+$, 732.4 (100) $[M + K]^{2+}$.

Calix[4]arene 10: A solution of ethyl 1-methyl-4-nitroimidazol-2-carboxylate (0.5 g, 2.5 mmol) in 200 mL of ethyl acetate and 100 mL of methanol was hydrogenated for 16 h at room temp. on Pd/C (0.15 g) at an H_2 pressure of 4 bar. The catalyst was removed by filtration, the solvent was distilled off in vacuo, CH_2Cl_2 (30 mL) and triethylamine (2 mL, 14 mmol) were added. The acyl chloride **5a** (0.5 g, 0.52 mmol) was added at 0°C, the reaction mixture was stirred for 16 h at room temp. and worked up as described for **9**. CC (CH_2Cl_2/MeOH, 97:3, $R_f = 0.26$) gave 70 mg (9%) of **10** as a solid. − ^{1}H NMR: $\delta = 9.91$ (s, 4 H), 7.43 (s, 4 H), 6.75 (s, 8 H), 4.80 (s, 8 H), 4.58 (d, $^2J = 13.1$ Hz, 4 H), 4.22 (q, $^3J = 7.1$ Hz, 8 H), 3.85 (s, 12 H), 3.23 (d, $^2J = 13.3$ Hz, 4 H), 1.22 (t, $^3J = 7.1$ Hz, 12 H), 1.01 (s, 36 H). − ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.4$ (C_{quat}), 158.8 (C_{quat}), 153.0 (C_{quat}), 145.6 (C_{quat}), 136.8 (C_{quat}), 132.7 (C_{quat}), 131.4 (C_{quat}), 129.3 (+), 125.7 (+), 74.7 (−), 61.1 (−), 35.8 (+), 33.8 (C_{quat}), 31.4 (−), 31.3 (+), 14.1 (+). − MS (ESI); *m/z* (%): 1507.6 (100) $[M + Na]^+$.

Calix[4]arene 11: To a solution of the acyl chloride **5a** (0.4 g, 0.42 mmol) and triethylamine (1.2 mL, 8.4 mmol) in 30 mL of CH_2Cl_2 was added benzylamine (0.2 mL, 1.8 mmol) at 0°C; the reaction mixture was stirred for 16 h at room temp. and worked up as described for **4a**. CC (CH_2Cl_2/MeOH, 49:1, $R_f = 0.30$) yielded 50 mg (10%) of **11** as a white solid, m.p. 277−278°C. − IR (KBr): $\tilde{\nu} = 3280\ cm^{-1}$, 1660, 1480, 1200. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (5.306), 202 (5.166), 276 (3.546). − ^{1}H NMR: $\delta =$ 7.81 (t, $^3J = 5.9$ Hz, 4 H), 7.23 (m, 20 H), 6.75 (s, 8 H), 4.40 (m, 20 H), 3.14 (d, $^2J = 13.1$ Hz, 4 H), 1.07 (s, 36 H). − ^{13}C NMR: $\delta = 169.5$ (C_{quat}), 152.8 (C_{quat}), 145.8 (C_{quat}), 138.3 (C_{quat}), 132.6 (C_{quat}), 128.5 (+), 127.6 (+), 127.2 (+), 125.8 (+), 74.4 (−), 42.9 (−), 33.8 (C_{quat}), 31.4 (−), 31.3 (+). − MS (ESI); *m/z* (%): 1259.8 (100) $[M + Na]^+$, 1237.6 (40) $[M + H]^+$. − $C_{80}H_{92}N_4O_8$ (1236.7): calcd. C 77.64, H 7.49, N 4.53; found C 77.34, H 7.78, N 4.43.

Calix[4]arene 14: To a suspension of *para-tert*-butylcalix[4]arene (**12**; 0.5 g, 0.77 mmol) and Na_2CO_3 (0.5 g, 4.7 mmol) in 70 mL of acetone was added 2.7 g (4.6 mmol) of **13** and the reaction mixture was refluxed for 10 d. The solvent was removed, the solid residue was extracted with 20 mL of CH_2Cl_2 and the resulting suspension was filtered. The organic phase was washed with sat. aqueous NH_4Cl solution, dried with Na_2SO_4, and the solvent was removed in vacuo. CC (PE/EA, 20:1; $R_f = 0.37$) of the crude product yielded 0.68 g (57%) of **14**, as a white solid, m.p. 210°C. − IR (KBr): $\tilde{\nu} = 3430\ cm^{-1}$, 1730, 1470, 1170. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (5.553), 230 (4.006), 286 (3.618). − ^{1}H NMR: $\delta = 7.65$ (s, 2 H), 7.03 (s, 4 H), 6.83 (s, 4 H), 5.34 (d, $^3J = 3.8$ Hz, 2 H), 4.62 (m, 2 H), 4.24 (d, $^2J = 12.9$ Hz, 4 H), 4.03 (t, $^3J = 5.9$ Hz, 4 H), 3.31 (d, $^2J = 12.9$ Hz, 4 H), 2.83 (t, $^3J = 7.2$ Hz, 4 H), 1.67 (m, 60 H), 1.27 (s, 18 H), 1.00 (s, 6 H), 0.99 (s, 18 H), 0.92 (d, $^3J = 6.5$ Hz, 6 H), 0.87 (d, $^3J = 6.6$ Hz, 6 H), 0.86 (d, $^3J = 6.6$ Hz, 6 H), 0.68 (s, 6 H). − ^{13}C NMR: $\delta = 172.7$ (C_{quat}), 150.7 (C_{quat}), 149.5 (C_{quat}), 146.9 (C_{quat}), 141.3 (C_{quat}), 139.7 (C_{quat}), 132.7 (C_{quat}), 127.6 (C_{quat}), 125.5 (+), 125.1 (+), 122.5 (+), 75.1 (−), 74.0 (+), 56.7 (+), 56.1 (+), 50.0 (+), 42.3 (C_{quat}), 39.7 (−), 39.5 (−), 38.1 (−), 37.0 (−), 36.6 (C_{quat}), 36.2 (−), 35.8 (+), 33.9 (C_{quat}), 33.8 (C_{quat}), 31.9 (−), 31.8 (+), 31.7 (+), 31.0 (+), 28.2 (−), 28.0 (+), 27.7 (−), 25.5 (−), 24.3 (−), 23.8 (−), 22.8 (+), 22.5 (+), 21.0 (−), 19.3 (+), 18.7 (+), 11.8 (+). − MS (ESI); *m/z* (%): 1580.9 (55) $[M + Na]^+$, 524.2 (100). − $C_{106}H_{156}O_8$ (1558.4): calcd. C 81.70, H 10.09; found C 81.44, H 10.21.

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