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Conformational Restriction of the Calix[6]arene Macrocycle by the Ritter Reaction

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Herein we report on the development of a novel and efficient approach to the restriction of the conformational mobility of calix[6]arenes. The method involves the addition of tertiary alcohols to calix[6]arenes with one, three and six cyanomethoxy groups attached to the lower rim under modified Ritter reaction conditions. Alkylation of monocyanomethoxy-*p*-*tert*-butylcalix[6]arene (**1**) and 37,39,41-trimethoxy-38,40,42-tricyanomethoxy-*p*-*tert*-butylcalix[6]arene (**2**) with 3-R-1-adamantanols (R = H, CH_2COOH) in trifluoroacetic acid afforded the corresponding mono- and triamides with cone-like conformations. The partial alkylation of hexanitrile derivatives showed unexpected regioselectivity. Addition of 1-adamantanol or *tert*-butyl alcohol to hexacyanomethoxy-*p*-X-calix[6]arenes **3a–c** (X = *tert*-butyl, 1-adamantyl, 3-methoxycarbonylmethyl-1-adamantyl) gave 37,40-dinitrile-38,39,41,42-tetraamides as the major products. These tetraamides are conformationally restricted in solution over a wide range of temperatures and adopt a flattened 1,2,3-alternate conformation, as shown by 2D and variable-temperature NMR experiments.

Introduction

Calix[6]arenes possess a cavity that is suitable for molecular recognition of large guest molecules. On the other hand effective methods need to be developed to conformationally restrict the high mobility of the macrocyclic ring.

It is known that bulky groups attached to the lower rim of calix[6]arene molecules can reduce the mobility of these flexible macrocycles. Mono-*O*-substitution of *p*-*tert*-butylcalix[6]arenes at the lower rim with groups as large as a butyl group slows ring inversion, while substitution with groups larger than benzyl freezes the conformation to produce cone-shaped molecules.[1] Proximal[2] or distal dibenzylation, dibenzoylation[3] or dithiophosphorylation[4] of *p*-*tert*-butylcalix[6]arene provide macro-rings with cone- and 1,2,3-alternate-like conformations. Three methoxy and three bulky alkoxy substituents in alternating positions on the lower rim stabilize calix[6]arenes in flattened cone conformations.[5] The 1,2,3-alternate conformation is preferred by calix[6]arenes symmetrically modified with four benzyl, benzoyl[1b,1e,3a] or 2-(2-methoxyethoxy)ethoxy[6] groups. Calix[6]arenes with six trimethylsilyl groups[7] or cholesteryl-containing ester groups[8] adopt 1,2,3-alternate conformations in solution over a wide range of temperatures, while six *p*-cyanobenzyl groups stabilize the cone conformation of the macrocycle.[1e]

Recently we demonstrated that the Ritter reaction performed in trifluoroacetic acid (TFA) is useful for preparing a wide range of amides in high yields.[9] Since bulky groups can be easily attached to a nitrile we have applied this method to calix[6]arene chemistry. We expected that the conformational mobility of the macrocycle would decrease and the resultant amides would be preorganized for molecular recognition.

Results and Discussion

Calix[6]arenes with nitriles attached to the lower rim have only been used until now as precursors of primary amides and amines. Thus, *p*-*tert*-butylcalix[6]arene bearing six cyanomethoxy groups was reduced to the corresponding hexaamine in order to obtain a host molecule for lanthanide ions.[10] The symmetrical tetraamine obtained from a calix[6]arene with four cyanomethoxy and two benzyloxy functions was used as a framework for the tetrakis[ruthenium tris(bipyridine)] derivative.[11] The mononitrile of *p*-SO_3H-calix[6]arene was converted into the corresponding monoamine in order to examine its interactions with amino acids in aqueous media.[12] To the best of our knowledge no significant conformational restriction has been obtained for cyanomethylated calix[6]arenes and their one-step derivatives.

In the study reported herein, the TFA-driven reactions of mono- (**1**), 1,3,5-tri- (**2**) and hexa- (**3**) cyanomethylated

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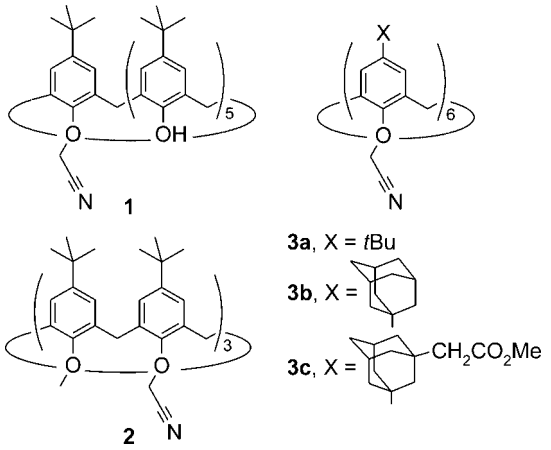
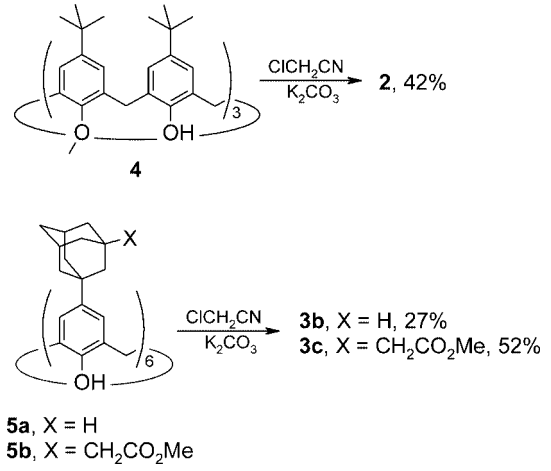
p-X-calix[6]arenes (Scheme 1) with 1-adamantanol, 3-carboxymethyl-1-adamantanol and *tert*-butyl alcohol were investigated.



Scheme 1. Cyanomethylated calix[6]arenes **1**–**3**.

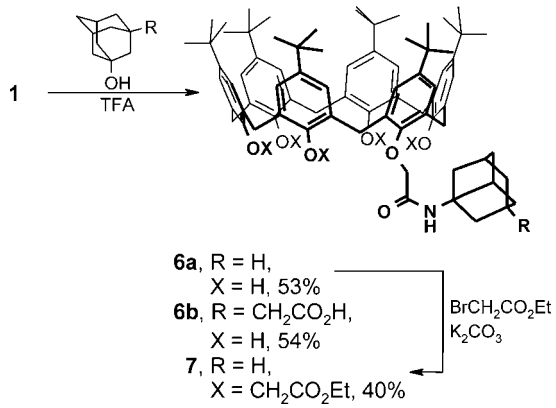
Compounds **1**[13] and **3a**[10] were synthesized according to published procedures. Trinitrile **2** as well as hexanitriles **3b** and **3c** were obtained by alkylation of triether **4**[1d,5a] or *p*-3-X-1-adamantylcalix[6]arenehexols **5a**,**b**[14] with chloroacetonitrile in the presence of K_2CO_3 in acetone (Scheme 2). As shown through room-temperature ^{1}H NMR studies all the synthesized nitriles are conformationally mobile.



Scheme 2. Syntheses of nitriles **2** and **3b**,**c**.

Synthesis and Structures of the Mono- and Triamides: The addition of 1-adamantanol and 3-carboxymethyl-1-adamantanol to the conformationally mobile mononitrile **1** in TFA/1,2-dichloroethane at 65–75 °C leads to the monoamides **6a** and **6b**, respectively (Scheme 3).

p-*tert*-Butylcalix[6]arenes with one bulky group attached to the lower rim have been reported to adopt the cone conformation as a result of the cyclic array of hydrogen bonds at the lower rim of the calix[6]arenes and the steric effects of the substituents.[1a–c,e] Analysis of the characteristic patterns of aromatic, $ArCH_2Ar$ bridge and *tert*-butyl protons in the ^{1}H NMR spectra, in particular, suggested the calix[6]-



Scheme 3. Syntheses of monoamides **6**.

arenes to be conformationally restricted. We found the same spectral patterns for monoamides **6a** (Figure 1) and **6b**.

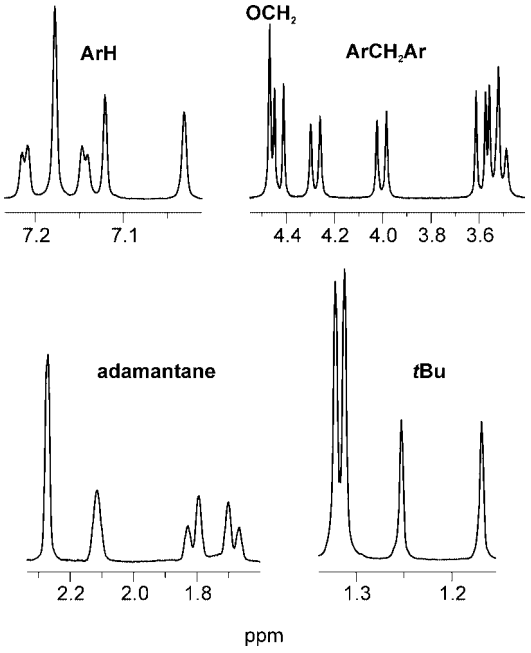


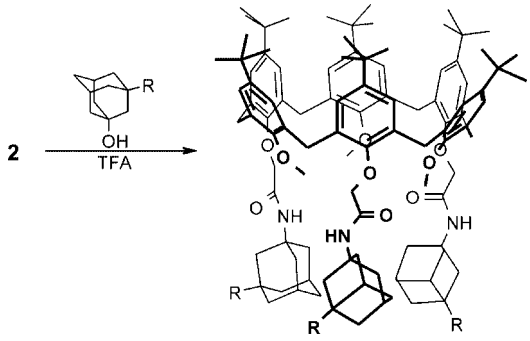
Figure 1. Characteristic patterns in the ^{1}H NMR spectrum of monoamide **6a**.

The ^{13}C NMR spectra of **6** exhibit one signal from the amide C=O, one OCH_2 signal, characteristic sets of aromatic and adamantane signals (four for **6a** and seven for **6b**), four pairs of signals from nonequivalent *tert*-butyl groups and also two signals from $ArCH_2Ar$ at δ = 32–33 ppm, which corresponds to a full *syn* arrangement of neighboring aromatic fragments. This data shows monoamides **6** to adopt rigid cone conformations in chloroform and that the adamantylamide unit acts as a conformational anchor blocking ring inversion.

Alkylation of the OH groups attached to the lower rim of **6a** with ethyl bromoacetate in the presence of K_2CO_3 in acetone resulted in the formation of pentaester **7** (Scheme 3).

In contrast to the data for **6**, the ^{1}H NMR spectrum of **7** exhibits broadened signals due to aromatic and $ArCH_2Ar$ protons as a result of fast conformational interconversion. The dramatic increase in macrocycle mobility upon alkylation of the residuary hydroxy groups supports the considerable contribution of hydrogen bonding at the lower rim of monoamide **6a** to the conformational preorganization of calix[6]arene molecules.

Adamantylation of trinitrile **2** under modified Ritter reaction conditions with 1-hydroxyadamantane and 3-carboxymethyl-1-adamantanol resulted in symmetrical triamides **8** (Scheme 4).



8a, R = H, 76%
8b, R = CH_2CO_2H, 64%

Scheme 4. Syntheses of triamides **8**.

The conformational properties of 1,3,5-trimethoxy-2,4,6-trialkoxy lower-rim-substituted calix[6]arenes have been widely studied.[5] For compounds of this type with three bulky alkoxy groups attached to the lower rim, the flattened cone conformation is preferred. Three methoxy groups were shown to be self-included inside the cavity and the cone-like conformation was stabilized through weak OMe–π interactions.

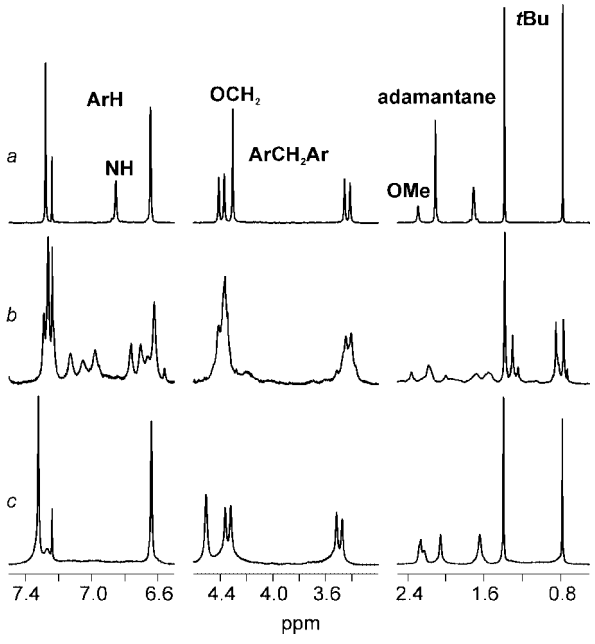
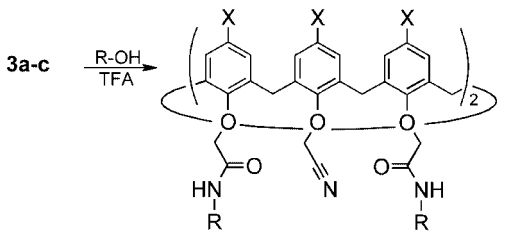


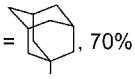
Figure 2. ^{1}H NMR spectra of (*a*) triamide **8a** and (*b*) triamide **8b** in $CDCl_3$ and (*c*) **8b** in $CDCl_3/CF_3CO_2D$.

The ^{1}H NMR spectrum of triamide **8a** exhibits two pairs of signals (1:1) arising from aromatic and *tert*-butyl protons and a pair of doublets due to nonequivalent axial and equatorial protons of the $ArCH_2Ar$ bridges (Figure 2, a). As for previously reported calix[6]arenes of this type the signal due to OMe in the case of triamide **8a** has a high-field shift (δ = 2.29 ppm). The ^{13}C NMR spectrum of **8a** exhibits signals corresponding to a C_{3v} symmetry with an $ArCH_2Ar$ resonance only at δ = 29.75 ppm, showing that all the neighboring aromatic fragments have a *syn* orientation.

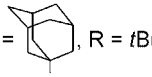
In pure $CDCl_3$ the ^{1}H NMR spectrum of **8b** is considerably more complicated (Figure 2, b), probably due to intra- and/or intermolecular bonding between the acid groups in the adamantane substituents. Upon the addition of a few drops of CF_3CO_2D both the ^{1}H and ^{13}C NMR spectra became distinct and similar to those obtained for **8a** (Figure 2, c). These data demonstrate that conformational restriction takes place in the case of **8b**.

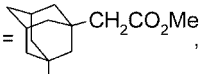
Selective Addition of Tertiary Alcohols to Hexanitriles: Unexpected behavior was observed for hexanitriles **3** under modified Ritter reaction conditions. It was found that even with an excess of 1-adamantanol or *tert*-butyl alcohol compounds **3** are converted into symmetrical tetraamides **9** as the major products in high yields instead of the expected hexaamides (Scheme 5).



9a, X = *t*Bu, R =  , 70%

9b, X = R = *t*Bu, 64%

9c, X =  , R = *t*Bu, 61%

9d, X = 

, R = *t*Bu, 56%

Scheme 5. Selective addition of tertiary alcohols to hexanitriles **3**.

The data obtained indicate that only four of the six nitrile groups are involved in the reaction while two remain inert. To the best of our knowledge this is the first example in calix[6]arene chemistry of a selective reaction at the lower rim in compounds with exhaustively modified OH groups. Usually selective modifications are achieved in calixarenes with free OH groups.

The structure of tetraamide **9a** was elucidated by means of ^{1}H, ^{13}C, H-C COSY, NOESY, temperature-dependent NMR and ESI-MS measurements. [Because of the low sol-

ubility of **9a** in chloroform ^{13}C and H-C COSY spectra were recorded in $CDCl_3/CF_3CO_2D$ (95:5); the NOESY spectrum was obtained in CD_2Cl_2.]

The molecular ion (m/z = 1839.26 $[M + Na]^+$) in the mass spectrum of **9a** corresponds to the product of the selective tetra-addition of 1-adamantanol to hexanitrile **3a**. No signals from molecules with a higher molecular weight were observed.

The ^1H NMR spectrum of **9a** (Figure 3) contains a pair of doublets (A, 4 H and D, 4 H) and two singlets (B, 4 H; C, 4 H) in the aromatic region, two pairs of doublets (E, 4 H and G, 4 H; F, 4 H and I, 4 H) and a singlet (H, 4 H) in the methylene region, a singlet (J, 4 H), two broadened signals in the adamantane region (K, 36 H; L, 24 H) and two singlets in the *tert*-butyl region (M, 18 H; N, 36 H). The ratios between the *tert*-butyl and adamantyl signals in the ^1H NMR spectrum confirm that molecule **9a** contains only four adamantane fragments. The presence of only two doublets and one singlet due to aromatic protons as well as the 1:2 ratio between the *tert*-butyl signals corresponds to a molecular symmetry with only two types of phenolic fragments (with equivalent and nonequivalent *meta* protons) in a 1:2 ratio.

The signals in the methylene region were assigned on the basis of H-C COSY experiments. Signals E and G correspond to the $OCH_2C(O)$ fragment, the pair of doublets F and I correspond to the methylene bridge between nonequivalent phenolic moieties, while the signal H corresponds to the bridge between equivalent ones. Also the signal J was assigned to the OCH_2CN group and the signal C, with no cross-peaks, to NH protons (see Figure 3).

The ^{13}C NMR spectrum, obtained at 300 K, exhibits two signals arising from C=O functions, 10 signals in the aromatic region, a signal characteristic of nitrile groups (δ = 115.28 ppm), only two signals from OCH_2CO (δ = 70.31 ppm) and OCH_2CN (δ = 58.26 ppm), two pairs of signals from *tert*-butyl groups, a double set of adamantane signals and two signals (1:2) at δ = 33.21 and 29.78 ppm corresponding to bridging $ArCH_2Ar$ carbon atoms. At 343 K ($C_2D_2Cl_4/CD_3CO_2D$) the ^{13}C NMR spectrum of **9a** contains only one averaged set of adamantylamide signals. Evidently, at 300 K slow N–C(O) bond rotation takes place. Thus, the ^{13}C NMR spectroscopic data support the proposed symmetry.

The data obtained confirm compound **9a** to be a *p*-*tert*-butylcalix[6]arene with four (1-adamantyl)amide fragments in the 1,2,4,5-positions and two cyanomethoxy groups in the 3,6-positions at the lower rim.

The well-resolved pattern of the calixarene methylene groups in the ^1H NMR spectrum implies a conformational restriction of the macrocycle on the NMR timescale. Only the 1,2,3- and 1,3,5-alternate conformations of 1,2,4,5-tetrasubstituted calix[6]arenes would generate a pair of doublets with an intervening singlet for methylene bridges (Figure 4).[3a] In both cases the adjacent adamantylamide moieties are *anti* to one another.

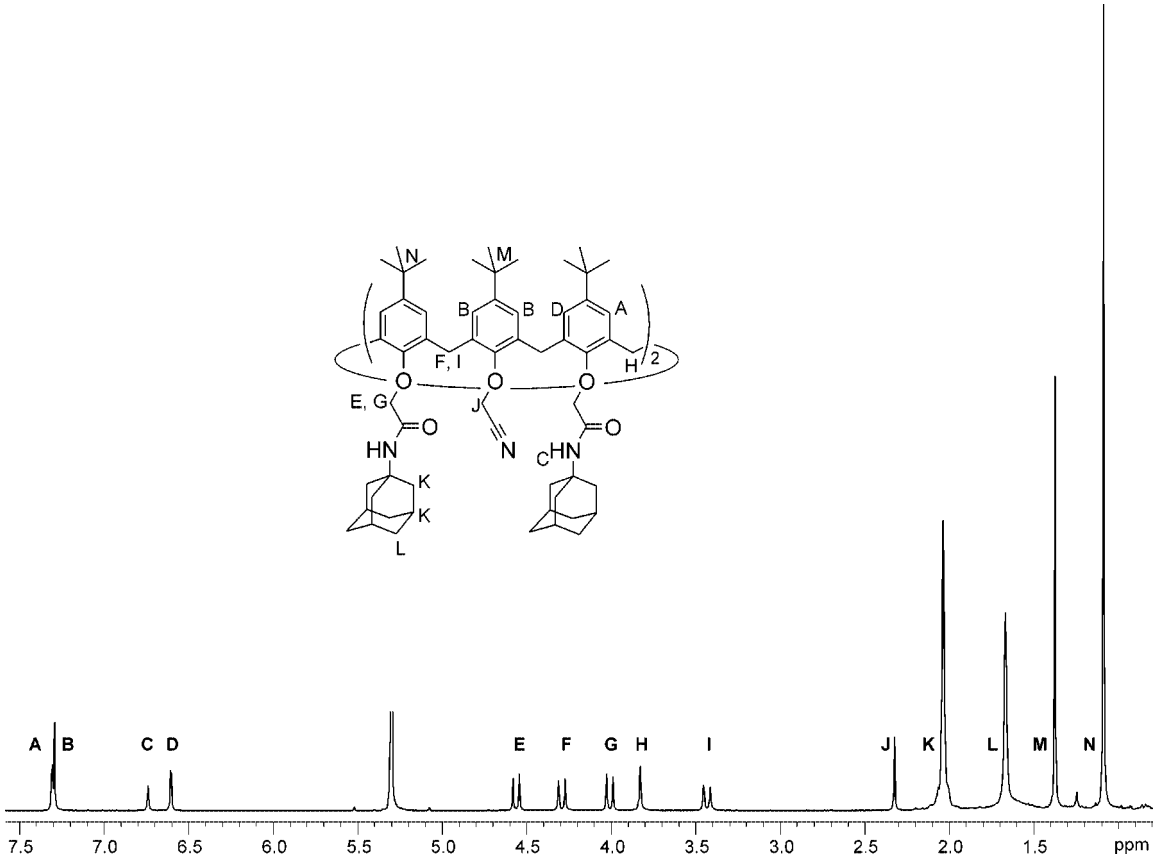


Figure 3. ^1H NMR spectrum of **9a** and its signal assignments.

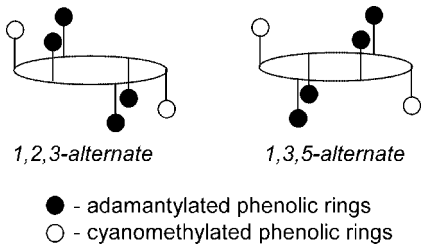


Figure 4. Possible conformations of tetraamide **9a**.

To choose between these two possibilities, a NOESY experiment was performed. Significant NOEs are given in Table 1 and are depicted by arrows in Figure 5.

Table 1. Significant NOEs between H_I and H_J in **9a**.[a,b]

H_I	H_J	NOE[c]
A	H	++
B	D	+
	I	+
C	B	+
	F	+
D	I	+
E	H	++
	K	++
F	C	+
	J	+
	K	++
G	I	++
	K	++
H	A	+++
	E	++
	K	+
I	B	+++
	D	+
	K	+
J	D	+
	F	+

[a] Measured by integration of the two-dimensional phase-sensitive NOESY spectrum (Bruker Avance 400, 2×10^{-3} M in CD_2Cl_2, 300 K). [b] See Figure 3 for notations. [c] All the observed NOEs are positive and denoted as +++ for strong (>4%), ++ for medium (2–4%) and + for weak (1–2%) effects, respectively.

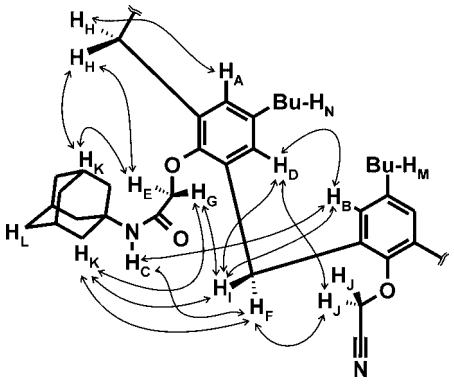


Figure 5. Significant NOEs in **9a**.

Cross-peaks A↔H and D↔I allowed the doublets in the aromatic region of the ^{1}H NMR spectrum to be correlated with the calixarene structure. The presence of NOEs between D and B and the fact that they have cross-peaks with only one proton of the neighboring $ArCH_2Ar$ moiety (signal I) show that the cyanomethylated and adamantylamide-containing phenolic rings have a *syn* orientation. Thus, the 1,2,3-alternate conformation appears to be the proper representation for compound **9a**. Moreover J has NOEs with D and F, indicating cyanomethoxy groups to be self-included in the calixarene cavity. This self-inclusion explains the high-field shift of CH_2CN fragments in the ^{1}H NMR spectrum of **9a** (δ = 2.31 ppm). In contrast, in the starting hexanitrile **3a**, the signal of these groups appears at δ = 4.00 ppm. Taking these observations into account the proposed conformation of tetranitrile **9a** is corrected to a flattened 1,2,3-alternate in which the two cyanomethylated phenolic moieties are closer to the average plane through the calixarene methylene groups than the adamantylamide-containing phenolic moieties. Other NOEs obtained allowed the methylene doublets to be assigned and the spatial orientation of adamantane fragments relative to the parent phenolic rings to be determined.

Next we calculated the molecular structures of the alternative configurations of calixarene **9a**. The calculations were performed with full geometry optimization using the semiempirical method AM1[15] in the Gaussian98 program package.[16]

The final molecular structure for tetraamide **9a** was determined from the experimental NOEs discussed above. The structure is presented in Figure 6.

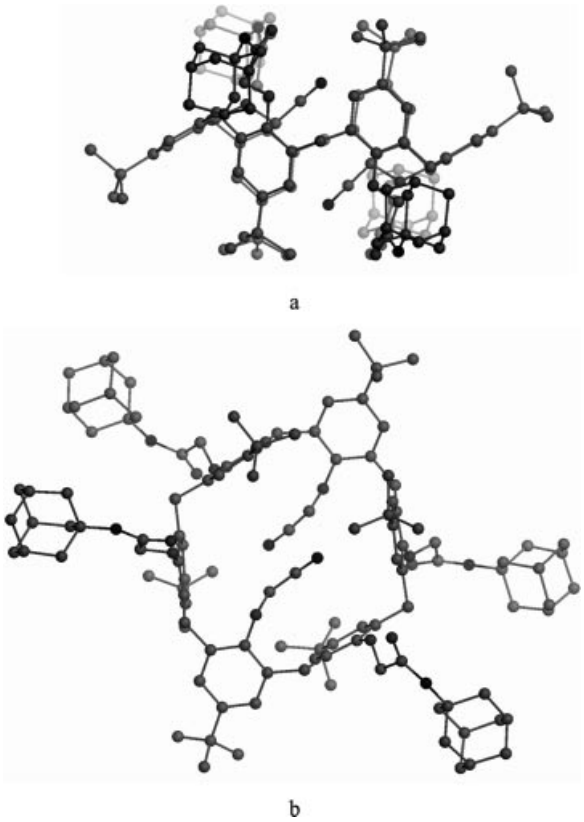


Figure 6. "Side" (a) and "top" (b) view of the calculated molecular structure of tetraamide **9a**.

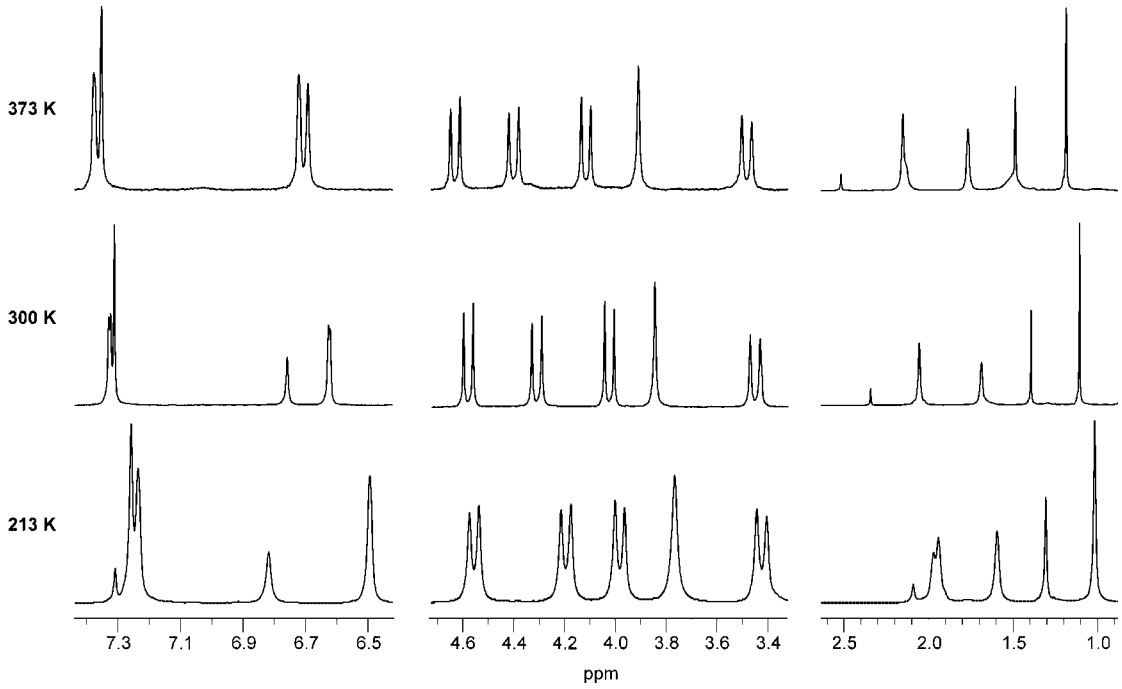


Figure 7. Parts of the ^{1}H NMR spectra of **9a** at different temperatures.

Important information on the conformational mobility of molecules can be obtained from variable-temperature NMR experiments. To investigate the mobility of the macrocycle ^{1}H NMR spectra of **9a** were recorded at different temperatures (low-temperature spectra were obtained in CD_2Cl_2 while high-temperature spectra were obtained in $C_2D_2Cl_4$). Selected spectra are presented in Figure 7.

Upon heating no significant change in the signals in the methylene region was observed showing that no conformational inversion takes place on the NMR timescale. At a low temperature no signals arising from minor conformations were observed in comparison, for instance, to *p-tert*-butylcalix[6]arene with alternating OMe and OCH_2Ph groups attached to the lower rim.[5c]

Nevertheless some changes in the chemical shifts of NH and CH_2CN protons were noted. Clearly while the general conformation of the calixarene platform is stable some substituents may undergo rotation. This is in good agreement with the calculations. Probably, at low temperatures molecules with more cavity-shielded CH_2CN protons are preferred among the mixture of rotamers, while at high temperatures molecules with less shielded ones are more stable. An inverse tendency is observed for NH-containing substituents in **9a**. Taking into account all the data discussed the tetraamide **9a** is stable in solution in a flattened 1,2,3-alternate conformation with less restricted rotation in the substituents.

Because all the NMR spectroscopic data for **9b**–**d** are in good agreement with those of **9a** the other tetraamides are assumed to have the same conformational properties.

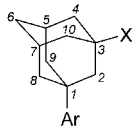
Conclusions

We have developed a procedure for the conversion of lower-rim cyanomethylated calix[6]arenes into the corresponding adamantylamides by a modified Ritter reaction performed in TFA. In the case of mono- and trinitriles conformationally restricted cone-shaped calix[6]arenes were obtained. Upon the addition of tertiary alcohols to calix[6]-arenes with six cyanomethoxy groups attached to the lower rim symmetrical tetraamide-dinitriles were formed with a unique regioselectivity. These derivatives are conformationally restricted over a wide range of temperatures and adopt a flattened 1,2,3-alternate conformation. Thus, in all cases, the Ritter reaction gave preorganized molecules containing 1–4 amide functions.

Experimental Section

The ^{1}H, ^{13}C, temperature-dependent, H-C COSY and NOESY NMR spectra were recorded with Bruker Avance 400 and AM 360 spectrometers with solvent signals as internal references. 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 with Micromass Ultima 3 and Agilent 1100 LC/MS instruments. Melting points were determined with a MEL TEMP 2 capillary melting point apparatus and are uncorrected. Because of its extremely low solubility in common organic solvents hexanitrile **3b** was used without performing a spectral analysis. To assign the chemical shifts in the ^{13}C NMR spectra the following symbols were used: δC_{calix} for carbon atoms of the calixarene skeleton, δCt_{Bu} for carbon atoms of the *tert*-butyl groups

attached to the upper rim, δC_{OR} for carbon atoms of substituents attached to the lower rim, δC_{Ad} for carbon atoms of monosubstituted adamantane fragments, $\delta C_{3\text{-}X\text{-}1\text{-}Ad}$ for carbon atoms of disubstituted adamantane fragments. The adamantane carbon atoms are numbered as given below.



Trinitrile 2: Under argon, a suspension of calixarene **4** (0.61 g, 0.6 mmol) and K_2CO_3 (4.98 g, 36 mmol) in dry acetone (40 mL) was stirred at room temperature for 30 min. KI (0.30 g, 1.8 mmol) and chloroacetonitrile (2.27 mL, 36 mmol) were added and the reaction mixture was stirred under reflux for 40 h. After cooling, the reaction mixture was filtered and the solvent was removed under reduced pressure. The remaining solid was taken up in chloroform and washed with water. The organic layer was dried with $MgSO_4$ and the solvent evaporated. The product was purified by column chromatography (gradient from hexane to hexane/THF, 5:1). Yield 42% (0.29 g); R_f = 0.25 (hexane/THF, 9:1); m.p. 155–157 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.13 (s, 6 H, ArH), 6.88 (s, 6 H, ArH), 4.38 (s, 6 H, OCH_2), 3.95 (s, 12 H, $ArCH_2Ar$), 2.79 (s, 9 H, OCH_3), 1.27 [s, 27 H, $C(CH_3)_3$], 1.04 [s, 27 H, $C(CH_3)_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δC_{calix} = 153.99, 150.56, 147.51, 146.16, 133.49, 132.63 (C_{Ar}), 126.98, 125.35 (CH_{Ar}), 30.76 ($ArCH_2Ar$) ppm; δCt_{Bu} = 34.07 [$C(CH_3)_3$], 31.32, 31.05 [$C(CH_3)_3$] ppm; δC_{OR} = 115.86 (CN), 59.99 (OCH_3), 57.24 (OCH_2) ppm. ESI-MS: *m*/*z* = 1150.7 $[M + NH_4]^+$; $C_{75}H_{93}N_3O_6{\cdot}NH_4$ (1150.6).

Hexanitrile 3b: Prepared in the same way as **2** using calixarene **5a** (0.72 g, 0.5 mmol), K_2CO_3 (0.83 g, 6.0 mmol), KI (0.13 g, 0.75 mmol) and chloroacetonitrile (0.38 mL, 6.0 mmol) in dry acetone (20 mL) under reflux for 28 h. After cooling to –12 °C, the reaction mixture was filtered and the solvent was removed under reduced pressure. The remaining solid was taken up in chloroform, filtered and washed with water. The organic layer was dried with $MgSO_4$ and the solvent evaporated. The remaining solid was washed with hot acetone. Yield 27% (0.23 g); R_f = 0.30 (chloroform/ethanol, 20:1); m.p. 272–274 °C.

Hexanitrile 3c: Prepared in the same way as **2** using calixarene **5b** (0.37 g, 0.2 mmol), K_2CO_3 (0.33 g, 2.4 mmol), KI (0.05 g, 0.3 mmol) and chloroacetonitrile (0.15 mL, 2.4 mmol) in dry acetone (20 mL) under reflux for 28 h. The product was purified by column chromatography (gradient from chloroform to chloroform/ethanol, 10:1). Yield 52% (0.22 g); R_f = 0.50 (chloroform/ethanol, 15:1); m.p. 138–140 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.00 (s, 12 H, ArH), 4.14 (s, 12 H, CH_2CN), 3.96 (s, 12 H, $ArCH_2Ar$), 3.60 (s, 18 H, OCH_3), 2.20–1.40 (m, 84 H, H_{Ad} + 12 H, CH_2CO) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δC_{calix} = 151.11, 147.52, 133.02 (C_{Ar}), 126.33 (CH_{Ar}), 31.70 ($ArCH_2Ar$) ppm; $\delta C_{3\text{-}X\text{-}1\text{-}Ad}$ = 171.81 (CO), 50.97 (OCH_3), 48.15 (C-2), 47.85 (CH_2CO), 42.22 (C-4,-10)*, 41.07 (C-8,-9)*, 36.61 (C-6), 35.53 (C-3), 33.44 (C-1), 28.97 (C-5,-7) ppm; δC_{OR} = 115.70 (CN), 57.60 (CH_2CN) ppm. ESI-MS: *m*/*z* = 2131.5 $[M + Na]^+$; $C_{132}H_{150}N_6NaO_{18}$ (2131.7).

Monoamide 6a: A mixture of calixarene **1** (0.51 g, 0.5 mmol), 1-adamantanol (0.15 g, 1 mmol), TFA (5 mL) and 1,2-dichloroethane (5 mL) was heated in a dry atmosphere at 70–75 °C for 7 h. After cooling, the solvent was evaporated under reduced pressure, the remaining solid was taken up in water and allowed to stand overnight. The precipitate formed was collected, washed with water and dried. The product was purified by column chromatography (chloroform/hexane, 1:2). Yield 53% (0.31 g); R_f = 0.45 (chloroform); m.p. 220–222 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.83 (s, 3 H, OH), 8.21 (s, 2 H, OH), 7.64 (s, 1 H, NH), 7.21 (d, *J* = 1.95 Hz, 2 H, ArH), 7.18 (s, 4 H, ArH), 7.14 (d, *J* = 1.95 Hz, 2 H, ArH), 7.12 (s, 2 H, ArH), 7.03 (s, 2 H, ArH), 4.47 (s, 2 H, OCH_2), 4.43 (d, *J* = 13.18 Hz, 2 H, $ArCH_2Ar$), 4.28 (d, *J* = 13.67 Hz, 2 H, $ArCH_2Ar$), 4.00 (d, *J* = 14.16 Hz, 2 H, $ArCH_2Ar$), 3.59 (d, *J* = 13.67 Hz, 2 H, $ArCH_2Ar$), 3.54 (d, *J* = 13.18 Hz, 2 H, $ArCH_2Ar$), 3.50 (d, *J* = 14.16 Hz, 2 H, $ArCH_2Ar$), 2.27 (s, 6 H, $CH_{2,Ad}$), 2.12 (s, 3 H, CH_{Ad}), 1.90–1.65 (m, 6 H, $CH_{2,Ad}$), 1.32 [s, 18 H, $C(CH_3)_3$], 1.31 [s, 18 H, $C(CH_3)_3$], 1.25 [s, 9 H, $C(CH_3)_3$], 1.17 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δC_{calix} = 149.80, 148.76, 148.21, 147.76, 146.22, 144.56, 143.87, 143.45, 127.84, 127.33, 126.91, 126.46 (C_{Ar}), 126.28, 126.18, 125.97, 125.93, 125.83, 125.70 (CH_{Ar}), 33.09, 32.41 ($ArCH_2Ar$) ppm; δCt_{Bu} = 34.13, 33.91, 33.88 [$C(CH_3)_3$], 31.80, 31.47, 31.90, 31.03 [$C(CH_3)_3$] ppm; δC_{OR} = 167.66 (CO), 74.55 (OCH_2) ppm; δC_{Ad} = 52.22 (C-1), 41.29 (C-2,-8,-9), 36.17 (C-4,-6,-10), 29.46 (C-3,-5,-7) ppm. ESI-MS: *m*/*z* = 1165.7 $[M + H]^+$; $C_{78}H_{101}NO_7{\cdot}H$ (1165.7).

Monoamide 6b: Prepared in the same way as **6a** using calixarene **1** (0.51 g, 0.5 mmol), 3-hydroxy-1-adamantylacetic acid (0.21 g, 1 mmol), TFA (5 mL) and 1,2-dichloroethane (5 mL) at 65–70 °C for 15 h. The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol, 20:1). Yield 54% (0.33 g); R_f = 0.45 (chloroform/ethanol, 20:1); m.p. 204–206 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.77 (s, 3 H, OH), 8.14 (s, 2 H, OH), 7.75 (s, 1 H, NH), 7.18 (d, *J* = 2.05 Hz, 2 H, ArH), 7.14 (s, 4 H, ArH), 7.11 (d, *J* = 2.05 Hz, 2 H, ArH), 7.09 (s, 2 H, ArH), 7.00 (s, 2 H, ArH), 4.46 (s, 2 H, CH_2CON), 4.38 (d, *J* = 13.45 Hz, 2 H, $ArCH_2Ar$), 4.24 (d, *J* = 13.45 Hz, 2 H, $ArCH_2Ar$), 3.96 (d, *J* = 13.97 Hz, 2 H, $ArCH_2Ar$), 3.57 (d, *J* = 13.45 Hz, 2 H, $ArCH_2Ar$), 3.52 (d, *J* = 13.45 Hz, 2 H, $ArCH_2Ar$), 3.49 (d, *J* = 13.97 Hz, 2 H, $ArCH_2Ar$), 2.35–1.95, 1.75–1.50 (m, 14 H, H_{Ad} + 2 H, CH_2COO), 1.29 [s, 18 H, $C(CH_3)_3$], 1.28 [s, 18 H, $C(CH_3)_3$], 1.22 [s, 9 H, $C(CH_3)_3$], 1.14 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δC_{calix} = 149.83, 148.70, 148.25, 147.75, 146.20, 144.55, 143.89, 143.46, 131.94, 127.71, 127.26, 126.88 (C_{Ar}), 126.40, 126.29, 126.21, 125.93, 125.87, 125.73 (CH_{Ar}), 33.01, 32.45 ($ArCH_2Ar$) ppm; δCt_{Bu} = 34.35, 33.91, 33.88 [$C(CH_3)_3$], 31.86, 31.48, 31.31, 31.03 [$C(CH_3)_3$] ppm; δC_{OR} = 168.12 (CON), 74.36 (OCH_2) ppm; $\delta C_{3\text{-}X\text{-}1\text{-}Ad}$ = 176.00 (COO), 52.86 (C-1), 47.50 (CH_2COO), 45.52 (C-2), 40.59 (C-4,-10)*, 40.57 (C-8,-9)*, 35.27 (C-6), 34.13 (C-3), 29.47 (C-5,-7) ppm. ESI-MS: *m*/*z* = 1223.7 $[M + H]^+$; $C_{80}H_{103}NO_9{\cdot}H$ (1223.7).

Monoamide-pentaester 7: Under argon, a suspension of calixarene **6a** (0.31 g, 0.266 mmol), K_2CO_3 (1.84 g, 13.3 mmol) and ethyl bromoacetate (1.47 mL, 13.3 mmol) in dry acetone (40 mL) was stirred under reflux for 40 h. After cooling, the reaction mixture was filtered and the solvent was removed under reduced pressure. The remaining solid was taken up in CH_2Cl_2 and washed with 2 M HCl and water. The organic layer was dried with $MgSO_4$ and the solvents evaporated. The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol, 10:1). Yield 40% (0.17 g); R_f = 0.30 (chloroform/ethanol, 15:1). m.p. 142–144 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.07 (br. s, 12 H, ArH), 5.80–3.20 (m, 12 H, $ArCH_2Ar$ + 10 H, OCH_2CH_3 + 12 H, CH_2CO), 2.25–1.55 (m, 15 H, H_{Ad}), 1.50–0.75 [m, 54 H, $C(CH_3)_3$], 0.66 (br. s, 15 H, CH_3) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δC_{calix} = 153.21 (br. s), 146.28, 132.86, 132.69, 132.60, 132.37, 132.11 (C_{Ar}), 126.41 (m, CH_{Ar}) ppm; δCt_{Bu} = 33.97, 33.90, 33.72, 33.65 [$C(CH_3)_3$], 31.33, 31.22, 30.91 [$C(CH_3)_3$] ppm; δC_{OR} = 169.15, 169.04 (COO), 167.92 (CON), 71.64, 70.55, 70.48, 70.29 (CH_2COO), 68.07 (CH_2CON), 60.84, 60.72, 60.62, 60.52

(O*C*H$_2$CH$_3$), 14.10, 14.06, 13.94 (CH$_3$) ppm; δC$_{Ad}$ = 51.79 (C-1), 41.33 (C-2,-8,-9), 36.27 (C-4,-6,-10), 29.41 (C-3,-5,-7) ppm. ESI-MS: *m*/*z* = 1617.8 [M + Na]$^+$; $C_{98}H_{131}NNaO_{17}$ (1618.1).

Triamide 8a: Prepared in the same way as **6a** using calixarene **2** (0.075 g, 0.066 mmol), 1-adamantanol (0.045 g, 0.297 mmol), TFA (0.46 mL, 5.84 mmol) and 1,2-dichloroethane (1 mL) at 60 °C for 6 h. The precipitate formed upon addition of water was collected, washed with methanol and dried. Yield 76% (0.08 g); R_f = 0.50 (chloroform/ethanol, 20:1); m.p. 242–244 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.28 (s, 6 H, ArH), 6.85 (s, 3 H, NH), 6.64 (s, 6 H, ArH), 4.39 (d, *J* = 15.13 Hz, 6 H, ArCH$_2$Ar), 4.30 (s, 6 H, OCH$_2$), 3.34 (d, *J* = 15.13 Hz, 6 H, ArCH$_2$Ar), 2.29 (s, 9 H, OCH$_3$), 2.11 (s, 27 H, CH$_{2,Ad}$), 1.71 (s, 9 H, CH$_{2,Ad}$ + 9 H, CH$_{Ad}$), 1.39 [s, 27 H, C(CH$_3$)$_3$], 0.78 [s, 27 H, C(CH$_3$)$_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δC$_{calix}$ = 154.26, 150.48, 146.63, 146.19, 133.07, 132.60 (C$_{Ar}$), 128.04, 123.90 (CH$_{Ar}$), 29.75 (ArCH$_2$Ar) ppm; δC*t*$_{Bu}$ = 34.17, 33.89 [*C*(CH$_3$)$_3$], 31.50, 30.93 [C(*C*H$_3$)$_3$] ppm; δC$_{OR}$ = 167.41 (CO), 71.75 (OCH$_2$), 60.04 (OCH$_3$) ppm; δC$_{Ad}$ = 51.78 (C-1), 41.48 (C-2,-8,-9), 36.23 (C-4,-6,-10), 29.40 (C-3,-5,-7) ppm. ESI-MS: *m*/*z* = 1612.1 [M + Na]$^+$; $C_{105}H_{141}N_3NaO_9$ (1612.3).

Triamide 8b: Prepared in the same way as **6a** using calixarene **2** (0.34 g, 0.3 mmol), 3-hydroxy-1-adamantylacetic acid (0.28 g, 1.35 mmol), TFA (1.35 mL) and 1,2-dichloroethane (1.35 mL) at 60–65 °C for 25 h. The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol, 10:1). Yield 64% (0.34 g); R_f = 0.25 (chloroform/ethanol, 15:1); m.p. 165–167 °C. ^{1}H NMR (360 MHz, $CDCl_3/CF_3CO_2D$): δ = 7.32 (s, 6 H, ArH), 6.64 (s, 6 H, ArH), 4.51 (s, 6 H, OCH$_2$), 4.34 (d, *J* = 15.26 Hz, 6 H, ArCH$_2$Ar), 3.49 (d, *J* = 15.26 Hz, 6 H, ArCH$_2$Ar), 2.35–1.50 (m, 9 H, OCH$_3$ + 6 H, CH$_2$COO + 42 H, H$_{Ad}$), 1.40 [s, 27 H, C(CH$_3$)$_3$], 0.78 [s, 27 H, C(CH$_3$)$_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3/CF_3CO_2D$): δC$_{calix}$ = 153.25, 149.92, 147.48, 147.28, 132.77, 132.16 (C$_{Ar}$), 128.60, 124.11 (CH$_{Ar}$), 29.59 (ArCH$_2$Ar) ppm; δC*t*$_{Bu}$ = 34.23, 33.94 [*C*(CH$_3$)$_3$], 31.35, 30.85 [C(*C*H$_3$)$_3$] ppm; δC$_{OR}$ = 170.82 (CON), 70.39 (OCH$_2$), 60.17 (OCH$_3$) ppm; δC$_{3\text{-}X\text{-}1\text{-}Ad}$ = 178.57 (COO), 53.28 (C-1), 47.26 (*C*H$_2$COO), 44.79 (C-2), 40.64 (C-4,-10), 39.90 (C-8,-9), 34.86 (C-6), 34.48 (C-3), 29.21 (C-5,-7) ppm. ESI-MS: *m*/*z* = 1786.4 [M + Na]$^+$; $C_{111}H_{147}N_3NaO_{15}$ (1786.4).

Tetraamide 9a: Prepared in the same way as **6a** using calixarene **3a** (0.18 g, 0.15 mmol), 1-adamantanol (0.27 g, 1.8 mmol), TFA (1.39 mL, 18 mmol) and 1,2-dichloroethane (2 mL) at 70–75 °C for 17 h. After cooling, the reaction mixture was evaporated under reduced pressure and the remaining oil was taken up in methanol. The precipitate formed was collected, washed with methanol and dried. Yield 70% (0.19 g); R_f = 0.50 (chloroform/ethanol, 20:1); m.p. > 350 °C. ^{1}H NMR (360 MHz, $CDCl_3/CF_3CO_2D$): δ = 7.34 (s, 4 H, ArH), 7.25 (d, *J* = 1.62 Hz, 4 H, ArH), 7.15 (s, 4 H, NH), 6.64 (d, *J* = 1.62 Hz, 4 H, ArH), 4.74 (d, *J* = 15.72 Hz, 4 H, OCH$_2$CO), 4.23 (d, *J* = 15.25 Hz, 4 H, ArCH$_2$Ar), 4.21 (d, *J* = 15.72 Hz, 4 H, OCH$_2$CO), 3.83 (s, 4 H, ArCH$_2$Ar), 3.46 (d, *J* = 15.25 Hz, 4 H, ArCH$_2$Ar), 2.28 (s, 4 H, OCH$_2$CN), 2.06 (s, 36 H, CH$_{2,Ad}$), 1.68 (s, 12 H, CH$_{2,Ad}$ + 12 H, CH$_{Ad}$), 1.42 [s, 18 H, C(CH$_3$)$_3$], 1.09 [s, 36 H, C(CH$_3$)$_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3/CF_3CO_2D$): δC$_{calix}$ = 153.32, 150.71, 148.44, 147.86, 133.30, 132.26, 131.78 (C$_{Ar}$), 128.64, 127.06, 124.47 (CH$_{Ar}$), 33.21, 29.78 (ArCH$_2$Ar) ppm; δC*t*$_{Bu}$ = 34.40, 34.15 [*C*(CH$_3$)$_3$], 31.37, 31.28 [C(*C*H$_3$)$_3$] ppm; δC$_{OR}$ = 170.17, 170.10 (CO), 115.28 (CN), 70.31 (O*C*H$_2$CO), 58.26 (O*C*H$_2$CN) ppm; δC$_{Ad}$ = 53.32, 53.20 (C-1), 41.07 (C-2,-8,-9), 36.00 (C-4,-6,-10), 29.30 (C-3,-5,-7) ppm. ESI-MS: *m*/*z* = 1839.26 [M + Na]$^+$; $C_{118}H_{154}N_6NaO_{10}$ (1839.54).

Tetraamide 9b: Prepared in the same way as **9a** using calixarene **3a** (0.12 g, 0.1 mmol), *tert*-butyl alcohol (0.089 g, 1.2 mmol), TFA (0.93 mL, 12 mmol) and 1,2-dichloroethane (1.35 mL) at 70–75 °C for 7 h. Yield 64% (0.095 g); R_f = 0.50 (chloroform/ethanol, 20:1); m.p. > 350 °C. ^{1}H NMR (360 MHz, $CDCl_3/CF_3CO_2D$): δ = 7.46 (s, 4 H, NH), 7.31 (s, 4 H, ArH), 7.27 (d, *J* = 1.52 Hz, 4 H, ArH), 6.65 (d, *J* = 1.52 Hz, 4 H, ArH), 4.94 (d, *J* = 16.02 Hz, 4 H, OCH$_2$CO), 4.23 (d, *J* = 16.02 Hz, 4 H, OCH$_2$CO), 4.14 (d, *J* = 15.26 Hz, 4 H, ArCH$_2$Ar), 3.82 (s, 4 H, ArCH$_2$Ar), 3.46 (d, *J* = 15.26 Hz, 4 H, ArCH$_2$Ar), 2.47 (s, 4 H, OCH$_2$CN), 1.40 [s, 18 H, ArC(CH$_3$)$_3$ + 36 H, NC(CH$_3$)$_3$], 1.10 [s, 36 H, ArC(CH$_3$)$_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3/CF_3CO_2D$): δC$_{calix}$ = 153.73, 151.00, 148.67, 148.01, 132.96, 131.99, 131.51 (C$_{Ar}$), 128.50, 127.17, 124.84 (CH$_{Ar}$), 33.86, 29.90 (ArCH$_2$Ar) ppm; δC*t*$_{Bu}$ = 34.38, 34.14 [*C*(CH$_3$)$_3$], 31.26, 31.19 [C(*C*H$_3$)$_3$] ppm; δC$_{OR}$ = 170.90, 170.85 (CO), 115.65 (CN), 70.08 (O*C*H$_2$CO), 58.55 (O*C*H$_2$CN), 52.68, 52.57 [N*C*(CH$_3$)$_3$], 28.40 [NC(*C*H$_3$)$_3$] ppm. ESI-MS: *m*/*z* = 1527.2 [M + Na]$^+$; $C_{94}H_{130}N_6NaO_{10}$ (1527.1).

Tetraamide 9c: Prepared in the same way as **9a** using calixarene **3b** (0.17 g, 0.1 mmol), *tert*-butyl alcohol (0.089 g, 1.2 mmol), TFA (0.93 mL, 12 mmol) and 1,2-dichloroethane (1.35 mL) at 70–75 °C for 7 h. The product was purified by column chromatography (chloroform). Yield 61% (0.12 g); R_f = 0.45 (chloroform/ethanol, 15:1); m.p. > 350 °C. ^{1}H NMR (360 MHz, $CDCl_3/CF_3CO_2D$): δ = 7.33 (s, 4 H, NH), 7.26 (s, 4 H, ArH), 7.19 (br. s, 4 H, ArH), 6.72 (br. s, 4 H, ArH), 5.00 (d, *J* = 15.80 Hz, 4 H, CH$_2$CO), 4.17 (d, *J* = 15.80 Hz, 4 H, CH$_2$CO), 4.11 (d, *J* = 15.26 Hz, 4 H, ArCH$_2$Ar), 3.81 (s, 4 H, ArCH$_2$Ar), 3.43 (d, *J* = 15.26 Hz, 4 H, ArCH$_2$Ar), 2.61 (s, 4 H, CH$_2$CN), 2.20–1.20 [m, 36 H, C(CH$_3$)$_3$ + 90 H, H$_{Ad}$] ppm. ^{13}C NMR (90 MHz, $CDCl_3/CF_3CO_2D$): δC$_{calix}$ = 154.01, 151.38, 148.53, 148.04, 132.65, 131.66, 131.02 (C$_{Ar}$), 127.98, 126.25, 125.14 (CH$_{Ar}$), 34.60, 29.88 (ArCH$_2$Ar) ppm; δC$_{Ad}$ = 43.53, 42.87 (C-2,-8,-9), 36.68, 36.42 (C-4,-6,-10), 35.96, 35.78 (C-1), 28.90, 28.71 (C-3,-5,-7) ppm; δC$_{OR}$ = 171.07, 171.00 (CO), 115.89 (CN), 69.96 (*C*H$_2$CO), 58.50 (*C*H$_2$CN), 52.47, 52.36 [*C*(CH$_3$)$_3$], 28.38 [C(*C*H$_3$)$_3$] ppm. ESI-MS: *m*/*z* = 1974.1 [M + H]$^+$; $C_{130}H_{166}N_6O_{10}$·H (1973.8).

Tetraamide 9d: Prepared in the same way as **9a** using calixarene **3c** (0.11 g, 0.05 mmol), *tert*-butyl alcohol (0.044 g, 0.6 mmol), TFA (0.47 mL, 6.1 mmol) and 1,2-dichloroethane (0.7 mL) at 70–75 °C for 14 h. After washing with methanol the solid was reprecipitated from chloroform solution upon addition of hexane, filtered and dried. Yield 56% (0.07 g); R_f = 0.45 (chloroform/ethanol, 20:1); m.p. 272–274 °C (decomp.). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.18 (br. s, 8 H, ArH), 7.04 (s, 4 H, NH), 6.62 (br. s, 4 H, ArH), 4.82 (d, *J* = 15.26 Hz, 4 H, OCH$_2$CO), 4.19 (d, *J* = 15.26 Hz, 4 H, ArCH$_2$Ar), 3.96 (d, *J* = 15.26 Hz, 4 H, OCH$_2$CO), 3.78 (s, 4 H, ArCH$_2$Ar), 3.63 (s, 6 H, OCH$_3$), 3.62 (s, 12 H, OCH$_3$), 3.36 (d, *J* = 15.26 Hz, 4 H, ArCH$_2$Ar), 2.59 (s, 4 H, CH$_2$CN), 2.30–1.40 (m, 12 H, C*H*$_2$COOCH$_3$ + 84 H, H$_{Ad}$), 1.35 [s, 36 H, C(CH$_3$)$_3$] ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δC$_{calix}$ = 153.91, 152.04, 147.28, 146.51, 132.82, 132.10, 131.12 (C$_{Ar}$), 127.71, 126.36, 124.51 (CH$_{Ar}$), 34.54, 29.88 (ArCH$_2$Ar) ppm; δC$_{3\text{-}X\text{-}1\text{-}Ad}$ = 171.67, 171.62 (CO), 51.03, 51.00 (OCH$_3$), 49.76 (C-2)*, 48.09, 48.05 (*C*H$_2$CO)*, 42.78 (C-4,-10)*, 41.11, 40.83 (C-8,-9)*, 36.69, 36.49 (C-6), 35.68, 35.30 (C-1), 33.49, 33.45 (C-3), 28.83, 28.74 (C-5,-7) ppm; δC$_{OR}$ = 167.71 (CO), 115.45 (CN), 71.18 (*C*H$_2$CO), 58.15 (*C*H$_2$CN), 50.89 [*C*(CH$_3$)$_3$], 29.05, 29.00 [C(*C*H$_3$)$_3$] ppm. ESI-MS: *m*/*z* = 2424.2 [M + H$_2$O + H]$^+$; $C_{148}H_{190}N_6O_{22}$·H$_2$O·H (2424.2).

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