Selective Monofunctionalization of Tri-urea-mono-acetamides of Calix[4]arenes on the Narrow Rim

Yuliya Rudzevich,*[a] Valentyn Rudzevich,[a,1] Michael Bolte,[b,2] Volker Böhmer*[a]

[a] Abteilung Lehramt Chemie, Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55099 Mainz, Germany
Fax +49(6131)3925419; E-mail: rudzevic@mail.uni-mainz.de; E-mail: vboehmer@mail.uni-mainz.de

[b] Fachbereich Chemie und Pharmazeutische Wissenschaften, Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität, Max-von-Laue-Str. 7, 60438 Frankfurt/Main, Germany
Fax +49(69)79829239; E-mail: bolte@chemie.uni-frankfurt.de

Received 4 October 2007; revised 16 November 2007

Abstract: The synthesis of calix[4]arenes substituted at their wide rim by three 3-aryl-urea and one acetamide group and at their narrow rim by three alkyl ether groups and one ether group ending in a carboxy function is described. The reaction sequence ensures that these functional groups are attached to the same phenolic unit. Two key intermediates have been additionally characterized by X-ray crystal structure analysis.

Key words: calixarenes, alkylations, carboxylic acids, self-assembly, supramolecular chemistry

Tetra-urea calix[4]arenes of type **1** form hydrogen-bonded, dimeric capsules (Figure 1, a) in apolar, aprotic solvents.[3] This dimerization can be used (and has been used) to construct various linear polymers from building blocks consisting of tetra-urea derivatives covalently connected via their narrow[4,5] rims. The construction of dendritic structures can be achieved in a similar way, which however, requires several independent (self) complementary motifs.[6] Recently we succeeded in building up dendrimers,[7] using the selective dimerization of tri-urea triphenylmethanes[8] for the core and the selective dimerization of tetra-urea calix[4]arenes for the formation of the shell.[9]

Tri-urea monoacetamide derivative **2** forms S_4-symmetrical tetrameric assemblies (Figure 1, b) in solution and in the crystalline state.[10] This tetramerization occurs independently from the dimerization of tetra-urea calix[4]arenes. Therefore, such tetramers would be ideal cores for the construction of dendrimers. For this purpose **2** has to be connected covalently to further calixarene derivatives via the narrow rim and, thus, must be further functionalized. To obtain structurally uniform dendrimers, an additional function must be introduced selectively either at the aromatic ring possessing an acetamide group or opposite to it.[11] Functionalization of one of the other phenolic units leads to chiral calix[4]arenes and hence to a mixture of diastereomeric dendritic assemblies. Statistical monofunctionalization would be even worse.

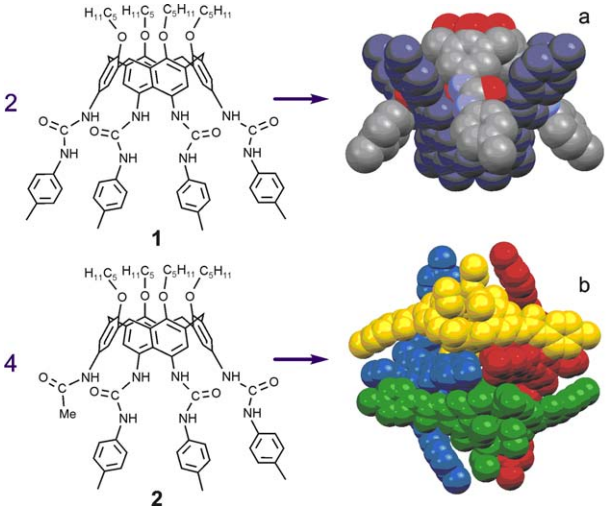


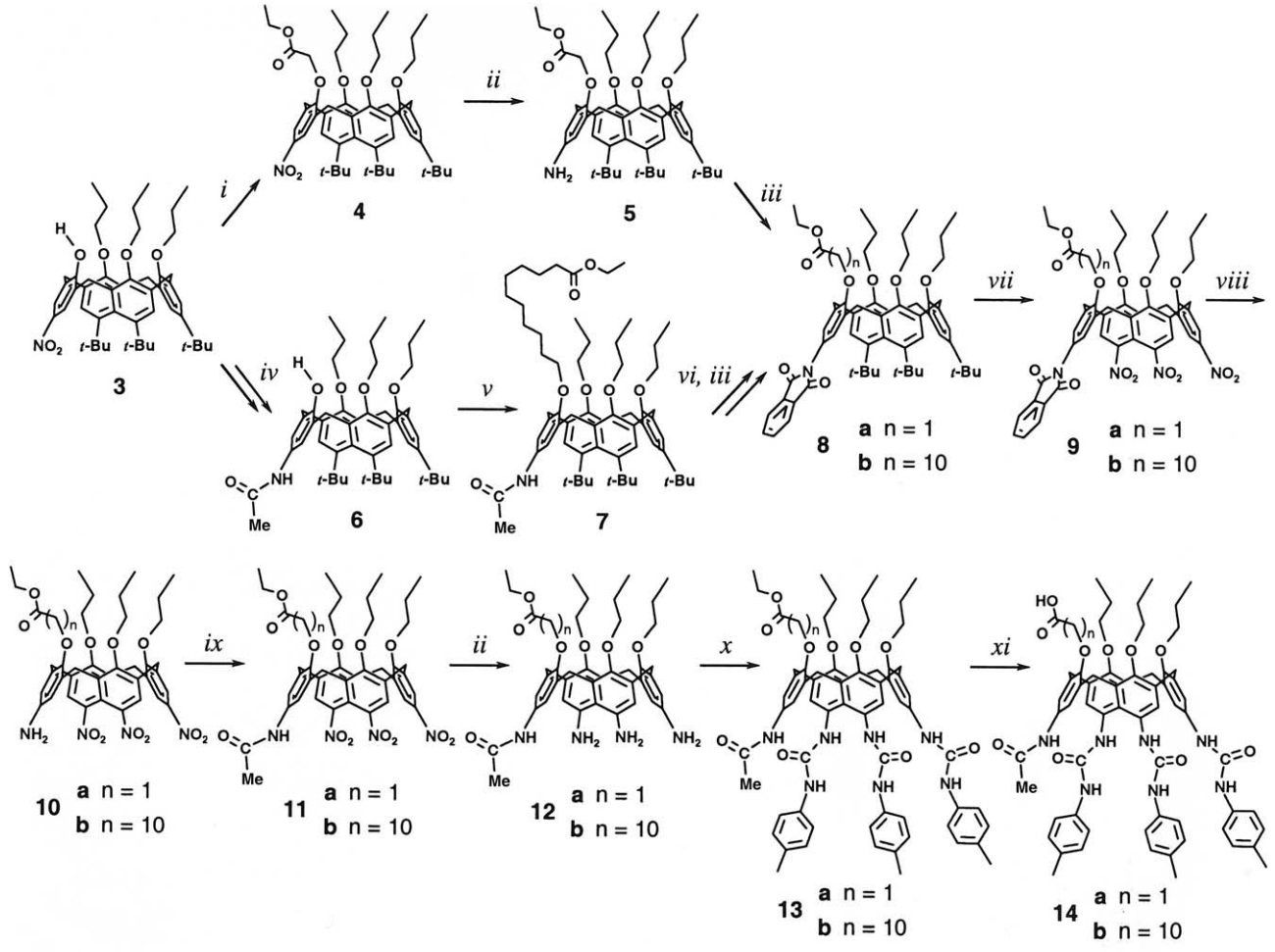
Figure 1 Dimeric capsule of tetra-urea calix[4]arenes **1** (a) and tetrameric assembly of tri-urea monoacetamide derivative **2** (b)

With this background we have tried to introduce a carboxylic group[12] as an additional functional group on the narrow rim in the phenolic ring bearing the acetamide group.[13] It is separated from the calixarene skeleton by a short (C_1) and a long (C_{10}) alkyl chain in order to vary the length of the spacer in the further dendrons. A synthetic sequence is described and discussed here.

The synthesis of **14a** started with the mononitro-tripropyl-calixarene **3**, which was easily prepared by selective *ipso*-nitration of the tripropyl ether of *tert*-butyl-calix[4]arene.[14] Alkylation with ethyl bromoacetate afforded **4** in 79% yield (Scheme 1). In principle, its nitro group could be easily reduced and then acetylated. However, the subsequent *ipso*-nitration of the remaining *tert*-butylphenol rings would lead to products (at least byproducts), in which the position *ortho* to the *N*-acylamino group is also substituted.[15] Recently it was shown that the protection of the amino groups by phthalimide allows *ipso*-nitration to be restricted to the desired replacement of *tert*-butyl groups.[16] Thus compound **4** was reduced and monoamine **5** was condensed with phthalic acid anhydride [$Zn(OAc)_2$, pyridine] to give **8a** in 73% yield.

For the synthesis of **14b** bearing the carboxylic function on a longer alkyl chain the analogous reaction sequence is

SYNTHESIS 2008, No. 5, pp 0754–0762
Advanced online publication: 08.02.2008
DOI: 10.1055/s-2008-1032155; Art ID: T15607SS



Scheme 1 Synthesis of the tri(tolyl)urea monoacetamides **14**. *Reagents and conditions*: (i) Na_2CO_3, MeCN, reflux; (ii) Raney Ni, toluene–EtOH; (iii) $Zn(OAc)_2$, phthalic anhydride, pyridine, reflux; (iv) Raney Ni, toluene–THF; Ac_2O, Et_3N; (v) $Br(CH_2)_{10}CO_2Et$, NaH, DMF; (vi) THF–MeOH, NaOH–H_2O, reflux; EtOH, H_2SO_4, reflux; (vii) HNO_3, CH_2Cl_2–AcOH; (viii) HCl, toluene–EtOH, reflux; (ix) Ac_2O, Et_3N, $CHCl_3$; (x) 4-TolNCO, CH_2Cl_2; (xi) THF–DMF, NaOH–H_2O (for **14a**), THF–MeOH, NaOH–H_2O (for **14b**).

not possible. The direct alkylation of the deactivated 4-nitrophenol ring in **3** with ethyl 11-bromoundecanoate failed due to the lower reactivity of the alkylating agent in comparison to ethyl bromoacetate. Therefore, the mono-nitro derivative **3** was reduced and acetylated in situ to **6** (99%) (Scheme 1). The following alkylation was easy, giving **7** in 93% yield. As discussed above, **7** cannot be directly nitrated to **11b**. In the next two steps the acetamide group was therefore replaced by the phthalimide group.

The *ipso*-nitration of compounds **8** gave trinitro mono-phthalimide derivatives **9** in 89–95% yield. The phthalimide group was readily cleaved with a threefold excess of hydrochloric acid and the resulting amines **10** were acylated with acetic anhydride. The calixacetamides **11**, in which the ester group at the narrow rim and the acetamide group at the wide rim are introduced at the same aromatic ring, were obtained in 76–98% yield. Finally, the reduction of the remaining nitro groups (83–85% of **12**), followed by acylation with 4-tolyl isocyanate (65–86% of **13**), and hydrolysis of the ester function afforded the target compounds **14** (98%).

The spectrum of **13a** in $CDCl_3$ shown in Figure 2 is very similar to that of compound **2** described previously.[10] This confirms the formation of a tetramer with the same symmetry. In the aromatic region the expected 21 signals were observed, from which six *ortho*-coupled doublets correspond to the aromatic protons of the tolyl residues. The eight *meta*-coupled doublets for the aromatic protons of calixarene rings were distinguished with the help of COSY-gs. The remaining six singlets were attributed to the NH protons of the urea and amide residues, while one singlet is covered by the signal of the solvent. In the aliphatic part of the spectrum eight doublets for the methylene bridges, three singlets for the tolyl CH_3 protons and one signal for amide CH_3 are found.

^1H NMR (Figure 2) and COSY-gs NMR spectra confirmed the ability of the **13a** and **13b** to form a tetramer in spite of the ester group at the narrow rim.

A single crystal of the mono-nitro calix[4]arene **4** was obtained by slow evaporation of an acetonitrile solution. The compound crystallizes in the monoclinic space group $P2_1/n$.[17] The molecule adopts the flattened (pinched) cone conformation (Figure 3). This is revealed clearly by the

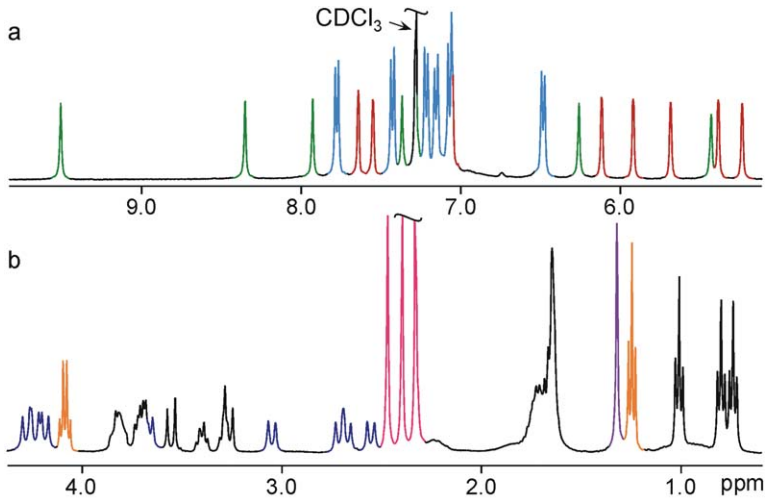


Figure 2 The ^{1}H NMR spectrum of **13a** in $CDCl_3$ (400 MHz, 25 °C): (a) NH and aromatic signals: NH (green); ArH of tolyl groups (light blue); ArH of calixarene skeleton (red); (b) aliphatic signals: $ArCH_2Ar$ (dark blue), OCH_2CH_3 (orange); $ArCH_3$ (pink); $C(O)CH_3$ (violet).

angles between the mean plane defined by the four methylene bridges linking the aromatic rings [C(1)–C(4)] and the planes of the individual phenyl rings: 147.5° [C(11)–C(16)], 88.1° [C(21)–C(26)], 135.8° [C(31)–C(36)], and 80.6° [C(41)–C(46)]. Thus, the two aromatic rings [C(21)–C(26)] and [C(41)–C(46)] are almost parallel to each other (interplanar angle 11.4°). The decrease of the NO_2 to *t*-Bu separation leads to an O(22)···O(42) distance of 5.67 Å. The two phenyl rings [C(11)–C(16)] and [C(31)–C(36)] are tilted so as to place the alkoxy groups inside the cavity (interplanar angle 103.3°), with an O(12)···O(32) separation of 3.33 Å. In this conformation it is not possible to have any solvent molecule enclathrated within the calixarene cup. One acetonitrile molecule is accommodated in continuous channels within the crystal lattice.

Compound **6** crystallizes from dimethyl sulfoxide solution in the triclinic space group *P*–1 as a 1:2 complex with dimethyl sulfoxide.[18] The conformation found for molecule **6** (Figure 4) is quite different from that of **4**. The calix[4]arene assumes a slightly distorted cone conformation as indicated by the interplanar angles between the mean plane of the bridging methylene carbon atoms [C(1)–C(4)] and the planes of the phenyl rings [C(n1)–C(n6)] (n = 1 to 4): 123.5, 119.4, 113.7, and 112.4, respectively. Thus aromatic rings [C(11)–C(16)] and [C(31)–C(36)] form a dihedral angle of 57.2° with an O(12)···O(32) separation of 4.12 Å; the value for the [C(21)–C(26)] and [C(41)–C(46)] dihedral angle is 51.8° [O(22)···O(42) separation of 4.46 Å]. A strong intramolecular hydrogen bond is found between the phenolic hydroxy group and one adjacent ether oxygen with O(12)···O(22) distance of 2.74 Å. The 'open' cone conformation facilitates the inclusion of one dimethyl sulfoxide molecule in the cavity of **6**. One methyl group of this dimethyl sulfoxide enters the cavity provided by the calix[4]arene and forms C–H···π interactions with the phenyl rings. The distances of the centroids of rings [C(n1)–C(n6)] (n = 1 to 4) to the included methyl carbon

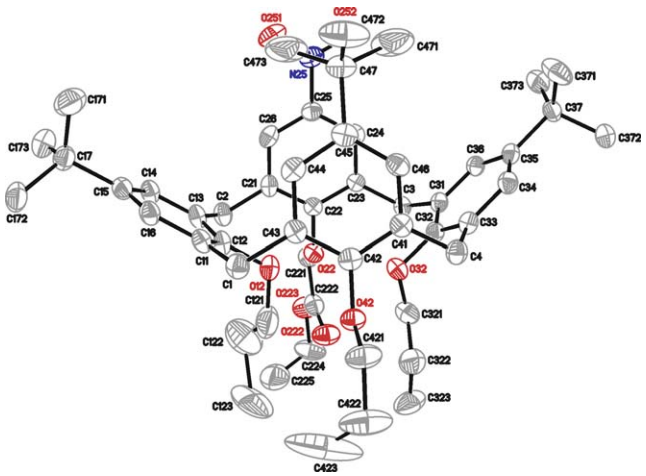


Figure 3 A view of the structure of **4** showing also the numbering scheme. The hydrogen atoms and solvent molecules are omitted for clarity.

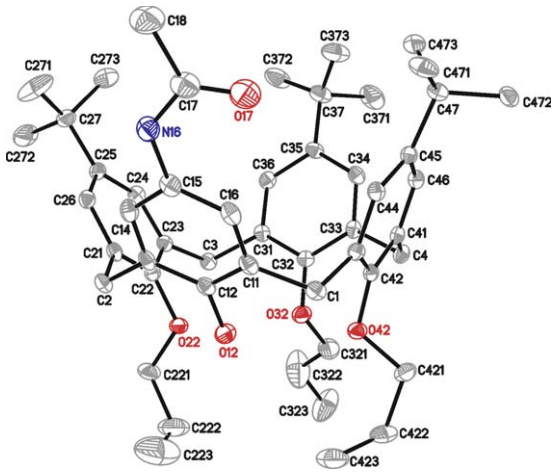


Figure 4 A view of the structure of **6** showing also the numbering scheme. The hydrogen atoms and solvent molecules are omitted for clarity.

are 3.71, 3.60, 3.72, and 3.82 Å, respectively. In addition, the amide hydrogen forms a hydrogen bond to the oxygen of the second dimethyl sulfoxide molecule [N(16)···O=S distance of 2.91 Å].

In summary, a multistep strategy for the synthesis of the calix[4]arene derivatives **14**, in which one carboxylic (narrow rim) and one acetamide (wide rim) function are introduced in the same aromatic ring was elaborated. The three remaining rings were substituted by urea and propyl groups at the wide and the narrow rim respectively. It was shown that the precursors **13** form the desired tetramers in apolar, aprotic solvents in spite of the presence of an additional polar group in the molecule. Derivatives of this type thus can be considered as cores for dendritic structures. Two intermediate compounds **4** and **6** were additionally characterized by X-ray crystal structure analysis.

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400 and 100.6 MHz respectively. Chemical shifts are with reference to the residual solvent peaks. Decoupling and DEPT experiments confirmed the assignments of the signals. Mass spectra were recorded on a Waters/Micromass QTof Ultima 3 mass spectrometer. All solvents were HPLC grade and used without further purification. Column chromatography was performed on silica gel 60 (0.035–0.070 mm, Acros).

As previously verified,[19] data for elemental analyses of organic calixarenes are often misleading, due to inclusion of solvent molecules, and cannot be considered appropriate criteria of purity. However, the identities of the reported compounds were unambiguously established by their spectroscopic data.

Intensity data for compounds **4** and **6** were collected on a STOE IPDS-II image plate diffractometer using graphite-monochromated Mo-Kα radiation. The data were corrected for Lorentz and polarization effects, but only for **6** for absorption effects.[20] The structures were solved using direct methods (SHELXS[21]) and refined by full-matrix least-squares techniques against Fo^2 (SHELXL-97[22]). Hydrogen atoms were included at calculated positions with fixed displacement parameters. Two H atoms bonded to O and N in **6** were freely refined. All non-hydrogen atoms were refined anisotropically. Two *tert*-butyl groups in **4** and two *tert*-butyl groups and two S atoms of the DMSO molecules in **6** are disordered over two positions. The disordered *tert*-butyl groups in **6** were restrained to have similar geometric parameters.[23]

5-Nitro-11,17,23-tri-*tert*-butyl-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (4)

A mixture of calix[4]arene **3**[14] (4.30 g, 5.63 mmol), Na_2CO_3 (0.89 g, 8.40 mmol), and ethyl bromoacetate (1.41 g, 8.44 mmol) was refluxed for 4 d in MeCN (50 mL). The sodium salts were filtered off, washed with $CHCl_3$ and the solvents were evaporated. The residue was dissolved in MeOH–acetone (5:1, 30 mL) and H_2O (30 mL) was added to the soln. The turbid aqueous phase was decanted and the residue was triturated with MeOH. The thus formed precipitate was filtered off and dried to afford calix[4]arene **4** (3.78 g, 79%) as a white powder; mp 195–197 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 [s, 9 H, $C(CH_3)_3$], 0.95 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.08 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.27 [s, 18 H, $C(CH_3)_3$], 1.31 (t, ^3J = 7.4 Hz, 3 H, OCH_2CH_3), 2.05–1.89 (m, 6 H, CH_2), 3.17 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 3.24 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 3.73 (t, ^3J = 7.4 Hz, 2 H, OCH_2), 3.92–3.85 (m, 2 H, OCH_2), 4.06–3.99 (m, 2 H, OCH_2), 4.24 (q, ^3J = 7.4 Hz, 2 H, OCH_2CH_3), 4.43 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 4.57 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 4.66 [s, 2 H, $OCH_2C(O)$], 6.40 (s, 2 H, ArH), 6.98 (d, ^4J = 2.3 Hz, 2 H, ArH), 7.05 (d, ^4J = 2.3 Hz, 2 H, ArH), 7.42 (s, 2 H, ArH).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 10.1 (CH_3), 10.7 (CH_3), 14.2 (CH_3), 23.1 (CH_2), 23.6 (CH_2), 30.9 [$C(CH_3)_3$], 31.1 (CH_2), 31.58 [$C(CH_3)_3$], 31.62 (CH_2), 33.3 [$C(CH_3)_3$], 34.1 [$C(CH_3)_3$], 61.0 (OCH_2), 71.3 (OCH_2), 76.8 (OCH_2), 77.2 (OCH_2), 123.4 (CH), 124.7 (CH), 125.0 (CH), 126.5 (CH), 132.5 (C), 133.2 (C), 135.4 (C), 142.9 (C), 144.5 (C), 145.3 (C), 153.0 (C), 154.4 (C), 160.1 (C), 168.9 (C).

MS (FD): *m/z* (%) = 851.2 (100) $[M + H]^+$.

5-Amino-11,17,23-tri-*tert*-butyl-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (5)

Calix[4]arene **4** (3.20 g, 3.76 mmol) was dissolved in toluene–EtOH (1:1, 40 mL) and hydrogenated at r.t. for 8 h in the presence of Raney Ni. The catalyst was filtered off and solvents were evaporated. The residue was triturated with MeOH; the thus formed precipitate was filtered off and dried. Compound **5** (2.84 g, 92%) was obtained as a white powder; mp 174–176 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 [s, 9 H, $C(CH_3)_3$], 0.92 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.08 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.27 [s, 18 H, $C(CH_3)_3$], 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.05–1.89 (m, 6 H, CH_2), 2.89 (br s, 2 H, NH_2), 3.03 (d, ^2J = 12.5 Hz, 2 H, $ArCH_2Ar$), 3.13 (d, ^2J = 12.5 Hz, 2 H, $ArCH_2Ar$), 3.73 (t, ^3J = 7.4 Hz, 2 H, OCH_2), 3.95 (t, ^3J = 7.4 Hz, 4 H, OCH_2), 4.23 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.43 [s, 2 H, $OCH_2C(O)$], 4.45 (d, ^2J = 12.5 Hz, 4 H, $ArCH_2Ar$), 5.78 (s, 2 H, ArH), 6.38 (s, 2 H, ArH), 6.93 (d, ^4J = 2.3 Hz, 2 H, ArH), 7.02 (d, ^4J = 2.3 Hz, 2 H, ArH).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 10.1 (CH_3), 10.7 (CH_3), 14.3 (CH_3), 23.0 (CH_2), 23.6 (CH_2), 31.1 [$C(CH_3)_3$], 31.2 (CH_2), 31.4 (CH_2), 31.7 [$C(CH_3)_3$], 33.5 [$C(CH_3)_3$], 34.0 [$C(CH_3)_3$], 60.5 (OCH_2), 72.0 (OCH_2), 76.6 (OCH_2), 77.0 (OCH_2), 115.0 (CH), 124.6 (CH), 125.1 (CH), 125.7 (CH), 132.7 (C), 134.0 (C), 134.7 (C), 135.4 (C), 140.4 (C), 143.8 (C), 144.3 (C), 148.1 (C), 153.2 (C), 154.8 (C), 169.8 (C).

MS (FD): *m/z* (%) = 820.8 (100) $[M + H]^+$.

5-Acetamido-11,17,23-tri-*tert*-butyl-25,26,27-tripropoxy-28-hydroxycalix[4]arene (6)

Calix[4]arene **3** (9.40 g, 12.30 mmol) was dissolved in a mixture of toluene–THF (3:1, 400 mL) and hydrogenated in the presence of Raney Ni (THF–hexane, 1:10, monitoring by TLC). When the reaction was finished, Ac_2O (25.1 g, 0.25 mol) and Et_3N (24.9 g, 0.25 mol) were added and the mixture was stirred for 4 h. The catalyst was filtered off and the soln was evaporated. The residue was dissolved in $CHCl_3$ (150 mL), washed with H_2O (3 × 70 mL), and dried ($MgSO_4$). The crude product was crystallized (MeCN) to give compound **6** (9.50 g, 99%) as white crystals; mp 214–216 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.92 [s, 18 H, $C(CH_3)_3$], 0.94 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.11 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.24 [s, 9 H, $C(CH_3)_3$], 1.96–1.83 (m, 4 H, CH_2), 1.96 [s, 3 H, $NHC(O)CH_3$], 2.18–2.08 (m, 2 H, CH_2), 3.19 (d, ^2J = 12.2 Hz, 2 H, $ArCH_2Ar$), 3.25 (d, ^2J = 12.2 Hz, 2 H, $ArCH_2Ar$), 3.69–3.63 (m, 2 H, OCH_2), 3.80–3.73 (m, 4 H, OCH_2), 4.16 (d, ^2J = 12.2 Hz, 2 H, $ArCH_2Ar$), 4.29 (d, ^2J = 12.2 Hz, 2 H, $ArCH_2Ar$), 6.34 (s, 1 H, OH), 6.59 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.79 (d, ^4J = 2.0 Hz, 2 H, ArH), 7.17 (s, 2 H, ArH), 7.26 (s, 2 H, ArH), 9.54 (s, 1 H, NH).

^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6): δ = 9.6 (CH_3), 10.5 (CH_3), 22.2 (CH_2), 22.9 (CH_2), 23.7 [$C(O)CH_3$], 30.1 (CH_2), 30.8 [$C(CH_3)_3$], 31.0 (CH_2), 31.2 [$C(CH_3)_3$], 33.4 [$C(CH_3)_3$], 33.7 [$C(CH_3)_3$], 76.1 (OCH_2), 77.1 (OCH_2), 119.5 (CH), 124.1 (CH), 125.0 (CH), 125.2 (CH), 128.1 (CH), 128.8 (CH), 129.2 (C), 130.7 (C), 131.3 (C), 133.0 (C), 134.7 (C), 144.7 (C), 144.8 (C), 148.5 (C), 151.5 (C), 153.0 (C), 167.3 (C).

MS (FD): *m/z* (%) = 776.6 (100) $[M + H]^+$.

5-Acetamido-11,17,23-tri-*tert*-butyl-25,26,27-tripropoxy-28-[10-(ethoxycarbonyl)decyloxy]calix[4]arene (7)

A slurry of the calix[4]arene **6** (10.70 g, 13.79 mmol) and NaH (0.50 g, 20.7 mmol) in DMF (200 mL) was stirred for 1 h. Then ethyl 11-bromoundecanoate (6.06 g, 20.68 mmol) was added and the stirring was continued at r.t. for 3 d. AcOH (5 mL) and then H_2O (200 mL) were added and the mixture was extracted with $CHCl_3$ (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography ($CHCl_3$–hexane, 2:1 then 6:1) to give **7** (12.7 g, 93%) as a light yellow oil.

^1H NMR (400 MHz, DMSO-d_6): δ = 0.75 [s, 9 H, $C(CH_3)_3$], 0.91 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.31–1.03 [m, 36 H, CH_3, CH_2, OCH_2CH_3, $C(CH_3)_3$], 1.50 (m, 4 H, CH_2), 1.80 [s, 3 H, $C(O)CH_3$], 1.99–1.81 (m, 6 H, CH_2), 2.24 [t, ^3J = 6.6 Hz, 2 H, $C(O)CH_2$], 3.02 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 3.09 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 3.67–3.60 (m, 4 H, OCH_2), 3.88–3.77 (m, 4 H, OCH_2), 4.03 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.27 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 4.31 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 6.30 (s, 2 H, ArH), 6.80 (s, 2 H, ArH), 6.89 (s, 2 H, ArH), 6.98 (s, 2 H, ArH), 9.01 (s, 1 H, NH).

$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ = 9.6 (CH_3), 10.5 (CH_3), 14.0 (CH_3), 22.6 (CH_2), 22.9 (CH_2), 23.8 [$C(O)CH_3$], 25.9 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.7 (CH_2), 30.4 (CH_2), 30.6 [$C(CH_3)_3$], 31.3 [$C(CH_3)_3$], 32.9 [$C(CH_3)_3$], 33.5 [$C(CH_3)_3$], 59.5 (OCH_2), 74.8 (OCH_2), 76.0 (OCH_2), 76.3 (OCH_2), 117.6 (CH), 124.2 (CH), 124.8 (CH), 125.4 (CH), 132.0 (C), 132.8 (C), 133.6 (C), 133.9 (C), 134.6 (C), 143.2 (C), 143.6 (C), 150.5 (C), 152.6 (C), 154.0 (C), 166.5 (C), 172.7 (C).

MS (FD): *m/z* (%) = 988.9 (100) $[M]^+$.

5-Phthalimido-11,17,23-tri-*tert*-butyl-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (8a)

A slurry of calix[4]arene **5** (2.36 g, 2.88 mmol), $Zn(OAc)_2$ (1.05 g, 5.75 mmol), and phthalic anhydride (0.85 g, 5.75 mmol) in pyridine (25 mL) was refluxed for 3 d. Then H_2O (30 mL) was added and the thus formed precipitate was filtered off and washed with 1 M HCl, H_2O, and MeOH. After drying in air, compound **8a** (2.00 g, 73%) was obtained as a beige powder; mp 207–209 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.97 [s, 18 H, $C(CH_3)_3$], 0.99 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.02 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.17 [s, 9 H, $C(CH_3)_3$], 1.29 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 2.14–1.88 (m, 2 H, CH_2), 1.97–1.88 (m, 4 H, CH_2), 3.14 (d, ^2J = 12.5 Hz, 2 H, $ArCH_2Ar$), 3.24 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 3.77–3.72 (m, 4 H, OCH_2), 3.87 (t, ^3J = 7.8 Hz, 2 H, OCH_2), 4.21 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.42 (d, ^2J = 12.5 Hz, 2 H, $ArCH_2Ar$), 4.70 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 5.00 [s, 2 H, $OCH_2C(O)$], 6.63–6.62 (m, 4 H, ArH), 6.94 (s, 2 H, ArH), 7.10 (s, 2 H, ArH), 7.75–7.73 (m, 2 H, H_{Phth}), 7.92–7.90 (m, 2 H, H_{Phth}).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 10.2 (CH_3), 10.6 (CH_3), 14.2 (CH_3), 23.4 (CH_2), 23.5 (CH_2), 31.0 (CH_2), 31.4 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$], 31.8 (CH_2), 33.8 [$C(CH_3)_3$], 33.9 [$C(CH_3)_3$], 60.4 (OCH_2), 70.3 (OCH_2), 76.9 (OCH_2), 77.3 (OCH_2), 123.5 (CH), 124.9 (CH), 125.1 (CH), 125.4 (CH), 126.0 (C), 126.1 (CH), 131.8 (C), 132.0 (C), 132.8 (C), 134.0 (CH), 134.9 (C), 136.0 (C), 144.6 (C), 144.7 (C), 153.3 (C), 154.2 (C), 155.1 (C), 167.2 (C), 170.6 (C).

MS (FD): *m/z* (%) = 950.8 (100) $[M + H]^+$.

5-Phthalimido-11,17,23-tri-*tert*-butyl-25,26,27-tripropoxy-28-[10-(ethoxycarbonyl)decyloxy]calix[4]arene (8b)

Hydrolysis of the acetamide: A soln of NaOH (10.30 g, 0.26 mol) in H_2O (40 mL) was added to the soln of calix[4]arene **7** (12.70 g, 12.84 mmol) in THF–MeOH (1:2, 210 mL) and the mixture was refluxed for 4 d. AcOH (20 mL) was added and the solvents were evaporated. The residue was dissolved in $CHCl_3$ (200 mL) and washed with H_2O (3 × 50 mL). The organic layer was dried ($MgSO_4$) and evaporated and the residue was refluxed in EtOH (200 mL) in the presence of H_2SO_4 (5 mL) for 8 h. After evaporation, the residue was dissolved in $CHCl_3$ (200 mL), washed with H_2O (3 × 50 mL) and 5% aq Et_3N (3 × 50 mL). The organic layer was dried ($MgSO_4$) and evaporated and the product was purified by column chromatography (EtOAc–hexane, 1:4). The desired amino compound (10.0 g, 80%) was obtained as a light yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.78 [s, 9 H, $C(CH_3)_3$], 0.89 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.09 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.24 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 1.30 (m, 8 H, CH_2), 1.33 [s, 18 H, $C(CH_3)_3$], 1.63–1.45 (m, 6 H, CH_2), 1.94–1.78 (m, 4 H, CH_2), 2.08–1.98 (m, 4 H, CH_2), 2.28 [t, ^3J = 7.6 Hz, 2 H, $C(O)CH_2$], 2.72 (s, 2 H, NH_2), 2.99 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 3.11 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 3.60 (t, ^3J = 6.9 Hz, 2 H, OCH_2), 3.69 (t, ^3J = 6.9 Hz, 2 H, OCH_2), 4.01–3.90 (m, 4 H, OCH_2), 4.11 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.34 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 4.43 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 5.67 (s, 2 H, Ar*H*), 6.26 (s, 2 H, Ar*H*), 7.00 (d, ^4J = 2.5 Hz, 2 H, Ar*H*), 7.08 (d, ^4J = 2.5 Hz, 2 H, Ar*H*).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 9.9 (CH_3), 10.8 (CH_3), 14.2 (CH_3), 23.0 (CH_2), 23.6 (CH_2), 25.0 (CH_2), 26.5 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 30.4 (CH_2), 31.0 [$C(CH_3)_3$], 31.1 (CH_2), 31.2 (CH_2), 31.7 [$C(CH_3)_3$], 33.5 (CH_2), 34.0 [$C(CH_3)_3$], 34.8 [$C(CH_3)_3$], 60.1 (OCH_2), 75.6 (OCH_2), 76.5 (OCH_2), 77.0 (OCH_2), 114.7 (CH), 124.5 (CH), 125.2 (CH), 125.7 (CH), 132.3 (C), 133.8 (C), 135.4 (C), 136.0 (C), 139.8 (C), 143.7 (C), 144.3 (C), 144.4 (C), 148.7 (C), 152.9 (C), 155.0 (C).

MS (FD): *m/z* (%) = 947.0 (100) $[M]^+$.

Protection by phthalimide: A mixture of the monoamino calix[4]arene (7.00 g, 7.39 mmol), $Zn(OAc)_2$ (4.06 g, 22.16 mmol), and phthalic anhydride (3.28 g, 22.16 mmol) was refluxed in pyridine (100 mL) for 3 d. H_2O (50 mL) was added to the suspension and the oily precipitate was separated, dissolved in $CHCl_3$ (150 mL), and washed with 1 M HCl (3 × 50 mL) and H_2O (5 × 50 mL). The residue obtained after evaporation was purified by column chromatography ($CHCl_3$–hexane, 2:1) to afford **8b** (4.80 g, 60%) as a glassy solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.01–0.97 (m, 9 H, CH_3), 1.02 [s, 9 H, $C(CH_3)_3$], 1.06 [s, 18 H, $C(CH_3)_3$], 1.25 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.39–1.32 (m, 12 H, CH_2), 1.63 (m, 2 H, CH_2), 2.07–1.95 (m, 8 H, CH_2), 2.29 [t, ^3J = 7.6 Hz, 2 H, $C(O)CH_2$], 3.12 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 3.17 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 3.81–3.77 (m, 4 H, OCH_2), 3.87 (t, ^3J = 7.6 Hz, 2 H, OCH_2), 3.95 (t, ^3J = 7.6 Hz, 2 H, OCH_2), 4.12 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.43 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 4.46 (d, ^2J = 12.7 Hz, 2 H, $ArCH_2Ar$), 6.74 (s, 4 H, ArH), 6.77 (s, 2 H, ArH), 7.03 (s, 2 H, ArH), 7.73–7.71 (m, 2 H, H_{Phth}), 7.89–7.87 (m, 2 H, H_{Phth}).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 10.3 (CH_3), 10.4 (CH_3), 14.3 (CH_3), 23.2 (CH_2), 23.3 (CH_2), 23.4 (CH_2), 25.0 (CH_2), 26.2 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.8 (CH_2), 31.0 (CH_2), 31.1 (CH_2), 31.2 [$C(CH_3)_3$], 31.4 [$C(CH_3)_3$], 33.7 (CH_2), 33.8 [$C(CH_3)_3$], 34.4 [$C(CH_3)_3$], 60.1 (OCH_2), 75.4 (OCH_2), 76.7 (OCH_2), 77.1 (OCH_2), 123.3 (CH), 124.9 (CH), 125.1 (CH), 125.3 (CH), 125.8 (C), 131.9 (C), 132.0 (C), 132.6 (C), 133.5 (C), 133.9 (CH), 134.2 (C), 135.8 (C), 144.3 (C), 144.4 (C), 144.47 (C), 144.50 (C), 153.6 (C), 153.8 (C), 155.7 (C), 167.0 (C), 173.9 (C).

MS (FD): *m/z* (%) = 1075.3 (100) $[M]^+$.

5-Phthalimido-11,17,23-trinitro-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (9a); Typical Procedure

Fuming HNO_3 (3.6 mL) was cautiously added to the vigorously stirred soln of calix[4]arene **8a** (2.60 g, 2.74 mmol) and AcOH (7.8 mL) in CH_2Cl_2 (260 mL). The mixture was stirred at r.t. for 1 h. The soln was washed with H_2O (5 × 50 mL), dried ($MgSO_4$), and evaporated. The residue was triturated with MeOH, the thus formed precipitate was filtered off and dried in air to yield calix[4]arene **9a** (2.23 g, 89%) as a beige powder; mp 225–227 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, ^3J = 7.2 Hz, 6 H, CH_3), 1.04 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.32 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 2.00–1.87 (m, 6 H, CH_2), 3.38 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 3.40 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 3.84 (t, ^3J = 7.2 Hz, 2 H, OCH_2), 4.09–4.03 (m, 2 H, OCH_2), 4.21–4.14 (m, 2 H, OCH_2), 4.26 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.54 [s, 2 H, $OCH_2C(O)$], 4.54 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 4.68 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 6.63 (s, 2 H, ArH), 7.47 (s, 2 H, ArH), 7.72–7.70 (m, 2 H, H_{Phth}), 7.77 (d, ^4J = 2.4 Hz, 2 H, ArH), 7.79 (d, ^4J = 2.4 Hz, 2 H, ArH), 7.85–7.83 (m, 2 H, H_{Phth}).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 10.1 (CH_3), 10.3 (CH_3), 14.3 (CH_3), 23.2 (CH_2), 23.3 (CH_2), 31.1 (CH_2), 31.3 (CH_2), 61.1 (OCH_2), 71.7 (OCH_2), 77.6 (OCH_2), 77.9 (OCH_2), 123.7 (CH), 124.0 (CH), 124.2 (CH), 124.6 (CH), 126.6 (CH), 127.3 (C), 131.5 (C), 133.5 (C), 134.3 (CH), 134.4 (C), 135.5 (C), 136.4 (C), 142.8 (C), 143.6 (C), 154.3 (C), 161.0 (C), 162.3 (C), 166.6 (C), 168.7 (C).

MS (FD): *m/z* (%) = 917.6 (100) $[M + H]^+$.

5-Phthalimido-11,17,23-trinitro-25,26,27-tripropoxy-28-[10-(ethoxycarbonyl)decyloxy]calix[4]arene (9b)

Following the typical procedure for **9a** produced calix[4]arene **9b** in 95% yield as a lightly yellow, glassy solid after column chromatography (EtOAc–hexane, 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.05 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.24 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.31 (m, 8 H, CH_2), 1.38 (m, 2 H, CH_2), 1.48 (m, 2 H, CH_2), 1.61 (m, 2 H, CH_2), 2.00–1.84 (m, 8 H, CH_2), 2.28 [t, ^3J = 7.6 Hz, 2 H, $C(O)CH_2$], 3.37 (d, ^2J = 13.7 Hz, 4 H, $ArCH_2Ar$), 3.85–3.81 (m, 4 H, OCH_2), 4.17–4.04 (m, 6 H, OCH_2CH_3, OCH_2), 4.51 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 4.53 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 7.39 (s, 2 H, ArH), 6.50 (s, 2 H, ArH), 7.70–7.68 (m, 2 H, H_{Phth}), 7.82–7.80 (m, 2 H, H_{Phth}), 7.86 (s, 4 H, ArH).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 9.9 (CH_3), 10.3 (CH_3), 14.2 (CH_3), 23.2 (CH_2), 23.3 (CH_2), 24.9 (CH_2), 26.3 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 30.3 (CH_2), 31.1 (CH_2), 34.3 (CH_2), 60.2 (OCH_2), 76.0 (OCH_2), 76.4 (OCH_2), 77.9 (OCH_2), 123.6 (CH), 124.1 (CH), 124.7 (CH), 126.3 (CH), 126.5 (C), 131.5 (C), 133.2 (C), 134.0 (C), 134.1 (CH), 135.6 (C), 136.8 (C), 142.8 (C), 143.7 (C), 154.9 (C), 160.7 (C), 162.5 (C), 166.6 (C), 173.8 (C).

MS (FD): *m/z* (%) = 1043.0 (100) $[M + H]^+$.

5-Amino-11,17,23-trinitro-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (10a); Typical Procedure

HCl (37%, 10 mL) was added to the soln of calix[4]arene **9a** (1.00 g, 1.11 mmol) in EtOH–toluene (1:1, 60 mL). The turbid mixture was refluxed until a clear soln was formed (~4 d) and then concentrated to ~20 mL. Then toluene (10 mL) was added and the excess HCl was neutralized by 1 M $NaHCO_3$. The organic layer was washed with H_2O (20 mL), dried ($MgSO_4$), and evaporated. The residue was triturated with MeOH, dried, dissolved in EtOAc and passed through a short column. Calix[4]arene **10a** (0.62 g, 72%) was obtained as a pale brown powder; mp 221–223 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.06 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.29 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.92–1.83 (m, 6 H, CH_2), 3.19 (d, ^2J = 14.1 Hz, 2 H, $ArCH_2Ar$), 3.36 (d, ^2J = 14.1 Hz, 2 H, $ArCH_2Ar$), 3.86 (t, ^3J = 7.4 Hz, 2 H, OCH_2), 3.99–3.93 (m, 2 H, OCH_2), 4.18–4.12 (m, 2 H, OCH_2), 4.22 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 4.37 [s, 2 H, $OCH_2C(O)$], 4.51 (d, ^2J = 14.1 Hz, 2 H, $ArCH_2Ar$), 4.54 (d, ^2J = 14.1 Hz, 2 H, $ArCH_2Ar$), 5.63 (s, 2 H, ArH), 7.29 (s, 2 H, ArH), 7.81 (s, 4 H, ArH).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 10.0 (CH_3), 10.3 (CH_3), 14.2 (CH_3), 23.2 (CH_2), 23.3 (CH_2), 31.1 (CH_2), 31.2 (CH_2), 60.8 (OCH_2), 71.7 (OCH_2), 77.5 (OCH_2), 77.6 (OCH_2), 114.7 (CH), 123.6 (CH), 123.7 (CH), 124.7 (CH), 133.2 (C), 135.0 (C), 135.8 (C), 137.3 (C), 142.4 (C), 142.5 (C), 142.6 (C), 147.6 (C), 161.4 (C), 162.9 (C), 169.1 (C).

MS (FD): *m/z* (%) = 787.2 (100) $[M + H]^+$.

5-Amino-11,17,23-trinitro-25,26,27-tripropoxy-28-[10-(ethoxycarbonyl)decyloxy]calix[4]arene (10b)

Following the typical procedure for **10a** gave calix[4]arene **10b** in 69% yield as a yellow foam after column chromatography (EtOAc–hexane, 1:4 then 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.07 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.24 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.29 (m, 8 H, CH_2), 1.33 (m, 2 H, CH_2), 1.44 (m, 2 H, CH_2), 1.60 (m, 2 H, CH_2), 1.82–1.75 (m, 2 H, CH_2), 1.93–1.85 (m, 6 H, CH_2), 2.27 [t, ^3J = 7.6 Hz, 2 H, $C(O)CH_2$], 3.07 (br s, 2 H, NH_2), 3.19 (d, ^2J = 14.2 Hz, 2 H, $ArCH_2Ar$), 3.35 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 3.67 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 3.84 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 4.00–3.93 (m, 2 H, OCH_2), 4.15–4.08 (m, 4 H, OCH_2), 4.37 (d, ^2J = 14.2 Hz, 2 H, $ArCH_2Ar$), 4.52 (d, ^2J = 13.7 Hz, 2 H, $ArCH_2Ar$), 5.55 (s, 2 H, ArH), 7.22 (s, 2 H, ArH), 7.89 (s, 4 H, ArH).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 9.9 (CH_3), 10.4 (CH_3), 14.2 (CH_3), 23.2 (CH_2), 23.3 (CH_2), 25.0 (CH_2), 26.4 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 30.2 (CH_2), 31.1 (CH_2), 34.3 (CH_2), 60.2 (OCH_2), 75.6 (OCH_2), 77.6 (OCH_2), 114.6 (CH), 123.5 (CH), 123.8 (CH), 124.9 (CH), 133.1 (C), 134.8 (C), 135.9 (C), 137.7 (C), 142.5 (C), 142.6 (C), 161.2 (C), 163.0 (C).

MS (FD): *m/z* (%) = 912.7 (100) $[M]^+$.

5-Acetamido-11,17,23-trinitro-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (11a); Typical Procedure

Ac_2O (4 mL) and Et_3N (5 mL) were added to the soln of calix[4]arene **10a** (1.50 g, 1.91 mmol) in $CHCl_3$ (10 mL) and the mixture was stirred for 10 h. After the addition of $CHCl_3$ (30 mL) the excess Ac_2O was quenched with 1 M $NaHCO_3$. The organic layer was washed with H_2O (4 × 20 mL), dried ($MgSO_4$), and evaporated. The residue was triturated (EtOH–H_2O, 1:2, 30 mL) and the thus formed solid was filtered off and dried in air to give calix[4]arene **11a** (1.20 g, 76%) as a brown powder; mp 173–175 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.07 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.30 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 1.94–1.83 (m, 6 H, CH_2), 2.01 [s, 3 H, $C(O)CH_3$], 3.32 (d, ^2J = 14.5 Hz, 2 H, $ArCH_2Ar$), 3.36 (d, ^2J = 14.5 Hz, 2 H, $ArCH_2Ar$), 3.85 (t, ^3J = 7.4 Hz, 2 H, OCH_2), 4.02–3.95 (m, 2 H, OCH_2), 4.18–4.11 (m, 2 H, OCH_2), 4.23 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.40 [s, 2 H, $OCH_2C(O)$], 4.52 (d, ^2J = 14.5 Hz, 2 H, $ArCH_2Ar$), 4.56 (d, ^2J = 14.5 Hz, 2 H, $ArCH_2Ar$), 6.42 (s, 2 H, Ar*H*), 6.63 (s, 1 H, NH), 7.20 (s, 2 H, ArH), 7.85 (s, 2 H, ArH), 7.86 (s, 2 H, ArH).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 9.9 (CH_3), 10.3 (CH_3), 14.2 (CH_3), 23.1 (CH_2), 23.3 (CH_2), 24.0 [$C(O)CH_3$], 31.0 (CH_2), 31.1 (CH_2), 60.9 (OCH_2), 71.5 (OCH_2), 77.6 (OCH_2), 77.7 (OCH_2), 120.5 (CH), 123.5 (CH), 123.9 (CH), 124.7 (CH), 133.2 (C), 133.4 (C), 135.1 (C), 135.8 (C), 137.0 (C), 142.5 (C), 151.6 (C), 161.5 (C), 162.7 (C), 168.4 (C), 168.8 (C).

MS (FD): *m/z* (%) = 829.5 (100) $[M + H]^+$.

5-Acetamido-11,17,23-trinitro-25,26,27-tripropoxy-28-[10-(ethoxycarbonyl)decyloxy]calix[4]arene (11b)

Following the typical procedure for **11a** gave monoacetamide **11b** in 98% yield as a yellow foam after column chromatography (EtOAc–hexane, 1:3 then 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.08 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.23 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.29 (m, 8 H, CH_2), 1.34 (m, 2 H, CH_2), 1.60 (m, 2 H, CH_2), 1.45 (m, 2 H, CH_2), 1.83–1.76 (m, 2 H, CH_2), 1.92–1.84 (m, 6 H, CH_2), 1.99 [s, 3 H, $C(O)CH_3$], 2.27 [t, ^3J = 7.6 Hz, 2 H, $C(O)CH_2$], 3.30 (d, ^2J = 14.2 Hz, 2 H, $ArCH_2Ar$), 3.36 (d, ^2J = 14.2 Hz, 2 H, $ArCH_2Ar$), 3.70 (t, ^3J = 6.9 Hz, 2 H, OCH_2), 3.83 (t, ^3J = 7.1 Hz, 2 H, OCH_2), 4.02–3.95 (m, 2 H, OCH_2), 4.13–4.07 (m, 4 H, OCH_2), 4.42 (d, ^2J = 14.2 Hz, 2 H, $ArCH_2Ar$), 4.51 (d, ^2J = 14.2 Hz, 2 H, $ArCH_2Ar$), 6.31 (s, 2 H, ArH), 6.57 (s, 1 H, NH), 7.13 (s, 2 H, ArH), 7.93 (s, 4 H, ArH).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 9.8 (CH_3), 10.4 (CH_3), 14.2 (CH_3), 23.2 (CH_2), 23.3 (CH_2), 24.0 [$C(O)CH_3$], 24.9 (CH_2), 26.3 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 30.2 (CH_2), 31.1 (CH_2), 34.3 (CH_2), 60.1 (OCH_2), 75.6 (OCH_2), 77.4 (OCH_2), 77.6 (OCH_2), 120.4 (CH), 123.4 (CH), 124.0 (CH), 124.9 (CH), 132.6 (C), 133.0 (C), 134.8 (C), 136.1 (C), 137.5 (C), 142.6 (C), 152.3 (C), 161.2 (C), 162.9 (C), 168.4 (C), 173.8 (C).

MS (FD): *m/z* (%) = 954.6 (100) $[M]^+$.

5-Acetamido-11,17,23-triamino-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (12a); Typical Procedure

Calix[4]arene **11a** (1.05 g, 1.27 mmol) was dissolved in toluene–EtOH (1:1, 30 mL) and hydrogenated at r.t. for 18 h in the presence of the Raney Ni monitored by TLC (THF). The catalyst was filtered off and the solvents were evaporated to leave calix[4]arene **12a** (0.78 g, 83%) as a brown powder; mp >190 °C (dec).

^{1}H NMR (400 MHz, THF-d_8): δ = 0.93 (t, ^3J = 7.6 Hz, 3 H, CH_3), 0.97 (t, ^3J = 7.6 Hz, 6 H, CH_3), 1.23 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.87–1.83 (m, 6 H, CH_2), 1.90 [s, 3 H, $C(O)CH_3$], 2.80 (d, ^2J = 13.3 Hz, 2 H, $ArCH_2Ar$), 2.94 (d, ^2J = 13.3 Hz, 2 H, $ArCH_2Ar$), 3.75–3.60 (m, 12 H, OCH_2 and NH_2), 4.13 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 4.28 (d, ^2J = 13.3 Hz, 2 H, $ArCH_2Ar$), 4.54 (d, ^2J = 13.3 Hz, 2 H, $ArCH_2Ar$), 4.60 [s, 2 H, $OCH_2C(O)$], 5.79 (s, 2 H, ArH), 5.81 (s, 2 H, ArH), 6.02 (s, 2 H, ArH), 6.87 (s, 2 H, ArH), 8.68 (s, 1 H, NH).

$^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8): δ = 10.7 (CH_3), 11.0 (CH_3), 14.6 (CH_3), 23.9 [$C(O)CH_3$], 24.0 (CH_2), 24.1 (CH_2), 32.1 (CH_2), 32.4 (CH_2), 60.5 (OCH_2), 71.4 (OCH_2), 77.4 (OCH_2), 115.51 (CH), 115.55 (CH), 115.59 (CH), 121.4 (CH), 134.7 (C), 135.1 (C), 135.6 (C), 136.4 (C), 136.6 (C), 142.9 (C), 143.5 (C), 149.4 (C), 150.1 (C), 153.5 (C), 167.4 (C), 170.4 (C).

MS (FD): *m/z* (%) = 739.4 (100) $[M + H]^+$.

5-Acetamido-11,17,23-triamino-25,26,27-tripropoxy-28-[10-(ethoxycarbonyl)decyloxy]calix[4]arene (12b)

Following the typical procedure for **12a** gave calix[4]arene **12b** in 85% yield as a pale solid; mp >117–120 °C (dec).

^{1}H NMR (400 MHz, DMSO–d_6, 75 °C): δ = 0.92 (t, ^3J = 7.6 Hz, 6 H, CH_3), 0.97 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.18 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.29 (m, 10 H, CH_2), 1.44 (m, 2 H, CH_2), 1.54 (m, 2 H, CH_2), 1.88–1.79 [m, 11 H, CH_2, $C(O)CH_3$], 2.25 [t, ^3J = 7.1 Hz, 2 H, $C(O)CH_2$], 2.82 (d, ^2J = 13.2 Hz, 2 H, $ArCH_2Ar$), 2.92 (d, ^2J = 13.2 Hz, 2 H, $ArCH_2Ar$), 3.64 (t, ^3J = 7.1 Hz, 2 H, OCH_2), 3.78–3.70 (m, 6 H, OCH_2), 4.09–4.00 (m, 8 H, OCH_2CH_3, NH_2), 4.21 (d, ^2J = 13.2 Hz, 2 H, $ArCH_2Ar$), 4.28 (d, ^2J = 13.2 Hz, 2 H, $ArCH_2Ar$), 5.86 (s, 2 H, ArH), 6.05 (s, 2 H, ArH), 6.06 (s, 2 H, ArH), 6.63 (s, 2 H, ArH), 9.19 (s, 1 H, NH).

$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ = 10.0 (CH_3), 10.2 (CH_3), 14.0 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 23.4 [$C(O)CH_3$], 24.3 (CH_2), 25.7 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.5 (CH_2), 30.6 (CH_2), 30.7 (CH_2), 33.4 (CH_2), 59.5 (OCH_2), 74.5 (OCH_2), 76.1 (OCH_2), 76.1 (OCH_2), 114.0 (CH), 114.3 (CH), 120.5 (CH), 132.6 (C), 134.0 (C), 134.1 (C), 134.3 (C), 134.9 (C), 141.7 (C), 142.2 (C), 147.4 (C), 147.6 (C), 152.2 (C), 167.4 (C), 172.7 (C).

MS (FD): *m/z* (%) = 864.4 (100) $[M]^+$.

5-Acetamido-11,17,23-tris[3-(4-methylphenyl)ureido]-25,26,27-tripropoxy-28-[(ethoxycarbonyl)methoxy]calix[4]arene (13a); Typical Procedure

4-Tolyl isocyanate (1.04 g, 7.80 mmol) was added to the soln of calix[4]arene **12a** (0.72 g, 0.97 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred for 6 h. MeOH (20 mL) was added and the solvents were evaporated. The residue was triturated with MeOH to form a solid that was filtered off and dried in air to yield calix[4]arene **13a** (0.71 g, 65%) as a white powder; mp >240 °C (dec).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.93 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.99 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.23 (t, ^3J = 7.6 Hz, 3 H, OCH_2CH_3), 1.88–1.83 (m, 6 H, CH_2), 1.94 [s, 3 H, $C(O)CH_3$], 2.21 (s, 6 H, $TolCH_3$), 2.22 (s, 3 H, $TolCH_3$), 3.09 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 3.10 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 3.82–3.67 (m, 6 H, OCH_2), 4.14 (q, ^3J = 7.6 Hz, 2 H, OCH_2CH_3), 4.33 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 4.55 (d, ^2J = 12.9 Hz, 2 H, $ArCH_2Ar$), 4.75 [s, 2 H, $OCH_2C(O)$], 6.59 (s, 2 H, ArH), 6.62 (s, 2 H, ArH), 6.98 (s, 2 H, ArH), 7.01 (d, ^3J = 8.2 Hz, 4 H, H_{Tol}), 7.05 (d, ^3J = 8.2 Hz, 2 H, H_{Tol}), 7.12 (s, 2 H, ArH), 7.17 (d, ^3J = 8.2 Hz, 4 H, H_{Tol}), 7.29 (d, ^3J = 8.2 Hz, 2 H, H_{Tol}), 8.02 (s, 2 H, NH), 8.13 (s, 2 H, NH), 8.26 (s, 1 H, NH), 8.34 (s, 1 H, NH), 9.61 [s, 1 H, $NHC(O)CH_3$].

$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ = 9.9 (CH_3), 10.3 (CH_3), 14.0 (CH_3), 20.2 ($TolCH_3$), 22.6 (CH_2), 23.8 [$C(O)CH_3$], 30.5 (CH_2), 31.1 (CH_2), 59.9 (OCH_2), 70.4 (OCH_2), 76.4 (OCH_2), 76.6 (OCH_2), 117.9 (CH), 118.0 (CH), 118.1 (CH), 118.2 (CH), 119.2 (CH), 128.9 (CH), 129.0 (CH), 130.1 (C), 130.2 (C), 133.3 (C), 133.4 (C), 133.6 (C), 133.7 (C), 134.6 (C), 135.0 (C), 137.2 (C), 150.6 (C), 151.3 (C), 152.3 (C), 152.4 (C), 167.6 (C), 169.7 (C).

MS (ESI): *m/z* (%) = 1160.5 (100) $[M + Na]^+$.

5-Acetamido-11,17,23-tris[3-(4-methylphenyl)ureido]-25,26,27-tripropoxy-28-[10-(ethoxycarbonyl)decyloxy]calix[4]arene (13b)

Following the typical procedure for **13a**, using MeCN in the last step instead of MeOH. Calix[4]arene **13b** was obtained in 86% yield as a white powder; mp >190–195 °C (dec).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.00–0.94 (m, 9 H, CH_3), 1.16 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.37–1.28 (m, 12 H, CH_2), 1.51 (m, 2 H, CH_2), 1.90 [m, 11 H, CH_2, $C(O)CH_3$], 2.22 (s, 9 H, $TolCH_3$), 2.26 [t, ^3J = 7.1 Hz, 2 H, $C(O)CH_2$], 3.11–3.06 (m, 4 H, $ArCH_2Ar$), 3.81–3.74 (m, 8 H, OCH_2), 4.04 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.33 (d, ^2J = 12.7 Hz, 4 H, $ArCH_2Ar$), 6.72 (s, 2 H, ArH), 6.77 (s, 2 H, ArH), 6.82 (s, 2 H, ArH), 7.03–6.99 (m, 8 H, ArH, H_{Tol}), 7.21 (d, ^3J = 8.3 Hz, 4 H, H_{Tol}), 7.27 (d, ^3J = 8.3 Hz, 2 H, H_{Tol}), 8.11 (s, 2 H, NH), 8.13 (s, 1 H, NH), 8.21 (s, 2 H, NH), 8.28 (s, 1 H, NH), 9.48 [s, 1 H, $NHC(O)CH_3$].

$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ = 10.0 (CH_3), 10.2 (CH_3), 14.0 (CH_3), 20.2 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 23.7 (CH_3), 24.3 (CH_2), 25.6 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.4 (CH_2), 30.6 (CH_2), 33.4 (CH_2), 59.5 (OCH_2), 74.7 (OCH_2), 76.2 (OCH_2), 76.4 (OCH_2), 117.9 (CH), 118.1 (CH), 119.0 (CH), 128.9 (CH), 129.0 (CH), 130.1 (C), 133.2 (C), 133.3 (C), 133.4 (C), 134.0 (C), 134.1 (C), 134.2 (C), 134.4

(C), 137.2 (C), 150.9 (C), 151.0 (C), 151.8 (C), 152.4 (C), 167.4 (C), 172.7 (C).

MS (ESI): *m/z* (%) = 1286.7 (100) $[M + Na]^+$.

5-Acetamido-11,17,23-tris[3-(4-methylphenyl)ureido]-25,26,27-tripropoxy-28-(carboxymethoxy)calix[4]arene (14a); Typical Procedure

A 3 M aq NaOH soln (2 mL) was added to the soln of calix[4]arene **13a** (0.60 g, 0.53 mmol) in THF–DMF (3:1, 28 mL). The mixture was stirred at r.t. for 12 h and AcOH (5 mL) was added to neutralize the excess NaOH. The soln was concentrated to ~15 mL, H_2O (35 mL) was added and the thus formed precipitate was filtered off and dried in air to give calix[4]arene **14a** (0.57 g, 98%) as a white powder; mp >260 °C (dec).

^{1}H NMR [400 MHz, DMSO-d_6 + CD_3CO_2D (10%)]: δ = 0.84 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.93 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.88–1.85 (m, 6 H, CH_2), 1.94 [s, 3 H, C(O)CH_3], 2.19 (s, 6 H, TolCH_3), 2.25 (s, 3 H, TolCH_3), 3.07 (d, ^2J = 12.9 Hz, 2 H, ArCH_2Ar), 3.08 (d, ^2J = 12.9 Hz, 2 H, ArCH_2Ar), 3.82–3.67 (m, 4 H, OCH_2), 3.80 (t, ^3J = 7.6 Hz, 2 H, OCH_2), 4.32 (d, ^2J = 12.9 Hz, 2 H, ArCH_2Ar), 4.47 (d, ^2J = 12.9 Hz, 2 H, ArCH_2Ar), 6.59 (d, ^4J = 2.0 Hz, 2 H, Ar*H*), 4.63 [s, 2 H, OCH_2C(O)], 6.65 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.68 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.98 (s, 2 H, ArH), 6.99 (d, ^3J = 8.2 Hz, 4 H, H_{Tol}), 7.00 (d, ^3J = 8.2 Hz, 2 H, H_{Tol}), 7.16 (d, ^3J = 8.2 Hz, 4 H, H_{Tol}), 7.15 (s, 2 H, ArH), 7.24 (d, ^3J = 8.2 Hz, 2 H, H_{Tol}), 8.01 (s, NH), 8.14 (s, NH), 8.25 (s, NH), 8.33 (s, NH). The intensity of NH protons is lower due to deuterium exchange.

^{13}C{^{1}H} NMR [100.6 MHz, DMSO-d_6 + CD_3CO_2D (10%)]: δ = 10.2 (CH_3), 10.5 (CH_3), 20.5 (TolCH_3), 22.9 (CH_2), 24.0 [C(O)CH_3], 25.4 (CH_2), 30.9 (CH_2), 31.4 (CH_2), 67.3 (OCH_2), 70.8 (OCH_2), 77.0 (OCH_2), 77.3 (OCH_2), 118.2 (CH), 118.3 (CH), 118.6 (CH), 119.7 (CH), 129.3 (CH), 129.4 (CH), 130.6 (C), 130.7 (C), 133.8 (C), 133.9 (C), 134.2 (C), 135.1 (C), 135.5 (C), 137.5 (C), 150.8 (C), 151.4 (C), 151.6 (C), 152.7 (C), 152.8 (C), 168.1 (C), 171.2 (C).

MS (ESI): *m/z* (%) = 1132.5 (100) $[M + Na]^+$.

5-Acetamido-11,17,23-tris-[3-(4-methylphenyl)ureido]-25,26,27-tripropoxy-28-(10-carboxydecyloxy)calix[4]arene (14b)

Following the typical procedure for **14a** using THF–MeOH (4:3) as solvent, gave **14b** in 98% yield as a white powder; mp >190–193 °C (dec).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.00–0.94 (m, 9 H, CH_3), 1.37–1.28 (m, 12 H, CH_2), 1.49 (m, 2 H, CH_2), 1.89 [m, 11 H, CH_2, C(O)CH_3], 2.19 [t, ^3J = 7.3 Hz, 2 H, C(O)CH_2], 2.22 (s, 9 H, TolCH_3), 3.11–3.06 (m, 4 H, ArCH_2Ar), 3.83–3.73 (m, 8 H, OCH_2), 4.33 (d, ^2J = 12.7 Hz, 2 H, ArCH_2Ar), 4.34 (d, ^2J = 12.7 Hz, 2 H, ArCH_2Ar), 6.72 (s, ^4J = 2.0 Hz, 2 H, ArH), 6.77 (s, ^4J = 2.0 Hz, 2 H, ArH), 6.83 (s, 2 H, ArH), 7.04–6.99 (m, 8 H, ArH, H_{Tol}), 7.21 (d, ^3J = 8.3 Hz, 4 H, H_{Tol}), 7.27 (d, ^3J = 8.3 Hz, 2 H, H_{Tol}), 8.10 (s, 2 H, NH), 8.13 (s, 1 H, NH), 8.21 (s, 2 H, NH), 8.28 (s, 1 H, NH), 9.48 [s, 1 H, N*H*C(O)CH_3], 11.95 (s, 1 H, COOH).

^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6): δ = 10.0 (CH_3), 10.2 (CH_3), 20.2 (TolCH_3), 22.6 (CH_2), 22.7 (CH_2), 23.7 [C(O)CH_3], 24.4 (CH_2), 25.6 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.4 (CH_2), 30.6 (CH_2), 33.6 (CH_2), 74.7 (OCH_2), 76.2 (OCH_2), 76.4 (OCH_2), 117.9 (CH), 118.1 (CH), 119.0 (CH), 128.9 (CH), 129.0 (CH), 130.1 (C), 133.2 (C), 133.3 (C), 133.4 (C), 134.0 (C), 134.1 (C), 134.2 (C), 134.4 (C), 137.2 (C), 150.8 (C), 151.0 (C), 151.8 (C), 152.4 (C), 167.4 (C), 174.4 (C).

MS (ESI): *m/z* (%) = 1258.6 (100) $[M + Na]^+$.

Acknowledgment

We thank the Deutsche Forschungsgemeinschaft for financial support (Bo 523/14 and SFB 625).

References

(1) Permanent address: Institute of Organic Chemistry, NAS of Ukraine, Murmanska str. 5, Kyiv-94, 02094 Ukraine.
(2) For X-ray crystal structure analysis.
(3) Rebek, J. Jr. *Chem. Commun.* **2000**, 637.
(4) (a) Castellano, R. K.; Rudkevich, D. M.; Rebek, J. Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 7132. (b) Castellano, R. K.; Rebek, J. Jr. *J. Am. Chem. Soc.* **1998**, *120*, 3657.
(5) For self-assembly of tetra-urea calix[4]arenes covalently connected via their wide rims see: (a) Brody, M. S.; Schalley, C. A.; Rudkevich, D. M.; Rebek, J. Jr. *Angew. Chem. Int. Ed.* **1999**, *38*, 1640. (b) Podoprygorina, G.; Janke, M.; Janshoff, A.; Böhmer, V. *Supramol. Chem.* in press.
(6) For self-sorting see: Braekers, D.; Peters, C.; Bogdan, A.; Rudzevich, Y.; Böhmer, V.; Desreux, J. F. *J. Org. Chem.* **2008**, *73*, 701.
(7) Rudzevich, Y.; Rudzevich, V.; Moon, C.; Schnell, I.; Fischer, K.; Böhmer, V. *J. Am. Chem. Soc.* **2005**, *127*, 14168.
(8) (a) Rudzevich, Y.; Rudzevich, V.; Schollmeyer, D.; Thondorf, I.; Böhmer, V. *Org. Lett.* **2005**, *7*, 613. (b) Rudzevich, Y.; Rudzevich, V.; Schollmeyer, D.; Thondorf, I.; Böhmer, V. *Org. Biomol. Chem.* **2006**, *4*, 3938.
(9) (a) Castellano, R. K.; Kim, B. H.; Rebek, J. Jr. *J. Am. Chem. Soc.* **1997**, *119*, 12671. (b) Thondorf, I.; Rudzevich, Y.; Rudzevich, V.; Böhmer, V. *Org. Biomol. Chem.* **2007**, *5*, 2775.
(10) Shivanyuk, A.; Saadioui, M.; Broda, F.; Thondorf, I.; Vysotsky, M. O.; Rissanen, K.; Kolehmainen, E.; Böhmer, V. *Chem. Eur. J.* **2004**, *10*, 2138.
(11) Also both positions might be functionalized, while the introduction of four functional groups (requiring no selectivity) most probably leads to sterical crowding, which would prevent the formation of dendrimers.
(12) For the monofunctionalization of tetra-urea derivatives see: Rudzevich, Y.; Fischer, K.; Schmidt, M.; Böhmer, V. *Org. Biomol. Chem.* **2005**, *3*, 3916.
(13) To use calix[4]arenes as universal building blocks, it would be ideal to functionalize all four positions at the wide rim (the *p*-positions of the phenolic units) and at the narrow rim (the four phenolic OH functions) selectively and independently.
(14) Rashidi-Ranjbar, P.; Taghvaei-Ganjali, S.; Shaabani, B.; Akbari, K. *Molecules* **2000**, *5*, 941.
(15) Verboom, W.; Bodewes, P. J.; van Essen, G.; Timmerman, P.; van Hummel, G. J.; Harkema, S.; Reinhoudt, D. N. *Tetrahedron* **1995**, *51*, 499.
(16) Bogdan, A.; Vysotsky, M. O.; Böhmer, V. *Collect. Czech. Chem. Commun.* **2004**, *69*, 1009.
(17) X-ray crystallographic data for **4**: $C_{53}H_{71}NO_8 \cdot C_2H_3N$ M = 891.16 g·mol^{-1}, colorless block, size 0.52 × 0.41 × 0.26 mm^3, monoclinic, space group $P2_1/n$, a = 18.4285 (13), b = 24.673 (2), c = 23.6687 (17) Å, β = 101.889 (6), V = 10531.0(14) Å^3, T = –100 °C, Z = 8, ρ_{calcd} = 1.124 g·cm^{-3}, μ (Mo-Kα) = 0.074 mm^{-1}, F(000) = 3856, 66424 reflections in h(–21/22), k(–29/29), l(–28/26), measured in the range 2.56° ≤ Θ ≤ 25.39°, completeness Θ_{max} = 98.3%, 19049 independent reflections, R_{int} = 0.0889, 8537 reflections with $F_o > 4\sigma(F_o)$, 1229 parameters, 0 restraints, $R1_{obs}$ = 0.0676, $wR2_{obs}$ = 0.1603,

$R1_{all}$ = 0.1406, $wR2_{all}$ = 0.1890, GOOF = 0.850, largest difference peak and hole: 0.928/–0.363 e·Å^{-3}.

(18) X-ray crystallographic data for **6**: $C_{51}H_{69}NO_5 \cdot 2\ C_2H_6OS$, M = 932.33 g·mol^{-1}, colorless rod, size 0.27 × 0.14 × 0.13 mm^3, triclinic, space group P–1, a = 12.3270 (8), b = 21.5880 (11), c = 22.6254 (12) Å, α = 65.959 (4), β = 83.687 (5), γ = 80.551 (5)°, V = 5417.9 (5) Å^3, T = –100 °C, Z = 4, ρ_{calcd} = 1.143 g·cm^{-3}, μ (Mo-Kα) = 0.147 mm^{-1}, F(000) = 2024, 52650 reflections in h(–14/12), k(–25/25), l(–26/26), measured in the range 3.35° ≤ Θ ≤ 25.03°, completeness Θ_{max} = 99.4%, 19028 independent reflections, R_{int} = 0.0624, 12643 reflections with $F_o > 4\sigma(F_o)$, 1263 parameters, 60 restraints, $R1_{obs}$ = 0.0895, $wR2_{obs}$ = 0.2316, $R1_{all}$ = 0.1274, $wR2_{all}$ = 0.2585, GOOF = 1.047, largest difference peak and hole: 1.318/–1.408 e·Å^{-3}.

(19) (a) Böhmer, V.; Jung, K.; Schön, M.; Wolff, A. *J. Org. Chem.* **1992**, *57*, 790. (b) Sansone, F.; Barboso, S.; Casnati, A.; Fabbi, M.; Pochini, A.; Ugozzoli, F.; Ungaro, R. *Eur. J. Org. Chem.* **1998**, 897.

(20) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(22) SHELXL-97 (Release 97-2), Sheldrick, G. M., University of Göttingen: Germany, **1997**.

(23) CCDC 662358 (**4**) and CCDC 662359 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033; email: deposit@ccdc.cam.ac.uk).