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Stepwise Synthesis and Selective Dimerisation of Bis- and Trisloop Tetra-urea Calix[4]arenes

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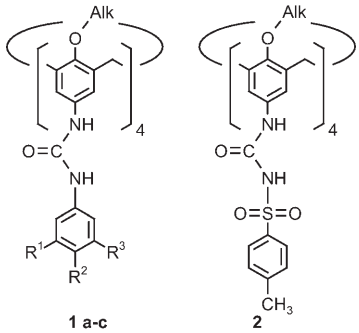
Abstract: Tetra-urea calix[4]arenes substituted with four mono- or bisalkenyl residues have been converted into bis- or tetraloop compounds by intramolecular olefin metathesis, with use of a tetratosylurea calix[4]arene as template. The same strategy has now been used to synthesise trisloop compounds and bisloop compounds with adjacent loops, completing the series of the loop-containing tetra-urea derivatives. A tetra-urea calix[4]arene of the AABB type, where A stands for a bisalkenyl- and B for a monoalkenyl-substituted urea unit, was used as precursor for the three loops. It was easily synthesised from a tetraamino calix[4]arene in which two adjacent amino groups were Boc-protected. The ABCB-type precursor for the two adjacent loops was prepared through protection of two opposite amino functions with trityl groups. The capabilities of the novel macrocyclic tetra-ureas for the selective formation of hydrogen-bonded dimers were studied.

Keywords: calixarenes · dimerization · metathesis · self-assembly · template synthesis

Introduction

Calix[4]arenes substituted at the wide rim with four arylurea functions (**1**) form dimeric capsules in aprotic, apolar solvents, held together by a seam of hydrogen bonds involving the urea functions of both calixarenes in an alternating pattern. This dimerisation, first described by Rebek,[1] has meanwhile been confirmed in numerous examples, including several crystal structures.[2] A solution of two different arylureas of type **1** normally contains not only the two homodimers but also the heterodimer (in a more or less statistical ratio) which is additional evidence of the dimerisation.[3]

Tetra-tosylureas **2** also form homodimers, but surprisingly a 1:1 mixture of **1** and **2** contains exclusively the heterodimer **1·2**. This observation could be utilisable, for instance, for the construction of "informational polymers" through self-assembly.[4]



Although a reasonable explanation for this exclusive formation of heterodimers was found only recently,[5] the preorganisation achieved in this way has frequently been used for intramolecular reactions between functional groups attached to the urea residues of **1**.[6] Bis- and tetra-loop compounds[7] **3** and **4**, in which adjacent urea groups are covalently interconnected, were obtained by olefin metathesis[8] (followed by hydrogenation) of tetra- or octaalkenyl derivatives **1b**

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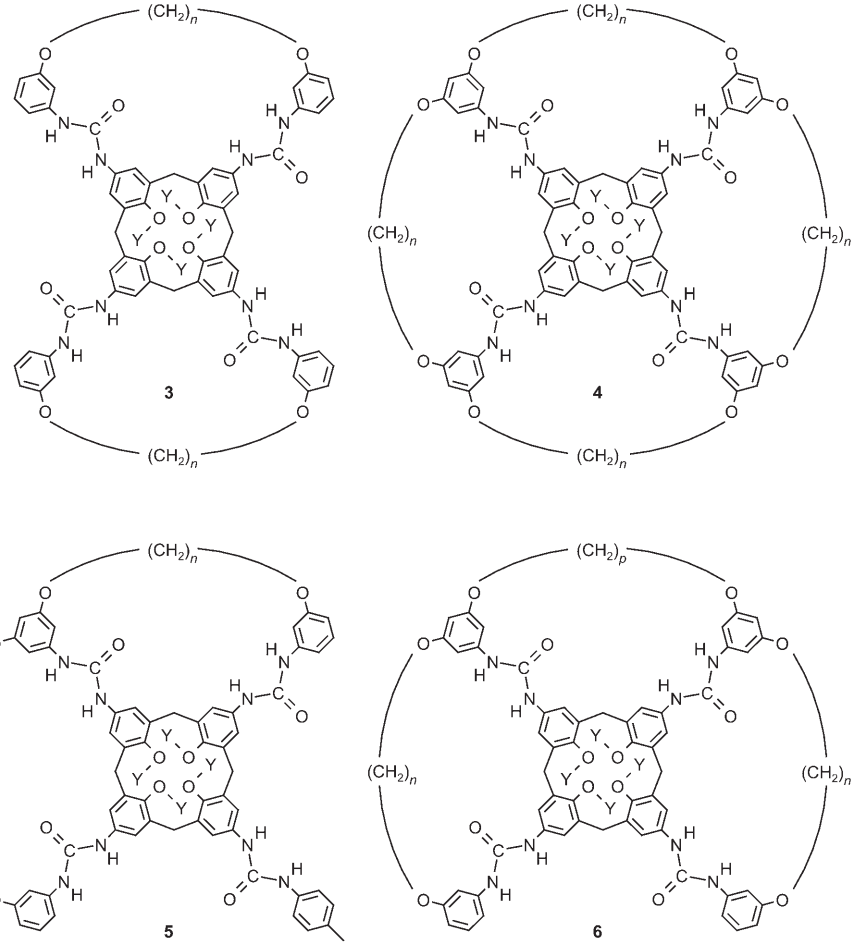
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: ^{1}H and ^{13}C NMR spectra of compounds **5** and **6**.

and **1c** with use of **2** as a template.[9] Compounds **3** and **4**[10] are not able to form homodimers, as this would require the sterically unfavourable overlap of the loops. However, they form heterodimers with tetra-ureas **1**, as long as their urea groups can pass through the loops. In a 1:1 mixture of **1** and **3** in an apolar solvent, *exclusively* the heterodimer **1·3** is present, since this represents the only possible means of having *all* urea functions involved in hydrogen bonding. This means that new selectivities for the dimerisation of tetra-ureas are possible. They have already been used for the synthesis of different catenanes[11,12] and rotaxanes,[13,14] and might be utilisable, for instance, for the controlled construction of larger assemblies.[15]



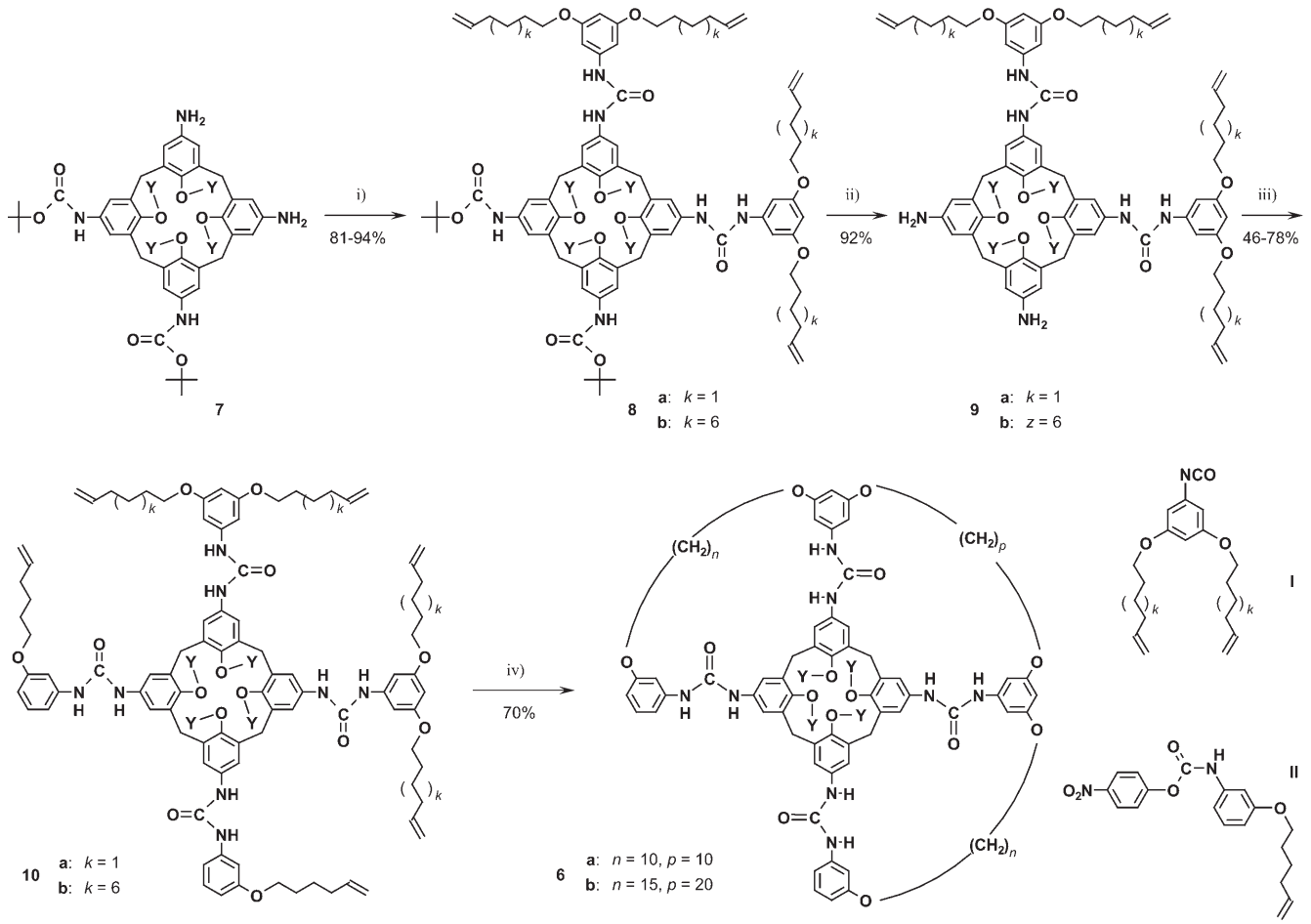
To extend this pattern of selective recognition and to complete the set of the multiloop tetra-urea derivatives, we have prepared compounds **5** and **6**, using tetra-tosylurea **2** as template, and have studied their dimerisation and self-sorting[16] properties.

Results and Discussion

Syntheses: Suitable precursors for compounds **6** are tetra-urea calix[4]arenes of the AABB-type, where A symbolises a phenolic unit substituted with a bisalkenyl urea group and B is a phenolic unit substituted with a monoalkenyl urea group. Their synthesis, from a starting 1,2-bis Boc-protected tetraamine **7**, is straightforward (Scheme 1). Compound **7** is acylated with an isocyanate **I**, prepared in situ from 3,5-dialkenyloxybenzoic acid, to afford **8**. After deprotection, the remaining two amino functions are acylated to provide **10**, with use of an activated urethane **II** as a milder reagent in this step.

The synthesis of the ABAC-type calix[4]arenes **5** requires more steps (Scheme 2). It is possible by use of the recently described 1,3-protection of a tetraamino calix[4]arene.[17] In a first step the 1,3-bistrityl tetraamine **11** is diacylated with a monoalkenyl isocyanate **III** as reagent to provide **12**. (All attempts to introduce two urea fragments by acylation with active urethanes failed, even at increased temperatures. Under these conditions the 1,3-ditrityl monourea is formed as main product.) Although the ditrityl-diurea **12** slowly decomposes under the conditions used for column chromatography (probably due to the slightly acidic silica gel), a product with about 95% purity (sufficient for the further steps) can be obtained by reprecipitation with methanol from a dichloromethane solution. The subsequent removal of the trityl groups under conditions (TFA in dichloromethane) recently described for a ditolyl analogue[17] results in a mixture of compounds. Obviously, the *m*-alkenyloxy aryl residue of the urea is nucleophilic enough to react with the trityl cation. This undesired substitution can be avoided by trapping the trityl cation with 3,5-dihydroxytoluene (**IV**, threefold excess). Reaction of diamine **13** with the corresponding active urethane **V** allows the triurea monoamine **14** to be obtained with high selectivity in relation to the same acylation with *p*-tolylisocyanate. Finally, the exhaustive acylation to afford **15** is easily achieved with the freshly prepared isocyanate **I**.

Olefin metathesis followed by hydrogenation of the initially formed double bonds finally gives the desired bis- and trisloop compounds **5** and **6**. The use of the tetra-tosyl urea **2** as template avoids the potentially possible *trans*-cavity bridging during metathesis, but does not exclude intercon-



Scheme 1. Synthesis of the trisloop tetra-urea calix[4]arene **6**: i) **I**, toluene; ii) $AlCl_3$, CH_2Cl_2; iii) **II**, Et_3N, THF, reflux; iv) **2**, Grubbs first-generation catalyst, CH_2Cl_2/C_6D_6; reduction (Pt_2O).

nection between the monoalkenyl residues in **10**. Nevertheless, the yield of this cyclisation step is "excellent".

Self-assembly: The novel bis- and trisloop compounds **5** and **6** can form neither homo- (**5·5**, **6·6**), nor heterodimers (**5·6**), as this would require the sterically unfavourable overlapping of loops. However, they easily form heterodimers in combinations with "open chain" tetra-urea calix[4]arenes, if small urea residues (e.g., tolylurea groups) to penetrate the loops are present. In combination with the use of bulky substituents that cannot pass through the loops, this leads to novel selectivities for the dimerisation of tetra-urea calix[4]arenes.[18]

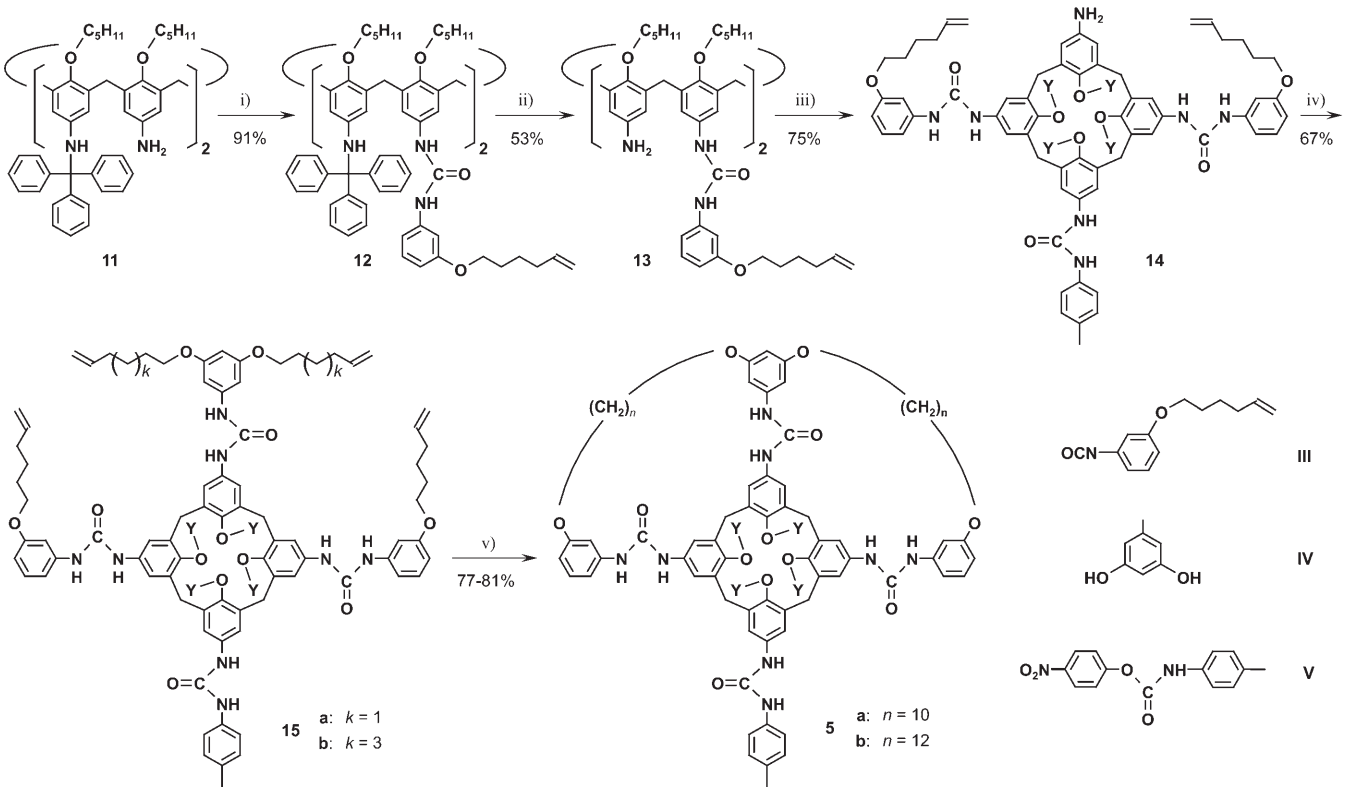
The underlying sorting process is based on two simple rules:

- dimers with overlapping loops are not formed,
- bulky residues do not penetrate the loops.

Statistically, six different tetra-urea calix[4]arenes can form 21 homo- and heterodimers, if all pairwise combinations can be achieved. With derivatives **D**–**F**, in which adjacent urea functions are covalently connected by two or three loops, this number of possible combinations can be reduced by six (first rule). If, in addition, the bulky residues of **A**–**C** cannot pass through the loops, only 11 possible dimers remain (second rule), as illustrated in Figure 1. (For some of these combinations several regioisomeric arrangements are possible.)

In a stoichiometric mixture the number of combinations achieved is further reduced to three, due to the fact that all tetra-urea calix[4]arenes "want to form dimers", since this is obviously the most stable arrangement. Only in this way can *all* urea functions be involved in a "hydrogen-bonded belt", in which each urea group acts simultaneously as hydrogen bond donor and acceptor.

Among the six tetra-ureas shown in Figure 1, the trisloop compound **F** can dimerise only with **A**, which is thus "consumed" in this way, and other dimers of **A** should not be formed. The bisloop compound **E** has only **B** as a potential partner (cf. Figure 2, where **E** = **5a** and **B** = **16**), and bisloop **D** can combine only with **C**. It is important to note that all six tetra-ureas do not even have to be present at the same concentration, only the appropriate pairs **A**/**F**, **B**/**E** and **C**/**D**. Thus, of the 11 possible dimeric combinations, only three dimers will be formed in the stoichiometric mixture.



Scheme 2. Synthesis of the bisloop tetra-urea calix[4]arene **5**: i) **III**, toluene; ii) **IV**, TFA, CH_2Cl_2; iii) **V**, $CHCl_3$; iv) **I**, toluene; v) **2**, Grubbs first-generation catalyst, CH_2Cl_2/C_6D_6; reduction (Pt_2O).

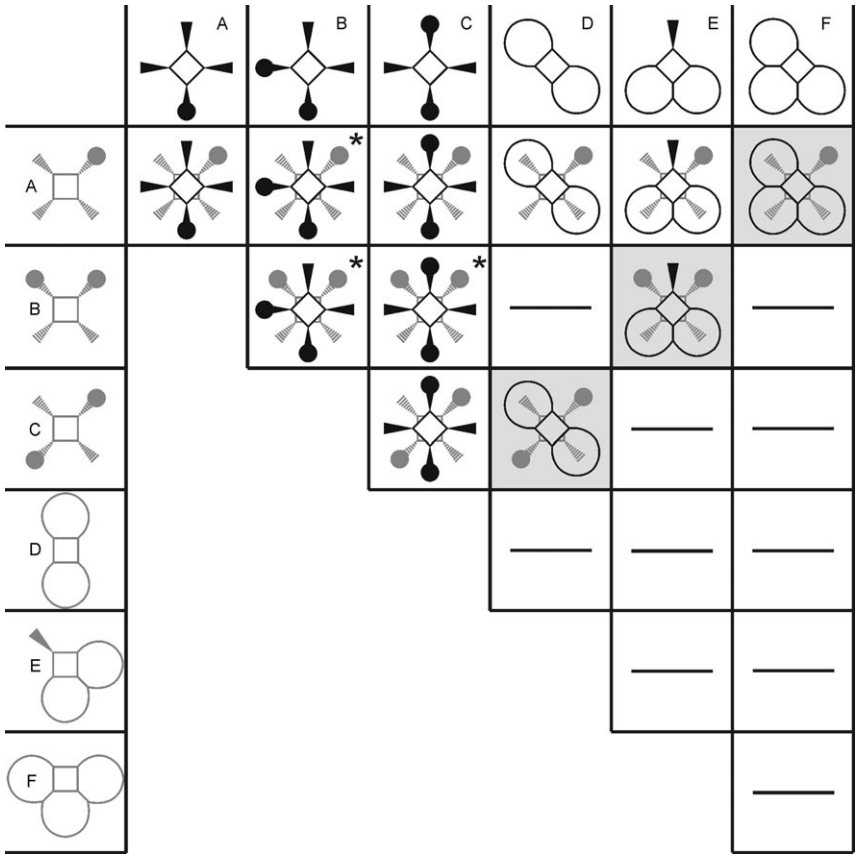


Figure 1. Schematic representation of the possible combinations of tetra-urea calix[4]arenes **A**–**F** to form dimeric capsules. Combinations for which regioisomeric arrangements are possible are marked with *.

The NMR spectra shown in Figure 2 confirm these predictions. The bisloop compound **5a** shows a broad, unresolved spectrum, typical for a mixture of ill-defined assemblies (Figure 2a). The tetra-urea **16**, with two bulky urea residues, forms two regioisomeric homodimers (Figure 2b). The stoichiometric mixture of the two tetra-urea compounds shows a sharp, well resolved spectrum, corresponding to the heterodimer **5a·16** (Figure 2c). In spite of the spectrum's complex and complicated pattern, the absence of the homodimer **16·16** can be unambiguously deduced. This principle also holds for the combination of trisloop derivative **6a** and tetra-urea **17** with one bulky residue (Figure 2d–f). Again, the NMR spectrum shows the formation of a single heterodimer **6a·17** (Figure 2f), while the homodimers **17·17** completely disappear.

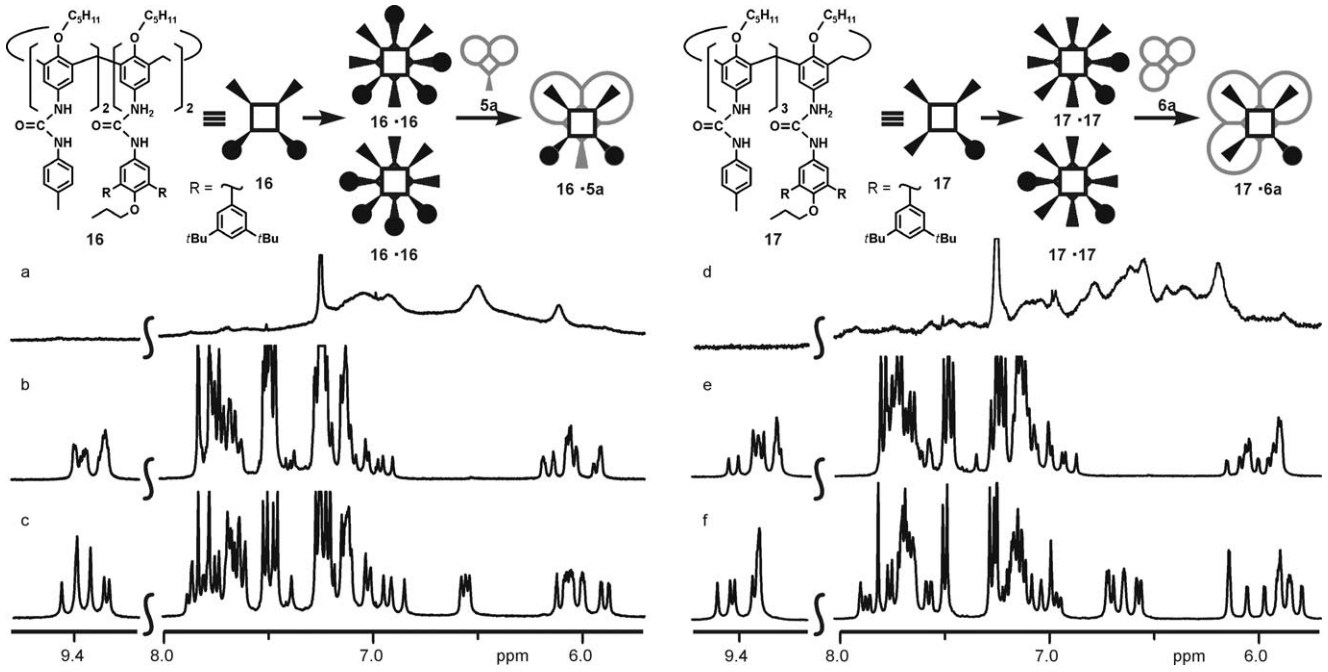


Figure 2. Sections of the ^{1}H NMR spectra ($CDCl_3$, 25 °C) of: a) the bisloop derivative **5a**, b) tetra-urea **16** (mixture of two regioisomeric homodimers), c) stoichiometric mixture of **5a** and **16** (heterodimer), d) trisloop derivative **6a**, e) tetra-urea **17** (mixture of two regioisomeric homodimers), and f) stoichiometric mixture of **6a** and **17** (heterodimer).

Conclusion

The recently described protection of two opposite amino functions in tetra-amino calix[4]arenes ("1,3-protection") by trityl groups paves the way for the controlled synthesis of tetra-urea calix[4]arenes, in which three urea functions are covalently connected by aliphatic chains to form bisloop derivatives. Trisloop derivatives were made analogously by use of "1,2-protection" with Boc groups. Tetra-urea calix[4]arenes with bulky urea groups are available by analogous strategies. These novel derivatives create novel possibilities for selective dimerisation, which may be utilisable, for instance, for the construction of structurally uniform, self-assembled dendrimers.[11]

Experimental Section

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 reported as δ values (ppm) with reference to the residual solvent peaks. Decoupling and DEPT experiments confirmed the assignments of the signals. ESI mass spectra were recorded on a Waters/Micromass QTof Ultima 3 mass spectrometer. ^{1}H and ^{13}C NMR spectra of compounds **5** and **6** are available as Supporting Information.

All solvents were HPLC grade and were used without further purification. Column chromatography was performed on silica gel 60 (0.035–0.070 mm, Acros). Grubbs′ catalyst—bis-(tricyclohexylphosphine)benzylidene ruthenium(IV) chloride—was purchased from Aldrich.

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. Nevertheless, the identities of the reported compounds, as well as their purities, were unambiguously established by their spectroscopic data.

1,3-Bis-[3-(hex-5-enyloxy)phenylureido]-2,4-bis-[triphenylmethylamino]-calix[4]arene (12): Bis(trichloromethyl) carbonate (1.52 g, 5.12 mmol) was added under nitrogen to a solution of 3-(hex-5-enyloxy)aniline[20] (0.98 g, 5.12 mmol) in toluene (20 mL). The solution was stirred for half an hour at room temperature, for 1 h at 50 °C and for 1 h at 80 °C and was finally concentrated under reduced pressure (bath temperature $>$70 °C). Toluene (20 mL) was added and evaporated again to remove the residues of phosgene.

Calix[4]arene **11**[17] (2.00 g, 1.60 mmol) was added under nitrogen to the solution of freshly prepared isocyanate in toluene (30 mL), and the reaction mixture was stirred overnight. Methanol (10 mL) was added, and the solvents were evaporated to a volume of $\approx$1–2 mL. The residue was treated with methanol (50 mL), and the resulting solid was filtered off, washed with methanol and dried in air to give compound **12** (2.45 g, 91 %) as a light brown powder. If necessary, additional purification can be performed by column chromatography (THF/hexane 1:5). M.p. 145–147 °C (decomposition); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.88 (t, ^3J(H,H) = 7.0 Hz, 6H; CH_3), 0.89(t, ^3J(H,H) = 7.0 Hz, 6H; CH_3), 1.16–1.52 (m, 20H; CH_2), 1.71 (m, 8H; CH_2), 1.90 (m, 4H; CH_2), 2.05 (m, 4H; CH_2), 2.69 (d, ^2J(H,H) = 12.4 Hz, 4H; ArCH_2Ar), 3.45 (t, ^3J(H,H) = 6.6 Hz, 4H; OCH_2), 3.82 (m, 4H; OCH_2), 3.93 (t, ^3J(H,H) = 6.6 Hz, 4H; OCH_2), 4.13 (d, ^2J(H,H) = 12.4 Hz, 4H; ArCH_2Ar), 4.97 (m, 4H; CH=CH_2), 5.21 (s, 2H; Ph_3CNH), 5.79 (m, 2H; CH=CH_2), 5.87 (s, 4H; ArH), 6.51 (d × d, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.1 Hz, 2H; PhH), 6.80 (s, 4H; ArH), 6.86 (br d × d, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.1 Hz, 2H; PhH), 6.99 (s, 30H; CPh_3H), 7.15 (d × d, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 8.3 Hz, 2H; PhH), 7.31 (d × d, ^4J(H,H) = 2.1 Hz, ^4J(H,H) = 2.1 Hz, 2H; PhH), 7.92 (s, 2H; NH), 8.38 ppm (s, 2H; NH); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO, 25 °C): δ = 13.7 (CH_3), 14.0 (CH_3), 22.2 (CH_2), 22.3 (CH_2), 24.6 (CH_2), 27.7 (CH_2), 28.0 (CH_2), 28.1 (CH_2), 29.0 (CH_2), 29.5 (CH_2), 30.6 (CH_2), 32.7 (CH_2), 66.9 (OCH_2), 70.8 (CPh_3), 74.3 (OCH_2), 74.7 (OCH_2), 104.1 (CH), 107.4 (CH), 110.0 (CH), 114.8 (CH=CH_2), 115.9 (CH), 117.9 (CH), 125.7 (CH), 127.1 (CH), 128.8 (CH), 129.3 (CH), 131.56 (C), 133.6 (C), 135.4 (C), 138.4 (CH=CH$_2$), 140.7 (C), 141.3 (C), 145.7 (C), 146.6 (C),

151.2 (*C*), 152.2 (*C*), 159.0 ppm (*C*); MS (ESI): *m/z* (%): calcd for $C_{112}H_{126}N_6O_8Na$: 1707.28; found: 1707.0 (100) $[M+Na]^+$.

1,3-Bis-[3-(hex-5-enyloxy)phenylureido]-2,4-diaminocalix[4]arene (13): Trifluoroacetic acid (1.35 g, 11.9 mmol) was added to a solution of calix[4]arene **12** (1.0 g, 0.59 mmol) and 3,5-dihydroxytoluene (**IV**, 0.59 g, 4.75 mmol) in dichloromethane (60 mL). After stirring for 2 h the reaction mixture was washed with water (2×20 mL), aqueous K_2CO_3 solution (5%, 4×20 mL) and again with water (2×20 mL) and dried ($MgSO_4$). The resulting mixture was purified by column chromatography (chloroform/acetone 3:1) to give the product **13** (0.38 g, 53%) as a beige solid mass. M.p. 147–150°C (decomposition); ^{1}H NMR (400 MHz, [D$_6$]DMSO+CD$_3$COOD (10%), 25°C): δ=0.87 (t, ^3J(H,H)=7.0 Hz, 6H; CH_3), 0.89 (t, ^3J(H,H)=7.0 Hz, 6H; CH_3), 1.17–1.53 (m, 20H; CH_2), 1.64–1.73 (m, 4H; CH_2), 1.76–1.85 (m, 8H; CH_2), 2.02–2.10 (m, 4H; CH_2), 3.03 (d, ^2J(H,H)=13.4 Hz, 4H; ArCH_2Ar), 3.66 (t, ^3J(H,H)=6.2 Hz, 4H; OCH_2), 3.83 (t, ^3J(H,H)=7.8 Hz, 4H; OCH_2), 3.89 (t, ^3J(H,H)=6.2 Hz, 4H; OCH_2), 4.28 (d, ^2J(H,H)=13.4 Hz, 4H; ArCH_2Ar), 4.90–5.03 (m, 4H; CH=CH_2), 5.73–5.85 (m, 2H; CH=CH$_2$), 5.88 (s, 4H; Ar*H*), 6.48 (d×d, ^3J(H,H)=8.2 Hz, ^4J(H,H)=2.0 Hz, 2H; Ph*H*), 6.83 (brd×d, ^3J(H,H)=8.2 Hz, ^4J(H,H)=2.0 Hz, 2H; Ph*H*), 7.05 (s, 4H; Ar*H*), 7.09 (d×d, ^3J(H,H)=8.2 Hz, ^3J(H,H)=8.2 Hz, 2H; Ph*H*), 7.16 (d×d, ^4J(H,H)=2.0 Hz, ^4J(H,H)=2.0 Hz, 2H; Ph*H*), 8.44 (s, {2H}; N*H*), 8.59 ppm (s, {2H}; N*H*) {the intensities of NH signals are lower because of deuterium exchange}; ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO+CD$_3$COOD (10%), 25°C): δ=14.2 (*C*H$_3$), 14.3 (*C*H$_3$), 22.7 (*C*H$_2$), 22.8 (*C*H$_2$), 25.2 (*C*H$_2$), 28.1 (*C*H$_2$), 28.6 (*C*H$_2$), 29.7 (*C*H$_2$), 30.0 (*C*H$_2$), 31.0 (*C*H$_2$), 33.3 (*C*H$_2$), 67.5 (O*C*H$_2$), 74.9 (O*C*H$_2$), 75.0 (O*C*H$_2$), 104.8 (*C*H), 107.9 (*C*H), 110.6 (*C*H), 115.2 (CH=*C*H$_2$), 117.6 (*C*H), 118.8 (*C*H), 129.8 (*C*H), 133.8 (*C*), 135.2 (*C*), 135.4 (*C*), 136.3 (*C*), 138.9 (*C*H=CH$_2$), 141.4 (*C*), 151.2 (*C*), 152.5 (*C*), 152.9 (*C*), 159.6 ppm (*C*); MS (ESI): *m/z* (%): calcd for $C_{74}H_{98}N_6O_8$: 1199.64; found: 1199.8 (100) $[M]^+$, 1221.8 (73) $[M+Na]^+$, 1239.8 (99) $[M+K]^+$, 2399.5 (31) $[2M]^+$, 2419.5 (5) $[2M+Na]^+$, 2439.5 (10) $[2M+K]^+$.

1,3-Bis-[3-(hex-5-enyloxy)phenylureido]-2-tolylureido-4-amino-calix[4]-arene (14): Et$_3$N (0.5 mL) was added to a solution of diamino-calix[4]arene **13** (0.36 g, 0.30 mmol) and the *p*-nitrophenyl ester **V**[21] (0.09 g, 0.33 mmol) in chloroform (50 mL). The reaction mixture was stirred for 3 h at room temperature, and was then washed with aqueous K_2CO_3 solution (10%, 3×20 mL) and water (2×20 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (THF/hexane 2:3) to yield calix[4]arene **14** (0.30 g, 75%) as a light yellow powder. M.p. 182–185°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C): δ=0.93 (t, ^3J(H,H)=6.6 Hz, 12H; CH_3), 1.28–1.54 (m, 20H; CH_2), 1.69 (m, 4H; CH_2), 1.89 (m, 8H; CH_2), 2.07 (m, 4H; CH_2), 2.21 (s, 3H; TolCH_3), 2.96 (d, ^2J(H,H)=12.8 Hz, 2H; ArCH_2Ar), 3.10 (d, ^2J(H,H)=12.8 Hz, 2H; ArCH_2Ar), 3.83 (m, 12H; OCH_2), 4.25 (d, ^2J(H,H)=12.8 Hz, 2H; ArCH_2Ar), 4.33 (d, ^2J(H,H)=12.8 Hz, 2H; ArCH_2Ar), 4.39 (brs, 2H; NH_2), 5.00 (m, 4H; CH=CH_2), 5.82 (m, 2H; CH=CH$_2$), 6.01 (s, 2H; Ar*H*), 6.48 (d×d, ^3J(H,H)=8.3 Hz, ^4J(H,H)=2.4 Hz, 2H; Ph*H*), 6.71 (d, ^4J(H,H)=2.3 Hz, 2H; Ar*H*), 6.75 (m, 4H; Ar*H* and Ph*H*), 6.82 (s, 2H; ArH), 7.03 (d, ^3J(H,H)=8.3 Hz, 2H; Tol*H*), 7.08 (m, 4H; *m*-Ph*H* and *o*-Ph*H*), 7.26 (d, ^3J(H,H)=8.3 Hz, 2H; Tol*H*), 8.11 (s, 2H; N*H*), 8.20 (s, 1H; N*H*), 8.24 (s, 1H; N*H*), 8.32 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO, 25°C): δ=13.9 (*C*H$_3$), 20.2 (Tol*C*H$_3$), 22.2 (*C*H$_2$), 22.3 (*C*H$_2$), 24.7 (*C*H$_2$), 27.8 (*C*H$_2$), 27.9 (*C*H$_2$), 28.1 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 30.6 (*C*H$_2$), 32.8 (*C*H$_2$), 66.9 (O*C*H$_2$), 74.7 (O*C*H$_2$), 104.2 (*C*H), 107.2 (*C*H), 110.1 (*C*H), 114.0 (*C*H), 114.8 (CH=*C*H$_2$), 117.9 (*C*H), 118.1 (*C*H), 118.4 (*C*H), 118.6 (*C*H), 129.0 (*C*H), 129.3 (*C*H), 130.2 (*C*), 133.0 (*C*), 133.3 (*C*), 134.1 (*C*), 134.2 (*C*), 134.5 (*C*), 134.6 (*C*), 137.2 (*C*), 138.4 (*C*H=CH$_2$), 141.0 (*C*), 147.3 (*C*), 151.1 (*C*), 151.2 (*C*), 152.3 (*C*), 152.5 (*C*), 159.0 ppm (*C*); MS (ESI): *m/z* (%): calcd for $C_{82}H_{105}N_7O_9Na$: 1355.78; found: 1354.8 (100) $[M+Na]^+$.

2-[3,5-Di(hex-5-enyloxy)phenylureido]-1,3-bis-[3-(hex-5-enyloxy)phenylureido]-4-tolylureido-calix[4]arene (15a): Diphenyl phosphoryl azide (DPPA, 0.061 g, 0.22 mmol) and Et$_3$N (0.023 g, 0.22 mmol) were added under nitrogen to a solution of 3,5-bis(hex-5-enyloxy)benzoic acid[22] (0.061 g, 0.19 mmol) in toluene (20 mL), and the mixture was stirred at 70°C for 4 h. A solution of calix[4]arene **14** (0.17 g, 0.13 mmol) in dichloromethane (3 mL) was added to the freshly prepared isocyanate, and the reaction mixture was stirred at 70°C for 4 h. Methanol (10 mL) was added, and the solvents were evaporated. Purification by column chromatography (CH_2Cl_2 followed by chloroform/acetone 30:1) afforded product **15a** (0.14 g, 67%) as a white powder. M.p. 158–160°C (decomposition); ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ=0.96 (m, 12H; CH_3), 1.36–1.59 (m, 24H; CH_2), 1.69 (m, 8H; CH_2), 1.94 (m, 8H; CH_2), 2.08 (m, 8H; CH_2), 2.19 (s, 3H; TolCH_3), 3.06 (d, ^2J(H,H)=13.2 Hz, 4H; ArCH_2Ar), 3.84 (m, 16H; OCH_2), 4.43 (d, ^2J(H,H)=13.2 Hz, 4H; ArCH_2Ar), 4.94 (m, 8H; CH=CH_2), 5.80 (m, 4H; CH=CH$_2$), 6.04 (brs, 1H; *p*-Ph*H*), 6.42 (d×d, ^3J(H,H)=8.0 Hz, ^4J(H,H)=1.8 Hz, 2H; Ph*H*), 6.57 (d, ^4J(H,H)=1.6 Hz, 2H; *o*-Ph*H*), 6.69 (brd, ^3J(H,H)=8.0 Hz, 2H; Ph*H*), 6.78 (s, 4H; Ar*H*), 6.83 (m, 4H; Ar*H*), 6.92 (d, ^3J(H,H)=8.2 Hz, 2H; Tol*H*), 6.97 (d×d, ^3J(H,H)=8.0 Hz, ^3J(H,H)=8.0 Hz, 2H; *m*-Ph*H*), 7.20 (m, 4H; Tol*H* and *o*-Ph*H*), 7.43 (s, 1H; N*H*), 7.52 (s, 1H; N*H*), 7.55 (s, 3H; N*H*), 7.58 (s, 1H; N*H*), 7.62 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25°C): δ=14.6 (*C*H$_3$), 20.8 (Tol*C*H$_3$), 23.8 (*C*H$_2$), 26.4 (*C*H$_2$), 29.49 (*C*H$_2$), 29.51 (*C*H$_2$), 29.8 (*C*H$_2$), 30.88 (*C*H$_2$), 30.91 (*C*H$_2$), 32.1 (*C*H$_2$), 34.4 (*C*H$_2$), 68.12 (O*C*H$_2$), 68.14 (O*C*H$_2$), 75.9 (O*C*H$_2$), 95.5 (*C*H), 97.7 (*C*H), 105.4 (*C*H), 108.3 (*C*H), 111.0 (*C*H), 114.9 (CH=*C*H$_2$), 119.1 (*C*H), 119.3 (*C*H), 129.7 (*C*H), 129.8 (*C*H), 131.3 (*C*), 134.8 (*C*), 134.88 (*C*), 134.94 (*C*), 135.79 (*C*), 135.82 (*C*), 136.00 (*C*), 136.02 (*C*), 138.7 (*C*), 139.5 (*C*H=CH$_2$), 142.4 (*C*), 142.8 (*C*), 152.6 (*C*), 152.7 (*C*), 152.8 (*C*), 153.2 (*C*), 153.3 (*C*), 153.5 (*C*), 160.7 (*C*), 161.4 ppm (*C*); MS (ESI): *m/z* (%): calcd for $C_{101}H_{130}N_8O_{12}$: 1648.21; found: 1649.1 (21) $[M+H]^+$, 1671.0 (100) $[M+Na]^+$.

2-[3,5-Di(oct-7-enyloxy)phenylureido]-1,3-bis-[3-(hex-5-enyloxy)phenylureido]-4-tolylureido-calix[4]arene (15b): This compound was prepared as described for **15a**; after column chromatography (CH_2Cl_2 followed by chloroform/acetone 15:1) **15b** was obtained in 68% yield. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C): δ=0.93 (t, ^3J(H,H)=7.0 Hz, 12H; CH_3), 1.23–1.53 (m, 32H; CH_2), 1.66 (m, 8H; CH_2), 1.90 (m, 8H; CH_2), 2.03 (m, 8H; CH_2), 2.20 (s, 3H; TolCH_3), 3.11 (d, ^2J(H,H)=12.8 Hz, 4H; ArCH_2Ar), 3.85 (m, 16H; OCH_2), 4.33 (d, ^2J(H,H)=12.8 Hz, 4H; ArCH_2Ar), 4.97 (m, 8H; CH=CH_2), 5.79 (m, 4H; CH=CH$_2$), 6.05 (t, ^4J(H,H)=2.1 Hz, 1H; *p*-Ph*H*), 6.47 (d×d, ^3J(H,H)=8.3 Hz, ^4J(H,H)=2.0 Hz, 2H; Ph*H*), 6.51 (d, ^4J(H,H)=2.1 Hz, 2H; *o*-Ph*H*), 6.78 (m, 10H; Ar*H* and Ph*H*), 6.99 (d, ^3J(H,H)=8.2 Hz, 2H; Tol*H*), 7.07 (d×d, ^3J(H,H)=8.3 Hz, ^3J(H,H)=8.3 Hz, 2H; *m*-Ph*H*), 7.08 (s, 2H; *o*-Ph*H*), 7.20 (d, ^3J(H,H)=8.2 Hz, 2H; Tol*H*), 8.12 (s, 1H; N*H*), 8.13 (s, 1H; N*H*), 8.17 (s, 2H; N*H*), 8.19 (s, 1H; N*H*), 8.27 (s, 1H; N*H*), 8.31 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO, 25°C): δ=13.9 (*C*H$_3$), 20.2 (Tol*C*H$_3$), 22.2 (*C*H$_2$), 24.7 (*C*H$_2$), 25.2 (*C*H$_2$), 27.9 (*C*H$_2$), 28.08 (*C*H$_2$), 28.12 (*C*H$_2$), 28.14 (*C*H$_2$), 28.5 (*C*H$_2$), 29.3 (*C*H$_2$), 30.6 (*C*H$_2$), 32.8 (*C*H$_2$), 33.0 (*C*H$_2$), 66.9 (O*C*H$_2$), 67.1 (O*C*H$_2$), 74.7 (O*C*H$_2$), 94.3 (*C*H), 96.6 (*C*H), 104.2 (*C*H), 107.2 (*C*H), 110.1 (*C*H), 114.5 (CH=*C*H$_2$), 114.8 (CH=*C*H$_2$), 117.9 (*C*H), 118.0 (*C*H), 118.1 (*C*H), 128.9 (*C*H), 129.2 (*C*H), 130.1 (*C*), 133.2 (*C*), 133.3 (*C*), 133.4 (*C*), 134.2 (*C*), 134.3 (*C*), 134.4 (*C*), 137.2 (*C*), 138.4 (*C*H=CH$_2$), 138.6 (*C*H=CH$_2$), 140.9 (*C*), 141.4 (*C*), 150.9 (*C*), 151.0 (*C*), 151.1 (*C*), 152.2 (*C*), 152.3 (*C*), 152.4 (*C*), 158.9 (*C*), 159.8 ppm (*C*); MS (ESI): *m/z* (%): calcd for $C_{105}H_{138}N_8O_{12}Na$: 1727.31; found: 1727.0 (100) $[M+Na]^+$.

Bisloop calix[4]arene 5a: A solution of tetra-urea **15a** (0.14 g, 0.085 mmol) and tetratosylurea **2**[23] (0.15 g, 0.093 mmol) in dichloromethane/benzene 3:1 (280 mL) was stirred until it became clear. Nitrogen was bubbled through the solution for 1 h, and Grubbs' catalyst, (0.014 g, 0.017 mmol) was added under nitrogen. The reaction mixture was stirred for 2 days. After addition of Et$_3$N (3 mL) the solvents were evaporated, and the residue was purified by column chromatography (THF/hexane 2:5 followed by THF/hexane 1:2). The obtained white solid was hydrogenated in THF/toluene 5:1 (60 mL) in the presence of PtO_2 (0.005 g, 0.022 mmol) as catalyst over 1.5 h. The catalyst was filtered off, solvents were evaporated, and the residue was precipitated with methanol from dichloromethane to yield compound **5a** (0.11 g, 81%) as a white powder. M.p. 290–300°C (decomposition); ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ=0.96 (t, ^3J(H,H)=7.0 Hz, 6H; CH_3), 0.97 (t, ^3J(H,H)=7.0 Hz, 6H; CH_3), 1.25–1.57 (m, 40H; CH_2), 1.67 (m, 8H; CH_2), 1.86–2.03 (m, 8H; CH_2), 2.16 (s, 3H; TolCH_3), 3.03 (d, ^2J(H,H)=13.0 Hz, 2H; ArCH_2Ar), 3.07 (d, ^2J(H,H)=13.0 Hz, 2H; ArCH_2Ar), 3.77 (m, 8H; OCH_2), 3.93 (t,

^3J(H,H) = 6.2 Hz, 4H; OCH_2), 3.98 (t, ^3J(H,H) = 7.8 Hz, 4H; OCH_2), 4.43 (d, ^2J(H,H) = 13.0 Hz, 4H; ArCH_2Ar), 5.99 (t, ^4J(H,H) = 2.1 Hz, 1H; *p*-Ph*H*), 6.44 (m, 4H; Ph*H* and *o*-Ph*H*), 6.54 (s, 2H; Ar*H*), 6.58 (s, 2H; Ar*H*), 6.83 (m, 4H; Ph*H* and Tol*H*), 6.98 (d, ^4J(H,H) = 2.1 Hz, 2H; Ar*H*), 7.02 (d × d, ^3J(H,H) = 8.2 Hz, ^3J(H,H) = 8.2 Hz, 2H; *m*-Ph*H*), 7.06 (d, ^3J(H,H) = 8.6 Hz, 2H; Tol*H*), 7.19 (s, 2H; *o*-Ph*H*), 7.22 (d, ^4J(H,H) = 2.1 Hz, 2H; Ar*H*), 7.24 (s, 1H; N*H*), 7.33 (s, 1H; N*H*), 7.43 (s, 1H; N*H*), 7.48 (s, 1H; N*H*), 7.76 (s, 2H; N*H*), 7.77 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 14.5 (*C*H$_3$), 14.7 (*C*H$_3$), 20.8 (Tol*C*H$_3$), 23.7 (*C*H$_2$), 23.9 (*C*H$_2$), 26.6 (*C*H$_2$), 26.7 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 29.7 (*C*H$_2$), 29.8 (*C*H$_2$), 30.0 (*C*H$_2$), 30.1 (*C*H$_2$), 30.7 (*C*H$_2$), 31.08 (*C*H$_2$), 31.10 (*C*H$_2$), 32.12 (*C*H$_2$), 67.8 (O*C*H$_2$), 68.1 (O*C*H$_2$), 75.8 (O*C*H$_2$), 75.9 (O*C*H$_2$), 76.0 (O*C*H$_2$), 95.6 (*C*H), 97.5 (*C*H), 105.7 (*C*H), 108.3 (*C*H), 111.1 (*C*H), 118.8 (*C*H), 119.0 (*C*H), 119.3 (*C*H), 119.4 (*C*H), 129.6 (*C*H), 129.9 (*C*H), 130.9 (*C*), 134.7 (*C*), 134.85 (*C*), 134.95 (*C*), 135.00 (*C*), 136.9 (*C*), 138.7 (*C*), 142.5 (*C*), 142.7 (*C*), 152.0 (*C*), 152.1 (*C*), 153.1 (*C*), 153.2 (*C*), 153.3 (*C*), 160.7 (*C*), 161.4 ppm (*C*); MS (ESI): *m*/*z* (%): calcd for $C_{97}H_{126}N_8O_{12}Na$: 1619.12; found: 1619.0 (100) [*M*+Na]$^+$.

Bisloop calix[4]arene 5b: Compound **5b** was prepared and purified as described for **5a**; yield 77%; m.p. 290–300 °C (decomposition); ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.96 (t, ^3J(H,H) = 7.0 Hz, 6H; C*H*$_3$), 0.97 (t, ^3J(H,H) = 7.0 Hz, 6H; C*H*$_3$), 1.22–1.54 (m, 48H; C*H*$_2$), 1.68 (m, 8H; C*H*$_2$), 1.95 (m, 8H; C*H*$_2$), 2.17 (s, 3H; Tol*CH*$_3$), 3.06 (d, ^2J(H,H) = 12.8 Hz, 2H; ArC*H*$_2$Ar), 3.07 (d, ^2J(H,H) = 12.8 Hz, 2H; ArC*H*$_2$Ar), 3.78 (m, 8H; OC*H*$_2$), 3.93 (m, 8H; OC*H*$_2$), 4.44 (d, ^2J(H,H) = 12.8 Hz, 4H; ArC*H*$_2$Ar), 6.00 (t, ^4J(H,H) = 1.3 Hz, 1H; *p*-Ph*H*), 6.44 (d × d, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.1 Hz, 2H; Ph*H*), 6.49 (d, ^4J(H,H) = 1.3 Hz, 2H; *o*-Ph*H*), 6.61 (s, 2H; Ar*H*), 6.64 (s, 2H; Ar*H*), 6.84 (br d, ^3J(H,H) = 8.2 Hz, 2H; Ph*H*), 6.87 (d, ^3J(H,H) = 8.2 Hz, 2H; Tol*H*), 6.95 (d, ^4J(H,H) = 2.1 Hz, 2H; Ar*H*), 7.02 (d × d, ^3J(H,H) = 8.2 Hz, ^3J(H,H) = 8.2 Hz, 2H; *m*-Ph*H*), 7.13 (d, ^4J(H,H) = 2.1 Hz, 2H; Ar*H*), 7.12 (d, ^3J(H,H) = 8.2 Hz, 2H; Tol*H*), 7.18 (s, 2H; *o*-Ph*H*), 7.24 (s, 1H; N*H*), 7.32 (s, 1H; N*H*), 7.36 (s, 1H; N*H*), 7.45 (s, 1H; N*H*), 7.60 (s, 2H; N*H*), 7.65 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 14.6 (*C*H$_3$), 14.7 (*C*H$_3$), 20.8 (Tol*C*H$_3$), 23.7 (*C*H$_2$), 23.9 (*C*H$_2$), 26.5 (*C*H$_2$), 26.6 (*C*H$_2$), 29.4 (*C*H$_2$), 29.6 (*C*H$_2$), 29.7 (*C*H$_2$), 29.8 (*C*H$_2$), 29.85 (*C*H$_2$), 29.87 (*C*H$_2$), 30.0 (*C*H$_2$), 30.1 (*C*H$_2$), 30.8 (*C*H$_2$), 31.1 (*C*H$_2$), 32.1 (*C*H$_2$), 67.9 (O*C*H$_2$), 68.0 (O*C*H$_2$), 75.9 (O*C*H$_2$), 75.97 (O*C*H$_2$), 76.02 (O*C*H$_2$), 95.3 (*C*H), 97.6 (*C*H), 105.5 (*C*H), 108.2 (*C*H), 110.9 (*C*H), 118.9 (*C*H), 119.1 (*C*H), 119.2 (*C*H), 129.7 (*C*H), 129.9 (*C*H), 131.1 (*C*), 134.96 (*C*), 135.01 (*C*), 135.04 (*C*), 136.7 (*C*), 138.8 (*C*), 142.5 (*C*), 142.8 (*C*), 152.1 (*C*), 152.2 (*C*), 152.9 (*C*), 153.0 (*C*), 153.2 (*C*), 160.7 (*C*), 161.4 ppm (*C*); MS (ESI): *m*/*z* (%): calcd for $C_{101}H_{134}N_8O_{12}Na$: 1675.23; found: 1675.0 (100) [*M*+Na]$^+$.

1,2-Bis-[3,5-di(hex-5-enyloxy)phenylureido]-3,4-di-Boc-calix[4]arene (8a): Compound **8a** was synthesised as described for **15a** from diamino calix[4]arene **7**[24] (0.48 g, 0.50 mmol) and the isocyanate freshly prepared from 3,5-bis(hex-5-enyloxy)benzoic acid[22] (0.35 g, 1.11 mmol), DPPA (0.36 g, 1.32 mmol) and Et$_3$N (0.13 g, 1.32 mmol). Purification by column chromatography (ethyl acetate/hexane 5:1) afforded **8a** (0.65 g, 81%) as a white solid. M.p. 151–153 °C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.96 (m, 12H; C*H*$_3$), 1.31–1.48 (m, 34H; C(C*H*$_3$)$_3$ and C*H*$_2$), 1.54 (m, 8H; C*H*$_2$), 1.72 (m, 8H; C*H*$_2$), 1.94 (m, 8H; C*H*$_2$), 2.09 (m, 8H; C*H*$_2$), 3.05 (d, ^2J(H,H) = 13.2 Hz, 4H; ArC*H*$_2$Ar), 3.87 (t, ^3J(H,H) = 6.2 Hz, 16H; OC*H*$_2$), 4.42 (d, ^2J(H,H) = 13.2 Hz, 4H; ArC*H*$_2$Ar), 4.95 (m, 8H; CH=C*H*$_2$), 5.80 (m, 4H; C*H*=CH$_2$), 6.04 (s, 2H; *p*-Ph*H*), 6.66 (s, 4H; *o*-Ph*H*), 6.75 (br s, 8H; Ar*H*), 7.46 (br s, 4H; N*H*), 8.16 ppm (br s, 2H; N*H*); MS (ESI): *m*/*z* (%): calcd for $C_{96}H_{134}N_6O_{14}Na$: 1617.99; found: 1619.0 (100) [*M*+Na]$^+$.

1,2-Bis-[3,5-di(undec-10-enyloxy)phenylureido]-3,4-di-Boc-calix[4]arene (8b): Compound **8b** was prepared and purified analogously to **8a**, yield 94%; m.p. 126–128 °C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.96 (m, 12H; C*H*$_3$), 1.22–1.51 (m, 82H; C(C*H*$_3$)$_3$ and C*H*$_2$), 1.69 (m, 8H; C*H*$_2$), 1.94 (m, 8H; C*H*$_2$), 2.03 (m, 8H; C*H*$_2$), 3.05 (d, ^2J(H,H) = 12.8 Hz, 4H; ArC*H*$_2$Ar), 3.86 (t, ^3J(H,H) = 6.3 Hz, 16H; OC*H*$_2$), 4.42 (d, ^2J(H,H) = 12.8 Hz, 4H; ArC*H*$_2$Ar), 4.91 (m, 8H; CH=C*H*$_2$), 5.78 (m, 4H; C*H*=CH$_2$), 6.03 (s, 2H; *p*-Ph*H*), 6.66 (s, 4H; *o*-Ph*H*), 6.76 (br s, 8H; Ar*H*), 7.45 (br s, 4H; N*H*), 8.17 ppm (br s, 2H; N*H*); MS (ESI): *m*/*z* (%): calcd for $C_{116}H_{174}N_6O_{14}Na$: 1898.30; found: 1899.4 (100) [*M*+Na]$^+$.

1,2-Bis-[3,5-di(hex-5-enyloxy)phenylureido]-3,4-diamino-calix[4]arene (9a): Aluminium chloride (0.12 g, 0.90 mmol) was added to a solution of **8a** (0.48 g, 0.30 mmol) in dichloromethane (30 mL) and the mixture was stirred for 4 h at room temperature. It was filtered through celite, washed with saturated aqueous NaHCO$_3$ (3 × 20 mL) and water (2 × 10 mL) and dried (MgSO$_4$). Evaporation of the solvent gave diamino-calix[4]arene **9a** (0.39 g, 92%) as a yellow powder. M.p. 153–154 °C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.94 (m, 12H; C*H*$_3$), 1.40 (m, 16H; C*H*$_2$), 1.52 (m, 8H; C*H*$_2$), 1.69 (m, 8H; C*H*$_2$), 1.87 (m, 8H; C*H*$_2$), 2.08 (m, 8H; C*H*$_2$), 2.51 (br s, 4H; N*H*$_2$), 2.80 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 2.94 (d, ^2J(H,H) = 13.2 Hz, 2H; ArC*H*$_2$Ar), 3.03 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 3.80 (m, 16H; OC*H*$_2$), 4.27 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 4.33 (d, ^2J(H,H) = 13.2 Hz, 2H; ArC*H*$_2$Ar), 4.40 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 4.95 (m, 8H; CH=C*H*$_2$), 5.80 (m, 4H; C*H*=CH$_2$), 5.94 (m, 4H; Ar*H*), 6.04 (s, 2H; *p*-Ph*H*), 6.49 (s, 2H; Ar*H*), 6.67 (s, 4H; *o*-Ph*H*), 6.77 (s, 2H; Ar*H*), 7.44 (br s, 2H; N*H*), 7.66 ppm (br s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 14.6 (*C*H$_3$), 23.76 (*C*H$_2$), 23.79 (*C*H$_2$), 26.4 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.8 (*C*H$_2$), 30.9 (*C*H$_2$), 32.1 (*C*H$_2$), 32.2 (*C*H$_2$), 34.4 (*C*H$_2$), 68.2 (O*C*H$_2$), 75.69 (O*C*H$_2$), 75.73 (O*C*H$_2$), 95.7 (*C*H), 97.8 (*C*H), 114.9 (CH=*C*H$_2$), 115.8 (*C*H), 121.8 (*C*H), 122.3 (*C*H), 134.1 (*C*), 135.9 (*C*), 136.6 (*C*), 139.5 (*C*H=CH$_2$), 142.9 (*C*), 149.8 (*C*), 153.8 (*C*), 161.4 ppm (*C*); MS (ESI): *m*/*z* (%): calcd for $C_{86}H_{118}N_6O_{10}Na$: 1417.88; found: 1417.9 (100) [*M*+Na]$^+$.

1,2-Bis-[3,5-di(undec-10-enyloxy)phenylureido]-3,4-diamino-calix[4]arene (9b): On application of the procedure described for the synthesis of **9a**, calix[4]arene **9b** was obtained in 93% yield. M.p. 128–130 °C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.94 (br s, 12H; C*H*$_3$), 1.22–1.49 (m, 64H; C*H*$_2$), 1.69 (m, 8H; C*H*$_2$), 1.87 (m, 8H; C*H*$_2$), 2.03 (m, 8H; C*H*$_2$), 2.55 (br s, 4H; N*H*$_2$), 2.80 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 2.94 (d, ^2J(H,H) = 13.2 Hz, 2H; ArC*H*$_2$Ar), 3.02 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 3.79 (m, 16H; OC*H*$_2$), 4.27 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 4.32 (d, ^2J(H,H) = 13.2 Hz, 2H; ArC*H*$_2$Ar), 4.39 (d, ^2J(H,H) = 13.2 Hz, 1H; ArC*H*$_2$Ar), 4.91 (m, 8H; CH=C*H*$_2$), 5.78 (m, 4H; C*H*=CH$_2$), 5.95 (m, 4H; Ar*H*), 6.03 (s, 2H; *p*-Ph*H*), 6.47 (s, 2H; Ar*H*), 6.67 (br s, 4H; *o*-Ph*H*), 6.80 (s, 2H; Ar*H*), 7.49 (br s, 2H; N*H*), 7.69 ppm (br s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 14.6 (*C*H$_3$), 23.8 (*C*H$_2$), 27.1 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.9 (*C*H$_2$), 30.1 (*C*H$_2$), 30.3 (*C*H$_2$), 30.4 (*C*H$_2$), 30.6 (*C*H$_2$), 30.9 (*C*H$_2$), 32.1 (*C*H$_2$), 32.2 (*C*H$_2$), 34.7 (*C*H$_2$), 68.4 (O*C*H$_2$), 75.7 (O*C*H$_2$), 95.5 (*C*H), 97.7 (*C*H), 114.6 (CH=*C*H$_2$), 115.8 (*C*H), 121.8 (*C*H), 122.3 (*C*H), 134.1 (*C*), 136.1 (*C*), 136.6 (*C*), 139.8 (*C*H=CH$_2$), 142.9 (*C*), 149.9 (*C*), 153.8 (*C*), 161.5 ppm (*C*); MS (ESI): *m*/*z* (%): calcd for $C_{106}H_{158}N_6O_{10}Na$: 1698.19; found: 1699.3 (100) [*M*+Na]$^+$.

1,2-Bis-[3,5-di(hex-5-enyloxy)phenylureido]-3,4-bis-[3-(hex-5-enyloxy)-phenylureido]calix[4]arene (10a): A solution of diamino-calix[4]arene **9a** (0.35 g, 0.25 mmol), *p*-nitrophenyl ester **II**[20] (0.19 g, 0.53 mmol) and Et$_3$N (0.5 mL) in THF (25 mL) was heated at reflux overnight. The residue obtained after evaporation was dissolved in dichloromethane (30 mL), washed with aqueous K$_2$CO$_3$ solution (5%, 4 × 20 mL) and water (2 × 20 mL) and dried (MgSO$_4$). The crude product was purified by column chromatography (ethyl acetate/hexane 1:5) to afford calix[4]arene **10a** (0.21 g, 46%) as a white solid. M.p. 208–210 °C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.96 (t, ^3J(H,H) = 6.6 Hz, 12H; C*H*$_3$), 1.44 (m, 16H; C*H*$_2$), 1.53 (m, 12H; C*H*$_2$), 1.69 (m, 12H; C*H*$_2$), 1.94 (m, 8H; C*H*$_2$), 2.09 (m, 12H; C*H*$_2$), 3.07 (d, ^2J(H,H) = 12.8 Hz, 4H; ArC*H*$_2$Ar), 3.85 (m, 20H; OC*H*$_2$), 4.44 (d, ^2J(H,H) = 12.8 Hz, 4H; ArC*H*$_2$Ar), 4.94 (m, 12H; CH=C*H*$_2$), 5.80 (m, 6H; C*H*=CH$_2$), 6.03 (br t, ^4J(H,H) = 1.7 Hz, 2H; *p*-Ph*H*), 6.41 (d × d, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.7 Hz, 2H; Ph*H*), 6.58 (m, 4H; *o*-Ph*H*), 6.66 (br d, ^3J(H,H) = 8.1 Hz, 2H; Ph*H*), 6.81 (s, 8H; Ar*H*), 6.97 (d × d, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 8.1 Hz, 2H; *m*-Ph*H*), 7.23 (br s, 2H; *o*-Ph*H*), 7.44 (s, 2H; N*H*), 7.46 (s, 2H; N*H*), 7.51 (s, 2H; N*H*), 7.55 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 14.6 (*C*H$_3$), 23.8 (*C*H$_2$), 26.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.8 (*C*H$_2$), 30.9 (*C*H$_2$), 32.1 (*C*H$_2$), 34.4 (*C*H$_2$), 68.1 (O*C*H$_2$), 75.9 (O*C*H$_2$), 95.5 (*C*H), 97.6 (*C*H), 105.3 (*C*H), 108.2 (*C*H), 111.0 (*C*H),

114.9 (CH=CH_2), 119.1 (*C*H), 129.8 (*C*H), 135.0 (*C*), 135.9 (*C*), 139.5 (*C*H=CH_2), 142.5 (*C*), 142.8 (*C*), 152.6 (*C*), 153.0 (*C*), 153.1 (*C*), 160.7 (*C*), 161.4 ppm (*C*); MS (FD): *m*/*z* (%): calcd for $C_{112}H_{148}N_8O_{14}$: 1829.11; found: 1830.2 (100) $[M+H]^+$.

1,2-Bis-[3,5-di(undec-10-enyloxy)phenylureido]-3,4-[3-(hex-5-enyloxy)-phenylureido]calix[4]arene (10b): Calix[4]arene **10b** was prepared as described for **10a**. The crude product was recrystallised from dichloromethane/methanol to afford **10b**, yield 78%. M.p. 144–146°C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ = 0.96 (br t, ^3J(H,H) = 7.0 Hz, 12H; CH_3), 1.23–1.59 (m, 72H; CH_2), 1.69 (m, 8H; CH_2), 1.89–2.14 (m, 20H; CH_2), 3.07 (d, ^2J(H,H) = 13.2 Hz, 4H; ArCH_2Ar), 3.76–3.92 (m, 20H; OCH_2), 4.43 (d, ^2J(H,H) = 13.2 Hz, 4H; ArCH_2Ar), 4.93 (m, 12H; CH=CH_2), 5.78 (m, 6H; C*H*=CH$_2$), 6.02 (br s, 2H; *p*-Ph*H*), 6.41 (d × d, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.4 Hz, 2H; Ph*H*), 6.58 (m, 4H; *o*-Ph*H*), 6.66 (br d, ^3J(H,H) = 8.1 Hz, 2H; Ph*H*), 6.80 (m, 8H; Ar*H*), 6.97 (d × d, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 8.1 Hz, 2H; *m*-Ph*H*), 7.23 (br s, 2H; *o*-Ph*H*), 7.44 (s, 2H; N*H*), 7.47 (s, 2H; N*H*), 7.51 (s, 2H; N*H*), 7.55 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25°C): δ = 14.6 (*C*H$_3$), 23.8 (*C*H$_2$), 26.4 (*C*H$_2$), 27.1 (*C*H$_2$), 29.5 (*C*H$_2$), 29.8 (*C*H$_2$), 29.9 (*C*H$_2$), 30.1 (*C*H$_2$), 30.3 (*C*H$_2$), 30.4 (*C*H$_2$), 30.6 (*C*H$_2$), 30.9 (*C*H$_2$), 32.2 (*C*H$_2$), 34.4 (*C*H$_2$), 34.7 (*C*H$_2$), 68.1 (O*C*H$_2$), 68.3 (O*C*H$_2$), 75.9 (O*C*H$_2$), 95.5 (*C*H), 97.6 (*C*H), 105.3 (*C*H), 108.3 (*C*H), 111.0 (*C*H), 114.6 (CH=*C*H$_2$), 114.9 (CH=*C*H$_2$), 119.2 (*C*H), 129.8 (*C*H), 135.0 (*C*), 135.9 (*C*), 139.5 (*C*H=CH$_2$), 139.8 (*C*H=CH$_2$), 142.5 (*C*), 142.8 (*C*), 152.7 (*C*), 153.0 (*C*), 153.1 (*C*), 160.7 (*C*), 161.5 ppm (*C*); MS (ESI): *m*/*z* (%): calcd for $C_{132}H_{188}N_8O_{14}Na$: 2132.41; found: 2133.4 (100) $[M+Na]^+$.

Trisloop calix[4]arene 6a: Compound **6a** was prepared from calix[4]arene **10a** (0.18 g, 0.11 mmol) as described for **5a**. Purification by column chromatography (THF/hexane 1:2) afforded **6a** (0.12 g, 70%) as a white solid. M.p. >300°C (decomposition); ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ = 0.97 (br t, ^3J(H,H) = 6.6 Hz, 12H; CH_3), 1.22–1.51 (m, 56H; CH_2), 1.68 (m, 8H; CH_2), 1.96 (m, 8H; CH_2), 3.067 (d, ^2J(H,H) = 12.8 Hz, 2H; ArCH_2Ar), 3.074 (d, ^2J(H,H) = 12.8 Hz, 2H; ArCH_2Ar), 3.85 (m, 20H; OCH_2), 4.44 (d, ^2J(H,H) = 12.8 Hz, 4H; ArCH_2Ar), 6.01 (t, ^4J(H,H) = 2.1 Hz, 2H; *p*-Ph*H*), 6.40 (d × d, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.1 Hz, 2H; Ph*H*), 6.56 (br s, 4H; *o*-Ph*H*), 6.73 (d, ^4J(H,H) = 2.1 Hz, 2H; Ar*H*), 6.76 (br d, ^3J(H,H) = 8.0 Hz, 2H; Ph*H*), 6.85 (br s, 2H; Ar*H*), 6.87 (br s, 2H; Ar*H*), 6.93 (d, ^4J(H,H) = 2.1 Hz, 2H; Ar*H*), 6.96 (d × d, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 8.0 Hz, 2H; *m*-Ph*H*), 7.05 (s, 2H; *o*-Ph*H*), 7.47 (s, 4H; N*H*), 7.51 ppm (s, 4H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25°C): δ = 14.6 (*C*H$_3$), 23.8 (*C*H$_2$), 26.58 (*C*H$_2$), 26.61 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 29.7 (*C*H$_2$), 29.98 (*C*H$_2$), 30.01 (*C*H$_2$), 30.09 (*C*H$_2$), 30.9 (*C*H$_2$), 31.0 (*C*H$_2$), 32.1 (*C*H$_2$), 32.2 (*C*H$_2$), 67.90 (O*C*H$_2$), 67.94 (O*C*H$_2$), 75.9 (O*C*H$_2$), 76.0 (O*C*H$_2$), 95.6 (*C*H), 97.3 (*C*H), 97.4 (*C*H), 105.5 (*C*H), 108.1 (*C*H), 111.0 (*C*H), 118.8 (*C*H), 118.88 (*C*H), 118.91 (*C*H), 119.1 (*C*H), 129.9 (*C*H), 135.0 (*C*), 135.1 (*C*), 135.8 (*C*), 142.5 (*C*), 142.8 (*C*), 152.5 (*C*), 152.9 (*C*), 153.0 (*C*), 160.7 (*C*), 161.4 (*C*), 161.5 ppm (*C*); MS (ESI): *m*/*z* (%): calcd for $C_{106}H_{143}N_8O_{14}$: 1752.07; found: 1753.14 (100) $[M+H]^+$.

Trisloop calix[4]arene 6b: Compound **6b** was prepared and purified as described for **6a**, yield 73%; m.p. >300°C (decomposition); ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ = 0.97 (br t, ^3J(H,H) = 6.6 Hz, 12H; CH_3), 1.20–1.51 (m, 96H; CH_2), 1.68 (m, 8H; CH_2), 1.95 (m, 8H; CH_2), 3.08 (d, ^2J(H,H) = 13.0 Hz, 4H; ArCH_2Ar), 3.77–3.92 (m, 20H; OCH_2), 4.44 (d, ^2J(H,H) = 13.0 Hz, 4H; ArCH_2Ar), 6.03 (s, 2H; *p*-Ph*H*), 6.41 (d × d, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 2.1 Hz, 2H; Ph*H*), 6.57 (s, 4H; *o*-Ph*H*), 6.60 (s, 2H; *o*-Ph*H*), 6.79 (m, 6H; Ar*H* and Ph*H*), 6.85 (s, 4H; Ar*H*), 6.98 (d × d, ^3J(H,H) = 8.2 Hz, ^3J(H,H) = 8.2 Hz, 2H; *m*-Ph*H*), 7.10 (s, 2H; *o*-Ph*H*), 7.44 (s, 2H; N*H*), 7.46 (s, 2H; N*H*), 7.51 (s, 2H; N*H*), 7.54 ppm (s, 2H; N*H*); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25°C): δ = 14.6 (*C*H$_3$), 23.8 (*C*H$_2$), 26.8 (*C*H$_2$), 26.9 (*C*H$_2$), 29.5 (*C*H$_2$), 29.8 (*C*H$_2$), 29.87 (*C*H$_2$), 29.91 (*C*H$_2$), 29.97 (*C*H$_2$), 30.00 (*C*H$_2$), 30.1 (*C*H$_2$), 30.2 (*C*H$_2$), 30.3 (*C*H$_2$), 30.9 (*C*H$_2$), 32.1 (*C*H$_2$), 32.2 (*C*H$_2$), 68.1 (O*C*H$_2$), 68.2 (O*C*H$_2$), 75.9 (O*C*H$_2$), 95.4 (*C*H), 97.6 (*C*H), 105.3 (*C*H), 108.1 (*C*H), 111.0 (*C*H), 119.0 (*C*H), 119.1 (*C*H), 119.2 (*C*H), 129.8 (*C*H), 134.97 (*C*), 135.00 (*C*), 135.8 (*C*), 142.5 (*C*), 142.8 (*C*), 152.6 (*C*), 152.9 (*C*), 153.0 (*C*), 160.7 (*C*), 161.5 ppm (*C*); MS (ESI): *m*/*z* (%): calcd for $C_{126}H_{182}N_8O_{14}Na$: 2054.37; found: 2055.36 (100) $[M+Na]^+$.

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[1] a) K. D. Shimizu, J. Rebek, Jr., *Proc. Natl. Acad. Sci. USA* **1995**, *92*, 12403–12407; b) B. C. Hamann, K. D. Shimizu, J. Rebek, Jr., *Angew. Chem.* **1996**, *108*, 1425–1427; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1326–1329.

[2] a) O. Mogck, E. F. Paulus, V. Böhmer, I. Thondorf, W. Vogt, *Chem. Commun.* **1996**, 2533–2534; b) I. Thondorf, F. Broda, K. Rissanen, M. Vysotsky, V. Böhmer, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1796–1800.

[3] O. Mogck, V. Böhmer, W. Vogt, *Tetrahedron* **1996**, *52*, 8489–8496.

[4] a) R. K. Castellano, B. H. Kim, J. Rebek, Jr., *J. Am. Chem. Soc.* **1997**, *119*, 12671–12672; b) R. K. Castellano, J. Rebek, Jr., *J. Am. Chem. Soc.* **1998**, *120*, 3657–3663.

[5] a) G.-K. Li, Y. Yang, C.-F. Chen, Z.-T. Huang, *Tetrahedron Lett.* **2007**, *48*, 6096–6099; b) I. Thondorf, Y. Rudzevich, V. Rudzevich, V. Böhmer, *Org. Biomol. Chem.* **2007**, *5*, 2775–2782; c) M. Bolte, I. Thondorf, V. Böhmer, Y. Rudzevich, V. Rudzevich, *Cryst. Eng. Commun.* **2008**, DOI: 10.1039/b716368a.

[6] A. Bogdan, Y. Rudzevich, M. O. Vysotsky, V. Böhmer, *Chem. Commun.* **2006**, 2941–2952.

[7] A. Bogdan, M. O. Vysotsky, L. Wang, V. Böhmer, *Chem. Commun.* **2004**, 1268–1269.

[8] For reviews on ring-closing metathesis, see: a) R. H. Grubbs, S. J. Miller, G. C. Fu, *Acc. Chem. Res.* **1995**, *28*, 446–452; b) H.-G. Schmalz, *Angew. Chem.* **1995**, *107*, 1981–1984; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1833–1836; c) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29.

[9] Examples of template synthesis of macrocycles, see: a) P. A. Chase, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten, *J. Mol. Catal. A* **2006**, *254*, 2–19; b) K. H. Song, S. O. Kang, J. Ko, *Chem. Eur. J.* **2007**, *13*, 5129–5134; c) N. Gimeno, R. Vilar, *Coord. Chem. Rev.* **2006**, *250*, 3161–3189; d) M. Bru, I. Alfonso, M. I. Burguete, S. V. Luis, *Angew. Chem.* **2006**, *118*, 6301–6305; *Angew. Chem. Int. Ed.* **2006**, *45*, 6155–6159.

[10] Cleavage of the urea links leads to huge macrocycles; see: Y. Cao, L. Wang, M. Bolte, M. O. Vysotsky, V. Böhmer, *Chem. Commun.* **2005**, 3132–3134.

[11] a) M. O. Vysotsky, A. Bogdan, T. Ikai, Y. Okamoto, V. Böhmer, *Chem. Eur. J.* **2004**, *10*, 3324–3330; b) O. Molokanova, A. Bogdan, M. O. Vysotsky, M. Bolte, T. Ikai, Y. Okamoto, V. Böhmer, *Chem. Eur. J.* **2007**, *13*, 6157–6170.

[12] For catenanes made with use of appropriate preorganisation: a) P. Baeuerle, M. Ammann, M. Wilde, G. Goetz, E. Mena-Osteritz, A. Rang, C. A. Schalley, *Angew. Chem.* **2007**, *119*, 367–372; *Angew. Chem. Int. Ed.* **2007**, *46*, 363–368; b) Y. Liu, L. M. Klivansky, S. I. Khan, X. Zhang, *Org. Lett.* **2007**, *9*, 2577–2580; c) E. Alcalde, L. Perez-Garcia, S. Ramos, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **2007**, *13*, 3964–3979; d) P. D. Beer, M. R. Sambrook, D. Curiel, *Chem. Commun.* **2006**, 2105–2117; e) M. Ammann, A. Rang, C. A. Schalley, P. Baeuerle, *Eur. J. Org. Chem.* **2006**, 1940–1948; f) J. Frey, T. Kraus, V. Heitz, J.-P. Sauvage, *Chem. Commun.* **2005**, 5310–5312; g) D. A. Leigh, P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong, *Angew. Chem.* **2001**, *113*, 1586–1591; *Angew. Chem. Int. Ed.* **2001**, *40*, 1538–1543.

[13] a) C. Gaeta, M. O. Vysotsky, A. Bogdan, V. Böhmer, *J. Am. Chem. Soc.* **2005**, *127*, 13136–13137; b) O. Molokanova, M. O. Vysotsky, Y. Cao, I. Thondorf, V. Böhmer, *Angew. Chem.* **2006**, *118*, 8220–8224; *Angew. Chem. Int. Ed.* **2006**, *45*, 8051–8055.

[14] For recent examples of rotaxanes made with use of preorganisation: a) J. Berná, J. D. Crowley, S. M. Goldup, K. D. Hänni, A.-L. Lee, D. A. Leigh, *Angew. Chem.* **2007**, *119*, 5811–5815; *Angew. Chem. Int. Ed.* **2007**, *46*, 5709–5713; b) A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, *Angew. Chem.* **2007**, *119*, 5103–5107; *Angew. Chem. Int. Ed.* **2007**, *46*, 5015–5019; c) C.-W. Chiu, C.-C. Lai, S.-H. Chiu, *J. Am.*

Chem. Soc. **2007**, *129*, 3500–3501; d) P. C. Haussmann, S. I. Khan, J. F. Stoddart, *J. Org. Chem.* **2007**, *72*, 6708–6713; e) W. R. Dichtel, O. Š. Miljanić, J. M. Spruell, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **2006**, *128*, 10388–10390; f) M. R. Sambrook, P. D. Beer, M. D. Lankshear, R. F. Ludlow, J. A. Wisner, *Org. Biomol. Chem.* **2006**, *4*, 1529–1538.

[15] Y. Rudzevich, V. Rudzevich, C. Moon, I. Schnell, K. Fischer, V. Böhmer, *J. Am. Chem. Soc.* **2005**, *127*, 14168–14169.

[16] a) A. Wu, L. Isaacs, *J. Am. Chem. Soc.* **2003**, *125*, 4831–4835; b) P. Mukhopadhyay, A. Wu, L. Isaacs, *J. Org. Chem.* **2004**, *69*, 6157–6164.

[17] Y. Rudzevich, V. Rudzevich, D. Schollmeyer, V. Böhmer, *Org. Lett.* **2007**, *9*, 957–960.

[18] For mass spectroscopic studies of selective dimerisations, see: D. Braekers, C. Peters, A. Bogdan, Y. Rudzevich, V. Böhmer, J. F. Desreux, *J. Org. Chem.*, in press.

[19] a) V. Böhmer, K. Jung, M. Schön, A. Wolff, *J. Org. Chem.* **1992**, *57*, 790–792; b) F. Sansone, S. Barboso, A. Casnati, M. Fabbi, A. Pochini, F. Ugozzoli, R. Ungaro, *Eur. J. Org. Chem.* **1998**, 897–905.

[20] A. Bogdan, M. O. Vysotsky, T. Ikai, Y. Okamoto, V. Böhmer, *Chem. Eur. J.* **2004**, *10*, 3324–3330.

[21] P. Y. Chong, S. Z. Janicki, P. A. Petillo, *J. Org. Chem.* **1998**, *63*, 8515–8521.

[22] Y. Rudzevich, V. Rudzevich, D. Schollmeyer, I. Thondorf, V. Böhmer, *Org. Biomol. Chem.* **2006**, *4*, 3938–3944.

[23] Y. Rudzevich, M. O. Vysotsky, V. Böhmer, M. S. Brody, J. Rebek, Jr., F. Broda, I. Thondorf, *Org. Biomol. Chem.* **2004**, *2*, 3080–3084.

[24] M. Saadioui, A. Shivanyuk, V. Böhmer, W. Vogt, *J. Org. Chem.* **1999**, *64*, 3774–3777.

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