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Multiple catenanes based on tetraloop derivatives of calix[4]arenes

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Dedicated to the memory of Dmitry M. Rudkevich

ABSTRACT

Four novel tetraarylurea calix[4]arenes (**4a–d**) have been synthesized, substituted by ω-alkenyloxy residues in 3,5-positions of the arylurea residues. The eight alkenyl groups were pairwise connected by olefin metathesis and subsequent hydrogenation. The ring-closure reaction was carried out with heterodimers exclusively formed by **4** with a tetratosylurea calix[4]arene **1**, which serves as a template in this reaction step. The potential trans-cavity bridging is entirely suppressed in this way. Bis- and tetraloop calix[4]arenes cannot form dimers due to overlapping loops. However, they readily form heterodimers with open-chain tetraureas, as long as their urea residues can pass through the loops. Thus, five heterodimeric capsules **8a–e** with bis[3]catenane structure were synthesized using again the olefin metathesis followed by hydrogenation. Two different strategies were compared for this reaction sequence, starting with heterodimers formed either by tetraloop derivatives **5** with tetraalkenyl tetraureas **6** (pathway A) or by bisloop derivatives **7** with octaalkenyl tetraureas **4** (pathway B). A distinct advantage of one of these pathways was not observed; the bis[3]catenanes were obtained with yields of 20–60%. Heterodimers formed by tetraloop derivatives **5b–d** and octaalkenyl ureas **4b–d** were converted analogous to three novel cyclic [8]catenanes **9a–c** in 30–42% yield. The structure of the novel catenanes was unambiguously proved by ^{1}H NMR and ESI MS, and for **8a** and **9a** additionally by single crystal X-ray analysis.

1. Introduction

The synthesis of various interlocked structures (such as catenanes, rotaxanes, knots,[1] Borromean rings,[2,3] etc.) is one of the most attractive topics in modern organic or supramolecular chemistry. Such compounds are interesting not only due to their topological properties but also they could find potential applications, e.g., for the design of controlled molecular-level machines and motors.[4,5] An important factor for the synthesis of such intricate molecules is the suitable preorganization of the reactive moieties to form selectively the desired covalent connections. A suitable arrangement of the functional groups in space can be achieved either by appropriate covalent linkage[6–8] or by reversible interactions,[9] such as hydrogen bonding,[10–12] π–π interactions,[13] or by coordination to metals[14–18] or anions.[19,20] Among numerous self-assembly motives, also the dimerization of calix[4]arenes bearing four urea functions at their wide rim, has been utilized for the preparation of novel structures with interesting topology and properties.[21]

Tetraurea derivatives of calix[4]arenes (further 'tetraureas') form dimeric capsules in apolar, aprotic solvents, such as benzene, toluene, chloroform, dichloromethane, etc. Their structure was first deduced from the ^{1}H NMR spectra[22,23] and proved later by several X-ray structures.[24,25] The two calix[4]arene molecules in such a dimer are turned by 45° with respect to each other allowing the formation of a cyclic array of 16 intermolecular hydrogen bonds between the NH and C=O groups of the interlocking urea functions at their wide rim (see Fig. 1a).

The internal volume of the tetraurea capsules is about 190–200 Å^3.[24] One molecule of the solvent is usually included as guest in the π-electron-rich cavity of the tetraurea dimer. It can be exchanged against other, more attractive guests, [26] e.g., neutral molecules (1,4-difluorobenzene)[27] or cations of appropriate size (tetraethylammonium,[25] cobaltocenium[28]).

In the presence of a polar solvent tetraurea dimers dis-assemble to monomers, which don't possess such host properties as the dimeric capsules.

2. Results and discussion

2.1. General considerations

In tetraurea dimers the residues attached to the calixarene skeleton via the urea functions are specifically arranged in space. If appropriate reactive groups are introduced to these residues,

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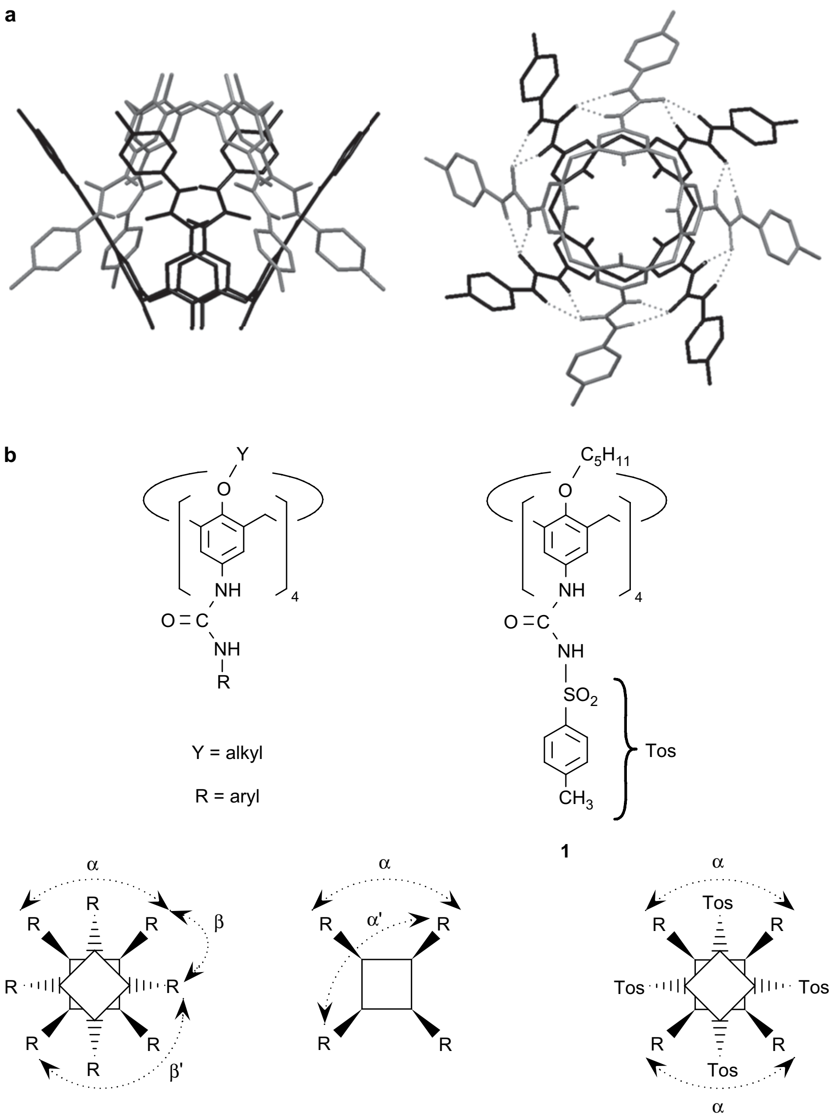


Figure 1. (a) Side and top views of the tetraurea dimer (oxygen functions omitted). (b) Possible connections by ring-closure reactions within a tetraurea dimer, a monomer, and a heterodimer with tetratosylurea **1**.

intramolecular or intermolecular connections (α- or β-connections) are possible between neighboring groups within a dimer. Additionally, β′-connections with remote functions have to be considered within a dimer, while an α′-connection should be possible only in a monomeric calix[4]arene (Fig. 1b). This assumption was fully confirmed by our early experiments in which the metathesis reaction and subsequent hydrogenation were applied to the dimer of a tetra-*m*-(ω-octenyloxy)phenylurea calix[4]arene.[29] The three expected isomers, the bis[2]catenane (four α-connections), the doubly bridged mono[2]catenane (two α- and two β-connections), and the tetra-bridged capsule (four β-connections), could be isolated. This first successful attempt inspired us to improve the selectivity of the synthesis.

The exclusive formation of 1:1 heterodimers between tetratosylurea calix[4]arene **1** and other tetraarylurea derivatives described by Rebek et al.[30] has provided us with a perfect template for the highly selective synthesis of a family of novel macrocycles. In these heterodimers, like in the tetraurea homodimers, residues attached to the urea groups of both tetratosyl- and tetraarylurea calixarenes are alternatingly entangled. Thus, reacting moieties attached to tetraarylurea become separated in space by the tosyl groups. This prevents automatically unfavored trans-cavity reactions (α′-connections), which are inevitable in the case of the monomeric form, and makes only α-connections possible. Consequently, ring-closure reactions between the neighboring arms within such a heterodimer should lead exclusively to compounds containing 'loop(s)' between adjacent urea groups.

Recently, we have successfully used this heterodimerization for the synthesis of various novel multi-macrocyclic tetraureas.[31–33] Several examples with two, three, and four 'loops' (Fig. 2) were prepared in good yields by the covalent connection of their adjacent alkenyl residues by metathesis reaction within the heterodimer with **1**.

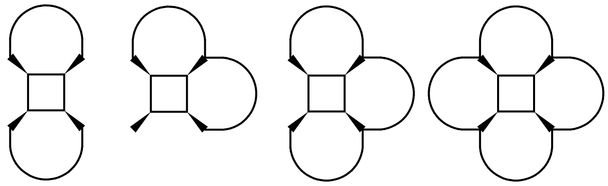
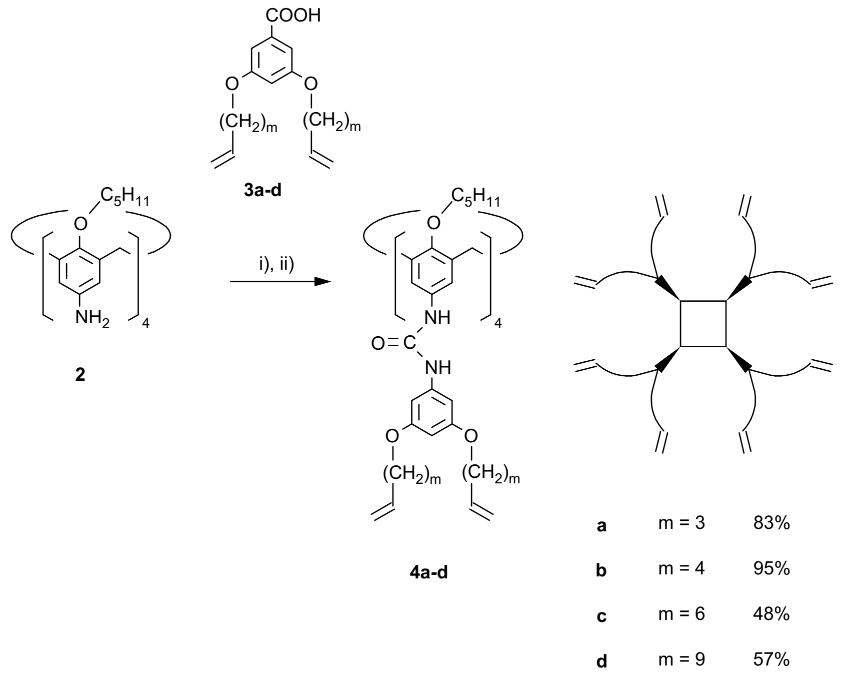


Figure 2. Schematic representation of bis-, tris-, and tetramacrocyclic tetraurea calix[4]arenes obtained by α-connections within the heterodimers formed between the corresponding precursors and tetratosylurea **1**.

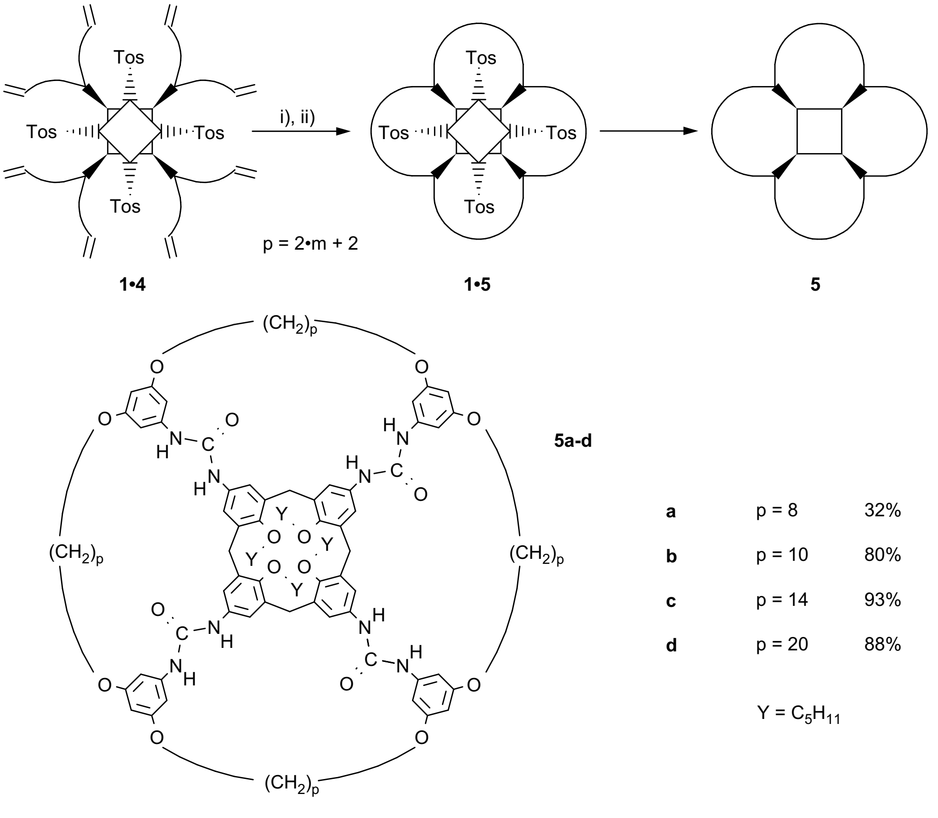


a	m = 3	83%
b	m = 4	95%
c	m = 6	48%
d	m = 9	57%

Figure 3. The synthesis of the octaalkenyl precursors **4** for tetraloop compounds. (i) DPPA, Et_3N, benzene, heating; (ii) benzene, heating.

Although these macrocyclic compounds possess four urea functions, they are not able to form homodimers due to the repulsion of their overlapping 'loops'. However, the multi-loop tetraureas readily form heterodimers with open-chain tetraureas provided the respective urea residues can pass through the loops. These heterodimers can be considered as pseudo-rotaxanes. They can be converted to catenanes[34,35] by ring closure[36] or to rotaxanes by stoppering reactions[37] if the open-chain tetraurea bears appropriate reactive groups.

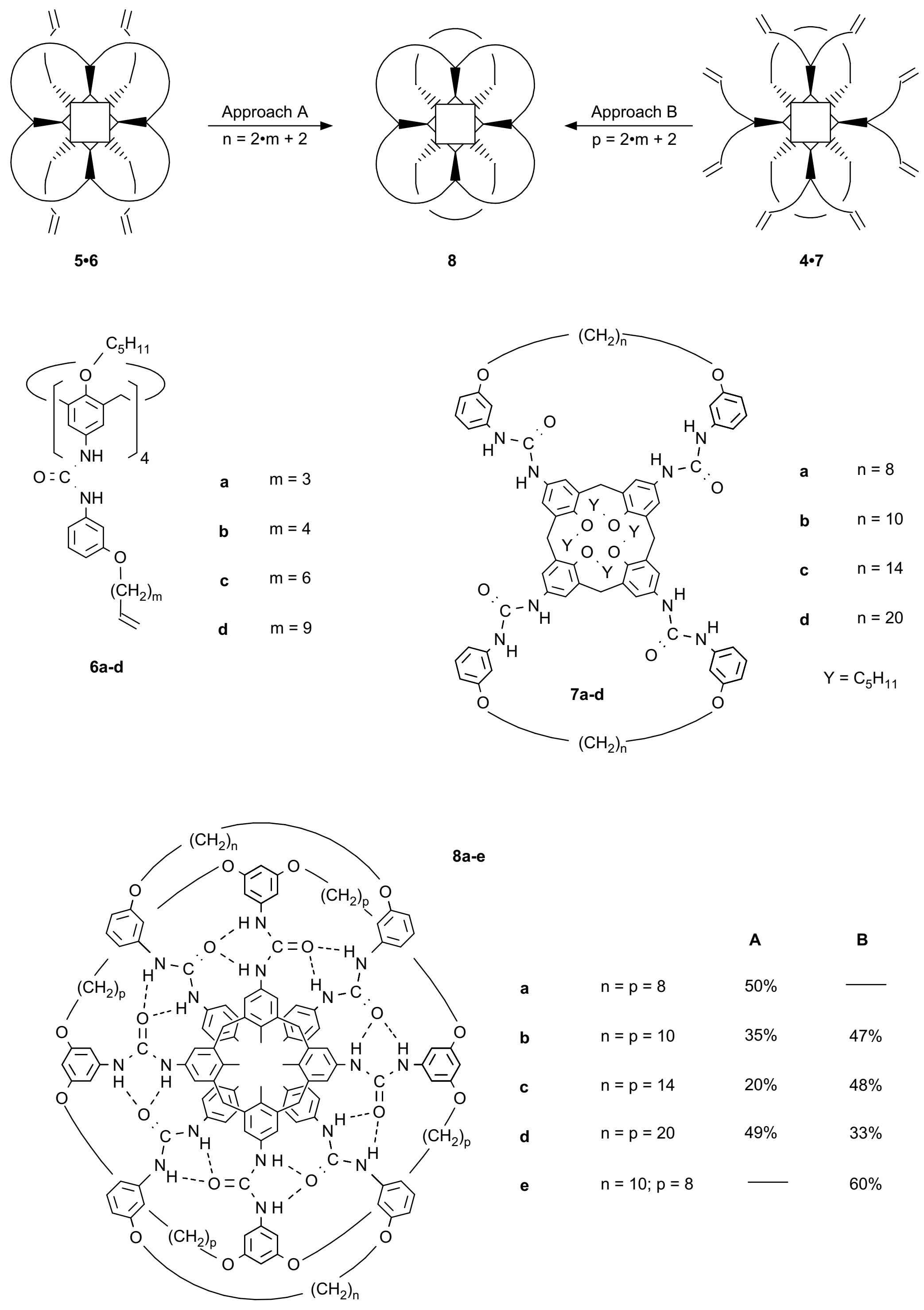
Obviously, variation of the length of the reacting alkenyl residues and the size of the loops may lead to combination(s) where either the heterodimer (pseudo-rotaxane) cannot be formed or the ring closure is impossible due to steric reasons. Thus, one of the



a	p = 8	32%
b	p = 10	80%
c	p = 14	93%
d	p = 20	88%

Y = C_5H_{11}

Figure 4. Schematic representation of the synthesis of tetraloop compounds **5a–d**. (i) Grubbs' catalyst, CH_2Cl_2, rt; (ii) H_2, PtO_2, THF, rt.



		A	B
a	n = p = 8	50%	——
b	n = p = 10	35%	47%
c	n = p = 14	20%	48%
d	n = p = 20	49%	33%
e	n = 10; p = 8	——	60%

Figure 5. Above: two strategies/approaches to synthesize bis[3]catenanes **8**. Below: formula survey of tetraureas with four *m*-ω-alkenyloxyphenyl groups **6a**–**d**, bisloop macrocycles **7a**–**d**, and bis[3]catenanes **8a**–**e** and their yields by approaches A and B. Pentoxy groups in **8** are omitted for clarity.

goals of our present work is an exploration of the scope and the limits for the synthesis of multiple catenanes derived from the available tetraloop tetraureas. In addition, it is interesting to investigate the influence of mechanical connections within tetraurea dimers on their host properties.

2.2. Synthesis of tetraloop compounds

Tetraureas with eight alkenyl chains, the precursors for tetraloop compounds, were prepared by acylation of the tetraamino calix[4]arene tetrapentylether **2** with isocyanates formed in situ via Curtius rearrangement from the corresponding acids in the presence of diphenylphosphorylazide (DPPA) and triethylamine (Fig. 3). The resulting octaalkenyl derivatives **4a**–**d** (m=3, 4, 6, 9) were purified by column chromatography and/or recrystallization and isolated in 48–95% yields.

As evidenced by ^{1}H NMR spectra tetraureas **4a**–**d** easily form homodimers and exclusively heterodimers with the tetratosylurea **1**. This property was used for the preparation of tetraloop compounds **5** by ring-closing olefin metathesis applied to the heterodimers **1**·**4** in benzene solution (Fig. 4). To exclude complications by

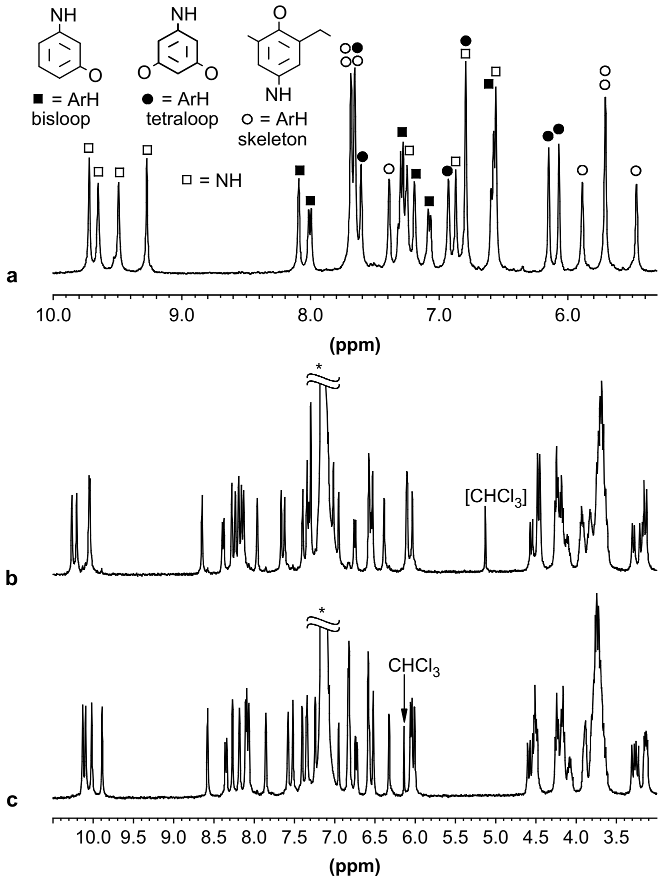


Figure 6. Sections of the ^{1}H NMR spectra (400 MHz, 25 °C) of bis[3]catenane **8a** (a) in THF-d_8, (b) with chloroform as guest in C_6D_6, and (c) with C_6D_6 as guest in C_6D_6. The solvent peaks are marked by asterisk.

cis- and trans-isomers the double bonds in the products were directly hydrogenated in the presence of platinum dioxide as catalyst. The macrocyclic compounds **5b**–**d** were easily 'liberated' from the tetratosylurea template by the addition of hydrogen bond breaking solvents (e.g., tetrahydrofuran) and isolated in 80–93% yield.

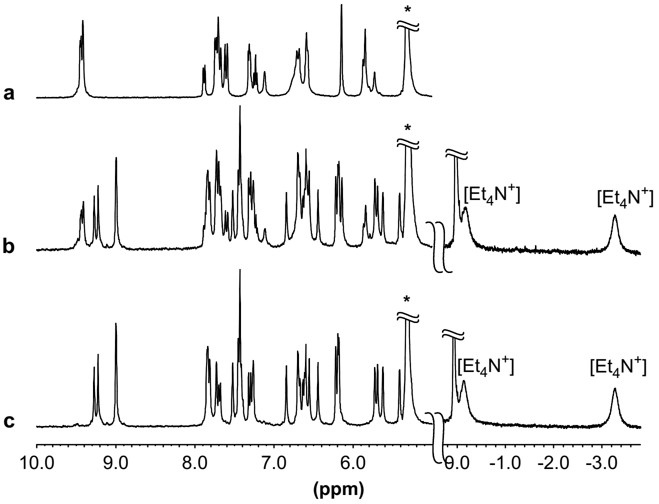


Figure 7. The inclusion of the tetraethylammonium cation in bis[3]catenane **8c** demonstrated by its ^{1}H NMR spectra (400 MHz, 25 °C) in CD_2Cl_2 (marked by asterisk). (a) Spectrum of pure **8c**, (b) the spectrum 3 min after addition of $Et_4N^+PF_6^-$ (a mixture of two complexes of **8c** with CD_2Cl_2 and Et_4N^+ as guests), and (c) the spectrum of **8c** with Et_4N^+ as guest.

The significantly lower yield for the tetraloop compound **5a** (32%) is due to the formation of the stable tetrakis[2]rotaxane-like structure **1·5a**, which was also isolated and characterized as individual species.[36] As mentioned before, the loops formed by ring-closure reactions within the heterodimer **1·4a** are too narrow in this case to easily release the relatively bulky tosyl units of the template **1**. Nevertheless, during the hydrogenation in tetrahydrofuran and the purification by column chromatography (ethyl acetate/*n*-hexane, 1:7) the dissociation process slowly takes place, allowing to isolate the tetraloop compound **5a** in 32% yield.

The structure and the purity of compounds **3a**–**d**, **4a**–**d**, and **5a**–**d** were confirmed by ^{1}H NMR spectroscopy and field-desorption (FD) or electrospray ionization (ESI) mass spectrometry.

2.3. Synthesis of bis[3]catenanes

There are two possible pathways (Fig. 5) to prepare the bis[3]-catenanes **8**: one, starting from the heterodimers between tetraloops **5** and tetralkenyl tetraureas **6** (approach A) and another one, starting with the heterodimers between bisloop compounds **7** and octaalkenyl tetraureas **4** (approach B). The only example of a bis[3]catenane **8** described previously was synthesized following the approach A,[34] while the second strategy B was not yet attempted. Consequently, a general comparison of both strategies is also lacking.

Tetraloop compounds **5a**–**d** readily form heterodimers with tetraureas **6a**–**d**, bearing four ω-alkenyloxyphenyl groups. Ring-closure by metathesis reaction followed by hydrogenation leads to bis[3]catenanes **8a**–**d** in 20–50% yield. The yields of these compounds show no correlation with the length of the alkenyl residues and the size of the loops; however, the procedure has not been optimized for each single case. Reaction conditions were similar to those published before:[34,35] olefin metathesis was carried out in dichloromethane solution under inert atmosphere using Grubbs' catalyst (first generation). The resultant products were directly hydrogenated in the presence of platinum dioxide.

Alternatively, the catenanes **8b**–**d** were prepared in 33–48% yield from heterodimers between bisloop macrocycles **7a**–**d** and octaalkenyl tetraureas **4b**–**d** using the same reaction steps.

In the case of bisloop compound **7a** (n=8) and tetraurea **4a** (m=3) the formation of heterodimers in dichloromethane solution was not observed. This might be explained by sterical reasons. Most probably, the 3,5-dialkenyloxyphenyl groups of the tetraurea **4a** are too voluminous to pass through the smallest loops of the series. In fact compound **7b**, which has loops larger only by two methylene groups dimerizes easily with tetraurea **4a**; ring closure of this heterodimer led to the corresponding 'hybrid' bis[3]catenane **8e** (n=10, p=8) in 60% yield.

By its topology a bis[3]catenane has C_{2v} symmetry. The formation of the hydrogen-bonded belt requires the orientation of the urea groups, which reduces the symmetry to C_2. This is reflected by their NMR spectra in apolar solvents ($CDCl_3$, CD_2Cl_2, C_6D_6). However, the spectra of bis[3]catenanes **8a**–**e** show a splitting of the signals, which is similar to that observed in apolar solvents also in a polar solvent such as tetrahydrofuran-d_8.

Table 1
Survey on the molecular peaks found by ESI MS for bis[3]catenanes **8a**–**e**

Bis[3]catenanes	Cations	Guests	Abundance (%)
8a	$2Na^+$	2 × acetonitrile	100
8b	Na^++H^+	Tetrahydrofuran+ethanol	100
8c	$2Na^+$	Acetonitrile	100
	$2Na^+$	Tetrahydrofuran	47
8d	$2H^+$	—	100
8e	Na^++H^+	2 × acetonitrile	100

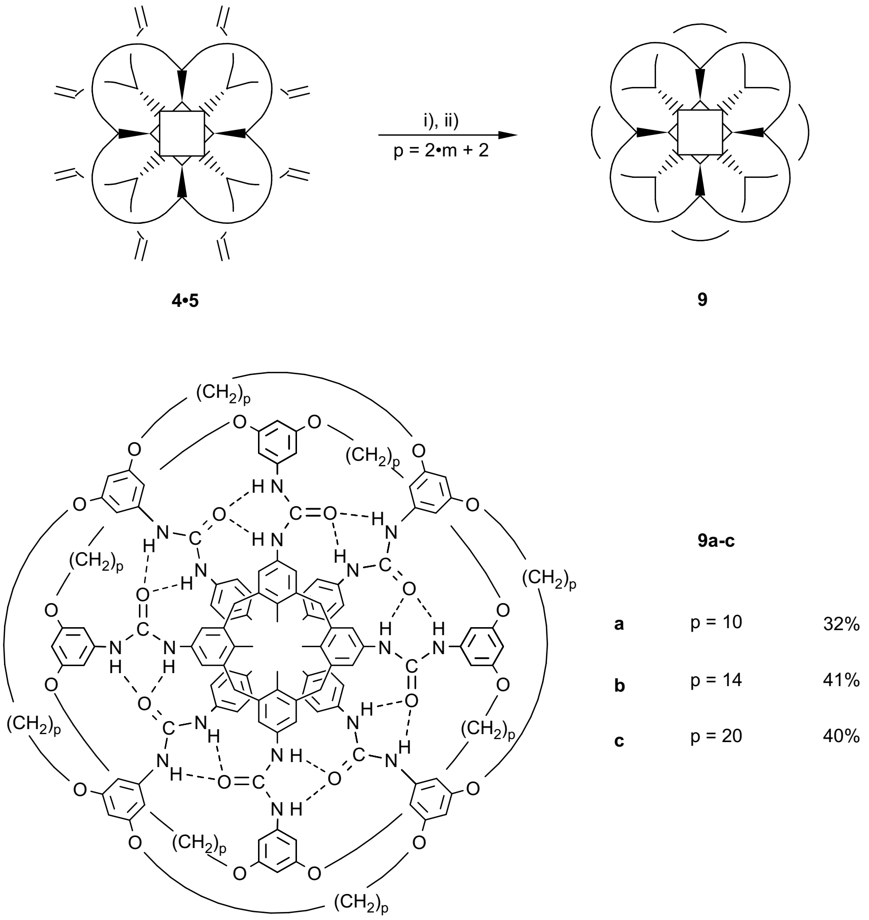


Figure 8. The synthesis of [8]catenanes **9a–c** (pentoxy groups at the phenolic oxygens of calix[4]arene skeletons are omitted for clarity). (i) Grubbs' catalyst, dichloromethane, rt; (ii) H_2, PtO_2, tetrahydrofuran, rt.

Figure 6a contains a representative part of a spectrum of compound **8a** recorded in THF-d_8. With the help of COSY spectra it was deduced that the signals for NH protons are split into two groups, four singlets shifted downfield and four upfield. The signals for the aromatic protons of calixarene skeletons and for the protons in 2,6-positions of the 3-alkoxyphenyl (bisloop) and 3,5-dialkoxyphenyl (tetraloop) units are also split and appear in the spectra as pairs of *m*-coupled doublets. All these are typical signs for the hydrogen-bonded 'dimeric' structure. Obviously, not only a complete separation of the two calixarenes forming the catenane is impossible, but also their individual solvatation. Thus, a hydrogen-bonded capsule seems to be still the energetically most favored structure for bis[3]catenanes in THF. The hydrogen-bonded belt can be broken, however, by pyridine, where the two NH protons appear as two somewhat broad signals separated by 0.06 ppm for **8c** ($n=p=14$).

The difference to bis[2]catenanes,[35] which show a broad, unresolved spectrum in THF is most probably due to the fact that the loops of the bisloop compound penetrate into two adjacent loops in bis[3]catenanes, which obviously limits their mobility drastically.

2.4. Guest inclusion of bis[3]catenanes

Like the dimers of open-chain tetraureas bis[3]catenanes **8a–e** include in their cavity small molecules as guest. For compounds with relatively large loops (**8b–d**) the exchange of included benzene or chloroform against benzene-d_6 takes place within seconds. The ^{1}H NMR spectra recorded immediately after a sample with pre-included guest was dissolved in C_6D_6 displayed already only the signals for the catenane containing C_6D_6.

Due to their shorter interlocking loops the guest exchange is relatively slow for the catenanes **8a** and **8e** and can be monitored by NMR spectroscopy. For example, chloroform included in the catenane **8a** is completely replaced by the solvent C_6D_6, the more favored guest, in 40–46 h. A section of the ^{1}H NMR spectrum of the complex of **8a** with chloroform in C_6D_6 is shown in Figure 6b. The signal for the encapsulated chloroform is shifted upfield and appears at 5.13 ppm. The signals of the complex of **8a** with deuterobenzene as guest are slightly shifted in comparison to the complex with chloroform (Fig. 6c). The appearance of the signal for the released chloroform at 6.13 ppm gives additional evidence for the formation of the complex with C_6D_6. The complete exchange of C_6H_6 against C_6D_6 in bis[3]catenanes **8a** and **8e** requires 7–8 days.[38]

The inclusion of a comparatively larger guest, such as the tetraethylammonium cation, in bis[3]catenanes was followed by ^{1}H NMR spectroscopy for compound **8c** ($n=p=14$) in dichloromethane. The signals for the capsules with tetraethylammonium appeared immediately after the addition of the tetraammonium hexafluorophosphate to the solution (Fig. 7). Like in the case of open-chain tetraureas, the ethyl groups of the included cation have pairwise different magnetic environments: two of them are within the 'equatorial plane' (the plane of the hydrogen-bonded belt), while the other two point toward the 'poles' of the capsule (the π-basic cavity) and hence are much more shielded by the aromatic rings.[39] This is reflected in their spectra, where two characteristic signals can be observed at high field at −0.13 and −3.27 ppm. The complete exchange of the guest in **8c** was achieved in 2 h.

ESI MS spectra for **8a**–**e** have shown peaks for molecular ions doubly charged by either two sodium cations, or two protons, or by one sodium cation and one proton 1:1. Different guest molecules were included (see Table 1) depending on the solvent for the preparation of the samples. The number of guest molecules varies between two (**8a**, **8b**, **8e**) and one (**8c**). For bis[3]catenane **8d** only the peak corresponding to 'empty' doubly charged species was found by ESI MS. Obviously, compounds **8** release guest molecules from their cavity with increasing size of the loops more easily.

2.5. Synthesis of [8]catenanes

Metathesis reaction of the heterodimers formed by the open-chain octaalkenyl tetraureas **4b**–**d** and the tetraloop calix[4]arenes **5b**–**d**, followed by hydrogenation produced the pure [8]catenanes **9a**–**c** in 32–41% yield (Fig. 8).

In the case of tetraloop **5b** (p=10) and tetraurea **4b** (m=4) we met difficulties with the formation of their heterodimer under the following standard conditions. Normally, stirring the solution of both compounds (where **5b** is taken in 5% excess) in dichloromethane at room temperature for 48 h is sufficient to complete the dimerization of the derivatives with larger loops **5c** (p=14) and **5d** (p=20) with the corresponding tetraureas **4c** and **4d**. However, for the pair with shorter residues only the signals for the homodimer of tetraurea **4b** and broad unclear signals for the tetraloop **5b** were observed in the ^{1}H NMR spectrum recorded in CD_2Cl_2 (Fig. 9a). Stirring for further 48 h at room temperature led to the appearance of some tiny signals of the heterodimer **4b·5b** in the spectrum. Refluxing the reaction mixture for 20 h resulted in a slight but insignificant growth of these signals. This showed us that the formation of the heterodimer **4b·5b** is possible in principle (in contrast to the heterodimer **4a·7a**), however, it is kinetically hindered due to steric reasons.

Of course, the homodimer **4b·4b** forms in solution much more rapidly than the heterodimer **4b·5b**, which requires that four 3,5-dialkoxyphenyl residues of **4b** are threaded through the loops of **5b**. For this sterically difficult process only the very small (usually not detectable) concentration of 'free' **4b** is available.

This brought us to the idea that the formation of heterodimers (the only dimers possible for the tetraloop compounds!) might be accelerated by the weakening of the urea–urea hydrogen bonds. Therefore, we added tetrahydrofuran (10 mL) to the solution of tetraloop **5b** and tetraurea **4b** in dichloromethane (100 mL) and kept it under reflux. The re-assembly process was regularly monitored by the growth of the signals for the heterodimers in the ^{1}H NMR spectrum (CD_2Cl_2). Finally, as shown in Figure 9b, after 11 days the signals for the heterodimer became dominant in the solution (although some tiny peaks of the signals for the homodimer **4b·4b** could be still observed). An increase of the content of tetrahydrofuran (to 20 mL) in the reaction mixture followed by stirring under reflux for further 11 days caused no changes in the ^{1}H NMR spectrum. Thus, the solution was evaporated, the resulting pseudo-rotaxanes were re-dissolved in dichloromethane, and subjected to olefin metathesis in the presence of Grubbs' catalyst. After hydrogenation, the corresponding [8]catenane **9a** (32% yield) and the unreacted tetraloop compound were separated from the reaction mixture by column chromatography.

2.6. Spectroscopic properties and guest inclusion of [8]catenanes

The ^{1}H NMR spectra of [8]catenanes **9a**–**c** in CD_2Cl_2 reflect the S_8 symmetry of the molecules (see an example in Fig. 9c) and remind of the spectra for homodimers of tetraureas **4a**–**d**. The signals for NH protons in **9a**–**c** are also split into two singlets due to the formation of two kinds of hydrogen bonds (weaker and stronger) to the neighboring urea groups and appear at 9.38–9.45 and 6.68–6.91 ppm. Two m-coupled doublets for the aryl protons of calixarene skeletons were observed in COSY spectra at 7.74–7.76 and 5.68–5.89 ppm. The aromatic protons of the 3,5-dialkoxyphenyl residues, which are adjacent to the urea functions are inequivalent for the same reasons as the protons of calixarene skeleton. They appear as m-coupled doublets at 7.50–7.72 and

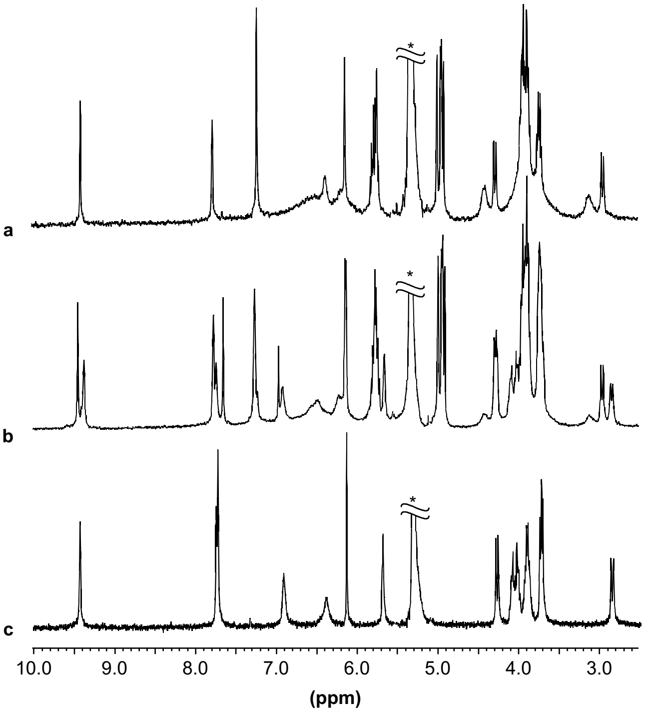


Figure 9. ^{1}H NMR spectra (400 MHz, 25 °C) in CD_2Cl_2 (marked by asterisk) of (a) the dimer **4b·4b** in the presence of tetraloop **5b**, 48 h after mixing, (b) the heterodimer **4b·5b**, formed after 16 days under reflux in dichloromethane/tetrahydrofuran solution, and (c) the resulting cyclic [8]catenane **9a**.

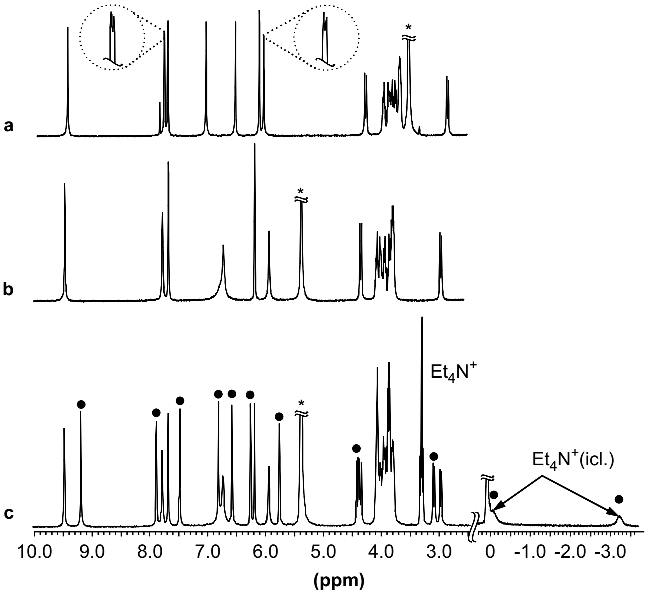


Figure 10. ^{1}H NMR spectra (400 MHz, 25 °C): (a) **9c** in THF-d_8; (b) **9c** in CD_2Cl_2 and (c) **9c** and **9c**·$Et_4N^+PF_6^-$ (marked by circles) in CD_2Cl_2 (the solvent peaks are marked by asterisk).

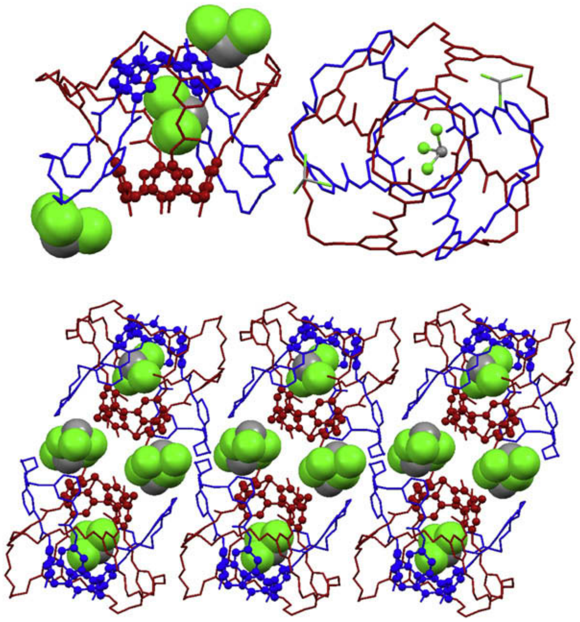


Figure 11. Side (left) and top (right) views of the X-ray structure of bis[3]catenane **8a** ($n=p=8$) and arrangement of the molecules in the crystal lattice. One molecule of *n*-hexane is included in the cavity of the catenane. Pentyl residues at the phenolic oxygens of calixarene skeletons and hydrogens are omitted.

Table 2
Comparison of some characteristic crystallographic data for the bis[3]catenane **8a** and the cyclic [8]catenane **9a**

Dimer	**8a**	**9a**	Tetraester[24]
Planes of calix-O-atoms			
Distance between centers [Å]	12.692	12.938	12.487
Angle [°]	4.59	5.99	0.0
Planes of methylene C atoms (=reference)			
Distance between centers [Å]	10.252	10.417	9.784
Angle [°]	4.54	3.99	0.0
Planes of carbonyl C atoms			
Distance between centers [Å]	1.502	1.606	1.100
Angle [°]	3.04	2.56	0.0
Calixarene A[a]			
O–O distance diagonal	5.188 3.647	5.166 3.649	4.376
C–C distance diagonal (reference plane) [Å]	7.163 7.155	7.112 7.267	
C–C distance diagonal (carbonyl groups) [Å]	10.227 11.253	9.831 11.370	
Angle calix-phenyl plane/ reference plane [°]	73.2[b] 48.0[b] 69.5[c] 56.4[c]	73.4 55.0 73.5 50.8	62.4
Calixarene B[a,d]			
O–O distance diagonal [Å]	5.076 3.813	5.057 3.732	4.469
C–C distance diagonal (reference plane) [Å]	7.466 7.035	7.127 7.256	
C–C distance diagonal (carbonyl groups) [Å]	10.330 11.130	10.809 10.391	
Angle calix-phenyl plane/reference plane [°]	70.6 54.2 70.7 58.7	69.1 59.0 71.3 53.0	64.1

Data for the first crystal structure of a dimeric capsule of tetraurea calix[4]arenes are included for comparison.

[a] Two calixarenes per catenane.

[b,c] Adjacent phenyl rings connected by the same loop.

[d] Bisloop calixarene in **8a**.

6.13 ppm. The proton in the *p*-position of the 3,5-dialkoxyphenyl residues is observed as a broad singlet at 6.39–6.68 ppm.

Similar to bis[3]catenanes **8a**–**e**, [8]catenanes **9a**–**c** keep their system of hydrogen bonds and stay as 'hydrogen-bonded dimers' in polar solvent such as tetrahydrofuran. The stability of this system was checked by NMR spectroscopy on [8]catenanes **9b** and **9c**, which were kept in THF-d_8 for more than one week and showed no signs of 'dissociation' of the hydrogen-bonded capsule in their spectra (see Fig. 10a in comparison to Fig. 10b).

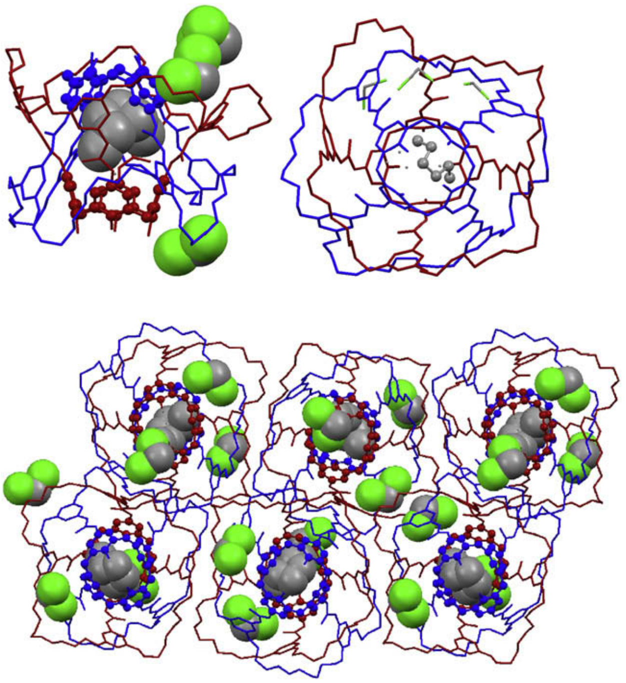


Figure 12. Side (left) and top (right) views of the X-ray structure of [8]catenane **9a** ($p=10$) and arrangement of the molecules in the crystal lattice. One molecule of *n*-hexane is included in the cavity of the catenane. Pentyl residues at the phenolic oxygens of calixarene skeletons and hydrogens are omitted.

The capsular structure with a hydrogen-bonded belt is stable even in pyridine, where two sharp singlets for NH protons are observed at 7.41 and 9.89 ppm for **9b** ($p=14$), a striking difference to the bis[3]catenane **8c** having the same size of the loops.

The inclusion of tetraethylammonium cation as guest was attempted for [8]catenane **9b** under the same conditions as for bis[3]catenane **8c**. Both compounds have an identical length of the loops ($n=p=14$), however, they show a significant difference in their host properties. As observed by ^{1}H NMR spectrometry, the cation inclusion for **8c** was complete in 2 h, while it needs about three weeks for [8]catenane **9b**. Obviously this is due to steric reasons. The growth of the signals in the spectra for the species **9b** containing tetraethylammonium as guest is illustrated in Figure 10c. It shows two sets of signals in the ratio 1:1 for **9c** still having a solvent molecule as guest and for the complex of **9c** with the cation. The signals for the complex **9c**$\cdot\mathrm{Et_4N^+}$ (as hexafluorophosphate) are marked by circles (compare with the spectrum of **9b** before the addition of $\mathrm{Et_4N^+PF_6^-}$ in Fig. 10b). The signals for the methyl groups of the included tetraethylammonium cation appear as two broad singlets at -0.07 and -3.22 ppm.

The structure of [8]catenanes **9a**–**c** was also proved by ESI MS. The peaks detected with high abundance by ESI MS correspond to the doubly charged (due to the presence of two sodium cations) molecular ions of [8]catenanes **9a**–**c**, all containing surprisingly one tetrahydrofuran molecule. The latter is one of the components of the solvent mixture, which was used for the preparation of the samples for the experiments. Tetrahydrofuran was obviously ‘imprisoned’ in the cavity of [8]catenanes as guest and couldn’t escape under conditions of ESI MS measurements.

For catenane **9a** with the smallest loops ($p=10$), besides the dominant peak for the molecular ion with tetrahydrofuran (100%), the peaks for doubly charged molecular ions with two molecules of acetonitrile (45%) and one molecule of trifluoroacetic acid (12%), which was added to all samples as a source of protons, were found. This shows that guest exchange is possible even for such sterically hindered structures as **9a**.

2.7. Crystal structures

Slow evaporation of the solution of bis[3]catenane **8a** ($n=p=8$) in chloroform/methanol and of [8]catenane **9a** ($p=10$) in dichloromethane/*n*-hexane produced single crystals suitable for X-ray analysis. The crystal structure reveals that in both cases the ‘dimeric’ system with a belt of hydrogen bonds is kept in the solid state (Fig. 11 and Fig. 12), although for **8a** a polar, hydrogen bond breaking solvent (methanol) was used. However, in contrast to a similar [8]catenane with larger loops ($p=14$)[34] both structures are noticeably deformed.

Some characteristic angles and distances between atoms and planes are collected for both structures in Table 2, and compared with the first crystal structure of a hydrogen-bonded dimer of a tetraurea calix[4]arene.[24] Technical details and a summary of crystallographic data are reported in Table 3.

In contrast to the C_4 symmetrical reference both structures are more or less distorted. The planes of the phenolic oxygens, of the methylene bridge carbons, and of the carbonyl carbon atoms are not parallel but tilted by 3.0–6.0°. The distances between the centers of these planes are insignificantly longer (0.40–0.63 Å).

For both catenanes the methylene bridges of the two calix[4]arenes form the corners of a (nearly) regular square. The diagonal distances differ by 6% or less. Unequal diagonal distances between the opposite phenolic oxygens for each single calixarene of the dimer (5.076/3.813 and 5.188/3.647 Å for **8a** and 5.057/3.733 and 5.166/3.649 Å for **9a**) together with the angles between the planes of the phenolic units and the reference plane of the methylene carbons characterize quantitatively the oval-like deformation. These angles (48–73° for **8a**, and 51–74° for **9a**) show, that both catenanes have practically the same shape. The distortion for single diphenylurea structures may be characterized by the interplanar angle of the aromatic rings. It varies between 16.4° and 31.6° (bisloop part) and 14.2° and 23.8° (tetraloop part) for **8a**, and 14.3° and 32.9° for **9a**. In spite of these distortions the capsules are glued together by a seam of strong intermolecular hydrogen bonds, indicated by $N_{phenyl}\cdots O_{carbonyl}$ distances between 2.787 and 2.900 Å (**8a**) and 2.783 and 2.883 Å (**9a**).[40]

Table 3
Crystal data and structure refinement

Compound	**8a**	**9a**
	$C_{410}H_{530}Cl_{30}N_{32}O_{56}$	$C_{120.5}H_{170}Cl_3N_8O_{16}$
Formula weight	7866.16	2093.08
Temperature [K]	173	173
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/c$
a [Å]	17.964(2)	23.7409(6)
b [Å]	21.996(3)	28.0178(11)
c [Å]	28.534(4)	37.0435(11)
α, [°]	101.345(10)	90
β [°]	106.437(9)	106.820(2)
γ [°]	99.404(10)	90
V [Å^3]	10,311(2)	23,586.0(13)
Z	1	8
D_{calcd} [g cm^{-3}]	1.267	1.179
μ(Mo Kα) [mm^{-1}]	0.267	0.143
Reflections collected	108,720	277,905
Independent reflections	36,360	41,652
Observed reflections, [$I>2\sigma(I)$]	7232	15,047
Data/restraints/parameters	36,360/382/1892	41,652/770/2639
Goodness of fit on F^2	1.448	1.133
Final R indices [$I>2\sigma(I)$], $R1$, $wR2$	0.2441, 0.4794	0.1503, 0.3669
R indices (all data), $R1$, $wR2$	0.4552, 0.5533	0.2713, 0.4331
Largest diff. peak and hole	2.306, −0.554	2.789, −0.747
CCDC deposition number	699485	699484

Surprisingly, one molecule of *n*-hexane is included as guest in the cavity of the catenane **9a** although usually tetraurea dimers encapsulate (like **8a**), other molecules, such as benzene, chloroform and dichloromethane, which are used as ‘classic’ solvents for the dimerization of tetraurea calix[4]arenes. Three dichloromethane molecules are also present in the crystal lattice outside the dimeric capsule, packed between disordered alkyl chains of the loops.

3. Conclusion and outlook

Tetraarylurea calix[4]arenes in which adjacent phenylurea residues are linked by four $-(CH_2)_8-$, $-(CH_2)_{10}-$, $-(CH_2)_{14}-$, and $-(CH_2)_{20}-$ loops were synthesized by ring-closing metathesis followed by hydrogenation. The exclusive formation of heterodimers between tetratosyl- and tetraarylureas substituted by two ω-alkenyl residues was successfully used to preorganize the reacting groups and to avoid trans-cavity bridging. While the originally resulting [4]rotaxane was difficult to split into the tetraloop calixarene and the template for the smallest ring size ($n=8$) the synthesis of calix[4]arenes with larger loops (longer (CH_2) chains with $n>20$) should be possible.

Since bis- and tetraloop tetraureas cannot form homodimers they form exclusively heterodimers with open-chain tetraurea calix[4]arenes. The reaction sequence olefin metathesis/hydrogenation applied to these heterodimers with tetraalkenyl or octaalkenyl tetraurea calix[4]arenes leads to various bis[3]catenanes on two different pathways and to cyclic [8]catenanes. Again we faced difficulties for calix[4]arenes with shorter loops ($n=8$) since their formation of heterodimers with bis-ω-alkenyl tetraureas is obviously sterically hindered. Reasonable yields were obtained, however, for loops with $n=10$, 14, and 20, and [8]catenanes with larger loops, including different loop sizes within the [8]catenane should be possible too.

In contrast to simple hydrogen-bonded dimers of tetraurea calix[4]arenes the multiple catenanes described offer the possibility for a (more or less) permanent inclusion of a guest, also in polar solvents. The strength of this inclusion can be controlled by the general structure (bis[2]catenanes, bis[3]catenanes, or [8]catenanes) and especially by the length of the interlocking rings. The easiness of the guest release may be modified also by the structure of the interlocking rings and by their attachment to the calix[4]arene. Further combinations, for instance a multi-catenane formed by a trisloop and a tetraloop calix[4]arene, are also possible.

4. Experimental

4.1. General

Solvents and all other chemicals were purchased from Acros, Aldrich, and Lancaster, and used without further purification. ^1H NMR spectra were recorded on a Bruker DRX400 Avance instrument (at 400 MHz). FD and ESI mass spectra were measured on a Finnigan MAT 8230 spectrometer and a Micromass Q-ToF

Ultima3 instrument, respectively. Melting points are uncorrected. *p*-Tetraamino calix[4]arene tetradecylether **1** and *p*-tosyltetraurea tetrapentylether **5** were prepared according to published procedures.[41]

4.2. Synthesis of 3,5-di-(ω-alkenyloxy)benzoic acids 3

4.2.1. *Benzoic acid **3a***

The mixture of 5-bromo-1-pentene (9.48 g, 60.5 mmol), methyl-3,5-dihydroxy benzoate (4.62 g, 27.5 mmol), and K_2CO_3 (8.34 g, 60.5 mmol) in DMF (140 mL) was vigorously stirred at 55 °C for 24 h. Then DMF was removed in vacuo, and the residue was partitioned between dichloromethane (2×120 mL) and water (120 mL). The organic layer was separated, washed with water (100 mL) and brine (100 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product as an oil. Purification by column chromatography (silica gel, ethyl acetate/*n*-hexane, 4:70) furnished the pure product as a viscous oil (6.43 g, 77%), which was used for the next step without characterization.

Methyl-3,5-di-(5-pentenyloxy)benzoate (6.43 g, 21.1 mmol) was dissolved in ethanol (170 mL) and mixed with the solution of potassium hydroxide (6.03 g, 0.108 mol) in H_2O (23 mL). The mixture was stirred at room temperature for 2 h, evaporated in vacuo, and the residue was partitioned between 5% HCl (130 mL) and ethyl acetate (130 mL). The organic layer was washed with water (100 mL) and brine (100 mL), and dried ($MgSO_4$). Evaporation of the filtrate gave the corresponding acid as a white, waxy solid; yield 5.15 g, 84%. Mp: 58.5–59.5 °C; ^{1}H NMR ($CDCl_3$): δ 11.7 (br s, 1H, COOH), 7.22 (d, *J*=2.3 Hz, 2H, ArH), 6.68 (t, *J*=2.3 Hz, 1H, ArH), 5.90–5.82 (m, 2H, CH=CH$_2$), 5.11–5.00 (m, 4H, CH=CH$_2$), 4.00 (t, *J*=7.4 Hz, 4H, OCH$_2$), 2.25 (m, 4H, C*H*$_2$CH=CH$_2$), 1.91 (m, 4H, –OCH$_2$C*H*$_2$); MS (FD) *m*/*z*: calcd for $C_{17}H_{22}O_4$ (M^+) 290.4, observed 290.2.[42]

4.2.2. *Benzoic acid **3b***

Methyl-3,5-di-(6-hexenyloxy)benzoate was obtained as described for **3a** from 6-bromo-1-hexene (7.48 g, 43.6 mmol), methyl-3,5-dihydroxy benzoate (3.51 g, 20.8 mmol), and K_2CO_3 (6.33 g, 45.9 mmol) in DMF (105 mL); yield 5.53 g, 80%.

The methylester (5.53 g, 16.6 mmol) was hydrolyzed in ethanol (140 mL) with potassium hydroxide (4.75 g, 84.8 mmol) in H_2O (18 mL). Pure **3b** was isolated as a white, wax-like solid; yield 4.43 g, 84%. Mp: 61 °C; ^{1}H NMR ($CDCl_3$): δ 7.24 (d, 2H, *J*=2.4 Hz, Ar*H*), 6.70 (t, 1H, *J*=2.4 Hz, Ar*H*), 5.90–5.82 (m, 2H, C*H*=CH$_2$), 5.10–5.00 (m, 4H, CH=C*H*$_2$), 4.00 (t, 4H, *J*=6.5 Hz, OC*H*$_2$), 2.20–2.10 (m, 4H, C*H*$_2$), 1.90–1.75 (m, 4H, C*H*$_2$), 1.60 (m, 4H, C*H*$_2$); MS (FD) *m*/*z*: calcd for $C_{19}H_{26}O_4$ (M^+) 318.4, observed 318.3.

4.2.3. *Benzoic acid **3c***

Methyl-3,5-di-(8-octenyloxy)benzoate was prepared as described for **3a** from 8-bromo-1-octene (10.0 g, 52.6 mmol), methyl-3,5-dihydroxy benzoate (4.02 g, 23.9 mmol), and K_2CO_3 (7.26 g, 52.6 mmol) in DMF (120 mL); yield 8.24 g, 89%.

The methylester (8.24 g, 21.2 mmol) was hydrolyzed in ethanol (175 mL) with potassium hydroxide (6.06 g, 108 mmol) in H_2O (25 mL). Pure **3c** was isolated as a white, waxy solid; yield 7.36 g, 93%. Mp: 39–43 °C; ^{1}H NMR ($CDCl_3$): δ 11.7 (br s, 1H, COO*H*), 7.23 (d, 2H, *J*=2.3 Hz, Ar*H*), 6.69 (t, 1H, *J*=2.2 Hz, Ar*H*), 5.90–5.75 (m, 2H, C*H*=CH$_2$), 5.00–4.95 (m, 4H, CH=C*H*$_2$), 4.00 (t, 4H, *J*=7.4 Hz, OC*H*$_2$), 2.07 (m, 4H, C*H*$_2$), 1.79 (m, 4H, C*H*$_2$), 1.50–1.35 (m, 12H, C*H*$_2$); MS (FD) *m*/*z*: calcd for $C_{23}H_{34}O_4$ (M^+) 374.5, observed 374.3.

4.2.4. *Benzoic acid **3d***

Methyl-3,5-di-(11-undecenyloxy)benzoate was prepared as described for **3a** from 11-bromo-1-octene (9.51 g, 38.8 mmol), methyl-3,5-dihydroxy benzoate (2.96 g, 17.6 mmol), and K_2CO_3 (5.35 g, 38.8 mmol) in DMF (90 mL); yield 8.10 g, 97%.

The methylester (8.10 g, 17.1 mmol) was hydrolyzed in ethanol (140 mL) with potassium hydroxide (4.89 g, 87.4 mmol) in H_2O (20 mL). Pure acid **3d** was isolated as a white, wax-like solid; yield 7.41 g, 94%. Mp: 46–48 °C; ^{1}H NMR ($CDCl_3$): δ 7.22 (d, 2H, *J*=2.0 Hz, Ar*H*), 6.68 (t, 1H, *J*=2.1 Hz, Ar*H*), 5.90–5.75 (m, 2H, C*H*=CH$_2$), 5.05–4.85 (m, 4H, CH=C*H*$_2$), 3.97 (t, 4H, *J*=6.5 Hz, OC*H*$_2$), 2.10–1.95 (m, 4H, C*H*$_2$), 1.85–1.70 (m, 4H, C*H*$_2$), 1.50–1.15 (m, 24H, C*H*$_2$); MS (FD) *m*/*z*: calcd for $C_{19}H_{26}O_4$ (M^+) 458.7, observed 458.6.

4.3. Synthesis of octaalkenyl derivatives 4

4.3.1. *Tetraurea **4a***

A solution of 3,5-di-(5-pentenyloxy)benzoic acid **3a** (0.30 g, 1.03 mmol), diphenylphosphorylazide (0.31 g, 0.25 mL, 1.1 mmol), and triethylamine (0.12 g, 0.016 mL, 1.1 mmol) in toluene (20 mL) was stirred for 2 h at 55 °C. Tetraamino calix[4]arene **2** (0.132 g, 0.172 mmol) was added and the mixture was stirred for 2 h at 85 °C. Then the solvent was evaporated and the residue was triturated with methanol. The solid was filtered off and dried to give the pure product as a gray powder; yield 0.272 g, 83%. The product can be additionally purified by column chromatography (silica gel, ethyl acetate/hexane, 1:14) followed by reprecipitation from methanol/dichloromethane. Mp 238 °C; ^{1}H NMR (DMSO-*d*$_6$): 8.29 (s, 4H, N*H*), 8.12 (s, 4H, N*H*), 6.76 (s, 8H, Ar*H*), 6.51 (s, 8H, Ar*H*), 6.04 (s, 4H, Ar*H*), 5.90–5.71 (m, 8H, C*H*=CH$_2$), 5.09–4.86 (m, 16H, CH=C*H*$_2$), 4.33 (d, 4H, *J*=13.3 Hz, ArC*H*$_2$Ar), 3.82 (pseudo t, 24H, *J*=6.1 Hz, OC*H*$_2$), 3.11 (d, 4H, *J*=12.9 Hz, ArC*H*$_2$Ar), 2.19–2.05 (m, 16H, C*H*$_2$), 1.88 (m, 8H, C*H*$_2$), 1.80–1.66 (m, 16H, C*H*$_2$), 1.46–1.30 (m, 16H, C*H*$_2$), 0.93 (br t, 12H, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{116}H_{152}N_8O_{16}$ (MNa^+) 1937.5, observed 1937.0.

4.3.2. *Tetraurea **4b***

Prepared as described for **4a** from 3,5-di-(6-hexenyloxy) benzoic acid **3b** (1.25 g, 3.92 mmol), diphenylphosphorylazide (1.2 g, 0.96 mL, 4.3 mmol), triethylamine (0.43 g, 0.61 mL, 4.3 mmol) in toluene (79 mL), and tetraamino calix[4]arene **2** (0.500 g, 0.654 mmol). Tetraurea **4b** was obtained as a powder; yield 1.264 g, 95%. Additional purification was carried out by column chromatography (silica gel, ethyl acetate/*n*-hexane, 1:22) followed by reprecipitation from methanol/dichloromethane. Mp 235 °C; ^{1}H NMR (DMSO-*d*$_6$): 8.27 (s, 4H, N*H*), 8.12 (s, 4H, N*H*), 6.76 (s, 8H, Ar*H*), 6.50 (s, 8H, Ar*H*), 6.03 (s, 4H, Ar*H*), 6.00–5.68 (m, 8H, C*H*=CH$_2$), 5.10–4.83 (m, 16H, CH=C*H*$_2$), 4.33 (d, 4H, *J*=12.5 Hz, ArC*H*$_2$Ar), 3.82 (m, 24H, OC*H*$_2$), 3.11 (d, 4H, *J*=11.0 Hz, ArC*H*$_2$Ar), 2.13–1.98 (m, 16H, C*H*$_2$), 1.88 (m, 8H, C*H*$_2$), 1.74–1.56 (m, 16H, C*H*$_2$), 1.54–1.30 (m, 32H, C*H*$_2$), 0.93 (s, 12H, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{124}H_{168}N_8O_{16}$ (MNa^+) 2049.7, observed 2049.1.

4.3.3. *Tetraurea **4c***

Prepared as described for **4a** from 3,5-di-(8-octenyloxy)benzoic acid **3c** (1.47 g, 3.92 mmol), diphenylphosphorylazide (1.19 mL, 4.31 mmol), triethylamine (0.436 g, 4.31 mmol), and tetraamino calix[4]arene **2** (0.500 g, 0.654 mmol). The crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane, 1:20) followed by reprecipitation from methanol/dichloromethane. Pure **4c** was obtained as a colorless powder; yield 0.714 g, 48%. Mp 232 °C; ^{1}H NMR (DMSO-*d*$_6$): 8.27 (s, 4H, NH), 8.11 (s, 4H, N*H*), 6.76 (s, 8H, Ar*H*), 6.49 (d, 8H, *J*=1.7 Hz, Ar*H*), 6.01 (br t, 4H, Ar*H*), 5.83–5.71 (m, 8H, C*H*=CH$_2$), 5.03–4.88 (m, 16H, CH=C*H*$_2$), 4.33 (d, 4H, *J*=13.3 Hz, ArC*H*$_2$Ar), 3.80 (pseudo t, 24H, *J*=6.0 Hz, OC*H*$_2$), 3.11 (d, 4H, *J*=12.3 Hz, ArC*H*$_2$Ar), 2.04–1.95 (m, 16H, C*H*$_2$), 1.89 (m, 8H, C*H*$_2$), 1.63 (m, 16H, C*H*$_2$), 1.45–1.22 (m, 64H, C*H*$_2$), 0.93 (br t, 12H, *J*=6.8 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{140}H_{200}N_8O_{16}$ (MH^+) 2252.2, observed 2251.5; ($M{+}2H^+$) 1126.6, observed 1126.3.

4.3.4. *Tetraurea **4d***

Prepared as described for **4a** from 3,5-di-(11-undecenyloxy)-benzoic acid **3d** (1.798 g, 3.921 mmol), diphenylphosphorylazide

(1.2 g, 0.96 mL, 4.3 mmol), triethylamine (0.43 g, 0.61 mL, 4.3 mmol), and tetraamino calix[4]arene **2** (0.500 g, 0.654 mmol). Purification was carried out by column chromatography (silica gel, tetrahydrofuran/*n*-hexane, 1:25) followed by reprecipitation from methanol/dichloromethane. Pure **4d** was obtained as a colorless powder; yield 0.967 g, 57%. Mp 229 °C; ^{1}H NMR (THF-d_8): 7.50 (s, 4H, N*H*), 7.43 (s, 4H, N*H*), 6.79 (s, 8H, Ar*H*), 6.57 (d, 8H, *J*=1.7 Hz, Ar*H*), 6.01 (br t, 4H, *J*=2.0 Hz, Ar*H*), 5.84–5.71 (m, 8H, C*H*=CH$_2$), 5.00–4.83 (m, 16H, CH=C*H*$_2$), 4.43 (d, 4H, *J*=12.9 Hz, ArC*H*$_2$Ar), 3.87 (t, 8H, *J*=7.3 Hz, OC*H*$_2$), 3.79 (t, 16H, *J*=6.5 Hz, OC*H*$_2$), 3.07 (d, 4H, *J*=13.3 Hz, ArC*H*$_2$Ar), 2.07–1.98 (m, 16H, C*H*$_2$), 1.94 (m, 8H, C*H*$_2$), 1.75–1.63 (m under the solvent peak, 16H, C*H*$_2$), 1.48–1.23 (m, 112H, C*H*$_2$), 0.96 (t, 12H, *J*=6.8 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{164}H_{248}N_8O_{16}$ (MNa$^+$) 2610.8, observed 2610.8; (M+2Na$^+$) 1316.9, observed 1316.4.

4.4. Synthesis of tetraloop derivatives 5

4.4.1. Tetraloop **5a**

Tetratosylurea **1** (0.243 g, 0.157 mmol) and tetraurea **4a** (0.20 g, 0.105 mmol) were dissolved in dichloromethane (320 mL) and stirred for 8 h at room temperature. The mixture was purged with nitrogen for 30 min, Grubbs' catalyst (34 mg, 0.042 mmol) was added, and then stirring was continued for 48 h at room temperature under nitrogen. Then triethylamine (1.0 mL) was added to destroy the catalyst and the complex with tetratosylurea **1**. After 1 h, the solvent was evaporated, the residue was dissolved in THF, and the solvent was evaporated again. The crude product was hydrogenated in THF (20 mL) for 24 h (room temperature, normal pressure) using platinum dioxide (83% Pt, 43 mg, 0.19 mmol) as catalyst. The residue obtained by evaporation was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane, 1:7). After reprecipitation from chloroform/methanol, the desired tetraloop calix[4]arene **5a** was finally obtained as a colorless powder; yield 61 mg, 32%. Mp >310 °C (decomposition); ^{1}H NMR (THF-d_8): 7.60 (s, 4H, N*H*), 7.53 (s, 4H, N*H*), 6.90 (s, 8H, Ar*H*), 6.54 (s, 8H, Ar*H*), 5.99 (s, 4H, Ar*H*), 4.44 (d, 4H, *J*=12.5 Hz, ArC*H*$_2$Ar), 3.94–3.76 (m, 24H, OC*H*$_2$), 3.07 (d, 4H, *J*=12.5 Hz, ArC*H*$_2$Ar), 2.14–1.92 (m, 8H, C*H*$_2$), 1.78–1.60 (m, 16H, C*H*$_2$), 1.50–1.20 (m, 48H, C*H*$_2$), 0.98 (t, 12H, *J*=6.5 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{108}H_{144}N_8O_{16}$ (MH$^+$) 1811.4, observed 1811.1; (M+2H$^+$) 906.2, observed 906.1.

4.4.2. Tetraloop **5b**

Tetratosylurea **1** (0.345 g, 0.222 mmol), tetraurea **4b** (0.300 g, 0.148 mmol), Grubbs' catalyst (49 mg, 0.059 mmol) in dichloromethane (600 mL), triethylamine (1.5 mL), and platinum dioxide (83% Pt, 0.0605 g; 0.266 mmol) in THF (25 mL) were reacted as described for **5a**. Purification by column chromatography (silica gel, THF/*n*-hexane, 1:3) followed by reprecipitation from chloroform/methanol gave the desired tetraloop calix[4]arene **5b** as a colorless powder; yield 0.228 g, 80%. Mp >300 °C (decomposition); ^{1}H NMR (THF-d_8): 7.51 (s, 8H, N*H*), 6.89 (s, 8H, Ar*H*), 6.56 (s, 8H, Ar*H*), 6.00 (s, 4H, Ar*H*), 4.44 (d, 4H, *J*=12.6 Hz, ArC*H*$_2$Ar), 3.94–3.76 (m, 24H, OC*H*$_2$), 3.08 (d, 4H, *J*=12.9 Hz, ArC*H*$_2$Ar), 1.99 (m, 8H, C*H*$_2$), 1.75–1.62 (m, 16H, C*H*$_2$), 1.50–1.20 (m, 64H, C*H*$_2$), 0.97 (t, 12H, *J*=6.5 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{116}H_{160}N_8O_{16}$ (MH$^+$) 1923.6, observed 1923.2; (M+2H$^+$) 962.3, observed 962.1.

4.4.3. Tetraloop **5c**

Tetratosylurea **1** (0.311 g, 0.200 mmol), tetraurea **4c** (0.300 g, 0.133 mmol), Grubbs' catalyst (44 mg, 0.0533 mmol) in dichloromethane (540 mL), triethylamine (2 mL), and platinum dioxide (83% Pt, 0.0545 g, 0.240 mmol) in THF (25 mL) were reacted as described for **5a**. Purification by column chromatography (silica gel, THF/*n*-hexane, 1:2) followed by reprecipitation from chloroform/methanol gave the desired tetraloop calix[4]arene **5c** as a colorless powder; yield 0.267 g, 93%. Mp >270 °C (decomposition); ^{1}H NMR (THF-d_8): 7.56 (s, 4H, N*H*), 7.47 (s, 4H, N*H*), 6.86 (s, 8H, Ar*H*), 6.57 (s, 8H, Ar*H*), 6.01 (s, 4H, Ar*H*), 4.44 (d, 4H, *J*=13.7 Hz, ArC*H*$_2$Ar), 3.94–3.70 (m, 24H, OC*H*$_2$), 3.07 (d, 4H, *J*=13.3 Hz, ArC*H*$_2$Ar), 1.96 (m, 8H, C*H*$_2$), 1.80–1.60 (m under the solvent peak, 16H, C*H*$_2$), 1.50–1.10 (m, 96H, C*H*$_2$), 0.97 (t, 12H, *J*=7.0 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{132}H_{192}N_8O_{16}$ (MH$^+$) 2148.0, observed 2147.4; (M+2H$^+$) 1074.5, observed 1074.2.

4.4.4. Tetraloop **5d**

Tetratosylurea **1** (0.2702 g, 0.1739 mmol), tetraurea **4d** (0.300 g, 0.116 mmol), Grubbs' catalyst (0.0381 g, 0.0464 mmol) in dichloromethane (480 mL), triethylamine (1.5 mL), and platinum dioxide (83% Pt, 0.047 g, 0.21 mmol) in THF (25 mL) were reacted as described for **5a**. Purification by column chromatography (silica gel, THF/*n*-hexane, 1:2) followed by reprecipitation from chloroform/methanol gave the desired tetraloop calix[4]arene **5d** as a colorless powder; yield 0.252 g, 88%. Mp 160 °C; ^{1}H NMR (THF-d_8): 7.51 (s, 4H, N*H*), 7.43 (s, 4H, N*H*), 6.82 (s, 8H, Ar*H*), 6.57 (s, 8H, Ar*H*), 6.01 (s, 4H, Ar*H*), 4.44 (d, 4H, *J*=13.3 Hz, ArC*H*$_2$Ar), 3.96–3.69 (m, 24H, OC*H*$_2$), 3.07 (d, 4H, *J*=13.6 Hz, ArC*H*$_2$Ar), 1.94 (m, 8H, C*H*$_2$), 1.80–1.60 (m under the solvent peak, 16H, C*H*$_2$), 1.50–1.20 (m, 144H, C*H*$_2$), 0.96 (br t, 12H, *J*=6.8 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{156}H_{240}N_8O_{16}$ (M+2H$^+$) 1242.8, observed 1242.4.

4.5. Synthesis of bis[3]catenanes 8

4.5.1. Approach A (starting from tetraloop compounds **5** and tetraalkenyl derivatives **6**)

A solution of the respective compounds **5** and **6** in freshly distilled and degassed dichloromethane was stirred at room temperature for 48 h; the complete formation of the heterodimer was verified by ^{1}H NMR. When the signals of the homodimer had disappeared, the reaction mixture was purged with nitrogen for 30 min and a solution of Grubbs' catalyst was added. After 48 h of stirring, triethylamine was added, the solution was stirred for 1 h, and evaporated. The crude product was dissolved in THF, and hydrogenated for 4 h (room temperature, normal pressure) using platinum dioxide (83% Pt) as catalyst. The crude product obtained by evaporation was finally purified by column chromatography followed by recrystallization.

4.5.2. Approach B (starting from bisloop compounds **7** and octaalkenyl derivatives **4**)

A solution of the respective compounds **4** and **7** was reacted as described in approach A.

4.5.3. Bis[3]catenane **8a**

Approach A: starting with tetraloop compound **5a** (58.0 mg, 0.0320 mmol), tetraalkenyl tetraurea **6a** (0.0459 g, 0.0291 mmol) in dichloromethane (120 mL), and Grubbs' catalyst (14.4 mg, 0.0175 mmol). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 5.9 mg; 0.0261 mmol). The final purification was achieved by column chromatography (silica gel, THF/*n*-hexane, 1:12; followed by THF/*n*-hexane, 1:6); recrystallization from chloroform/methanol gave the bis[3]catenane **8a** as a colorless, crystalline powder; yield 49 mg, 50%. Mp >320 °C (decomposition); ^{1}H NMR (C_6D_6): 10.13 (s, 2H, N*H*), 10.10 (s, 2H, N*H*), 10.02 (s, 2H, N*H*), 9.89 (s, 2H, N*H*), 8.58 (s, 2H, Ar*H*), 8.35 (d, 2H, *J*=8.4 Hz, Ar*H*), 8.27 (s, 2H, Ar*H*), 8.18 (d, 2H, *J*=2.2 Hz, Ar*H*), 8.11 (d, 2H, *J*=2.2 Hz, Ar*H*), 8.09 (s, 2H, Ar*H*), 8.07 (d, 2H, *J*=1.8 Hz, Ar*H*), 7.86 (d, 2H, *J*=2.2 Hz, Ar*H*), 7.58 (s, 2H, Ar*H*), 7.52 (s, 2H, N*H*), 7.40 (s, 2H, Ar*H*), 7.35 (d, 2H, *J*=8.0 Hz, Ar*H*), 7.30–7.00 (m under the solvent peak, 6H, Ar*H*), 6.83 (s, 2H, N*H*), 6.82 (s, 2H, N*H*), 6.81 (s, 2H, N*H*), 6.73 (dd, 2H, *J*=8.3 Hz, *J*=1.6 Hz, Ar*H*), 6.62–6.55 (m, 4H, Ar*H*), 6.52 (s, 2H, Ar*H*), 6.32 (d, 2H, *J*=2.2 Hz, Ar*H*), 6.06 (d, 2H, *J*=1.8 Hz, Ar*H*), 6.04 (d, 2H, *J*=2.2 Hz, Ar*H*), 6.01 (d, 2H, *J*=2.2 Hz, Ar*H*), 4.59 (d, 2H, *J*=11.7 Hz, ArC*H*$_2$Ar), 4.56–4.46 (m, 6H, ArC*H*$_2$Ar), 4.30–4.02 (m, 12H, OC*H*$_2$), 3.92–3.60 (m, 28H, OC*H*$_2$), 3.29 (d, 2H, *J*=12.1 Hz, ArC*H*$_2$Ar), 3.24 (d, 2H, *J*=11.7 Hz, ArC*H*$_2$Ar), 3.14 (d, 2H, *J*=11.4 Hz, ArC*H*$_2$Ar), 3.13 (d, 2H, *J*=11.7 Hz, ArC*H*$_2$Ar), 2.20–1.65 (m, 26H, C*H*$_2$), 1.55–1.09 (m, 82H, C*H*$_2$), 1.06–0.89 (m, 24H, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{200}H_{260}N_{16}O_{28}$ $(M+2Na^{+}+2CH_3CN)$ 1732.2, observed 1732.0.

4.5.4. *Bis[3]catenane* ***8b***

Approach A: starting with tetraloop compound **5b** (80.0 mg, 0.0416 mmol), tetraalkenyl tetraurea **6b** (64.7 mg, 0.0396 mmol) in dichloromethane (160 mL), Grubbs' catalyst (6.5 mg, 0.0079 mmol), and triethylamine (0.5 mL). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 8.0 mg, 0.036 mmol). The final purification by column chromatography (silica gel, THF/*n*-hexane, 1:15) followed by recrystallization from chloroform/methanol gave the bis[3]catenane **8b** as a colorless, crystalline powder; yield 48.1 mg, 35%.

Approach B: starting with bisloop compound **7b** (65.6 mg, 0.0414 mmol), octaalkenyl tetraurea **4b** (0.0800 g, 0.0395 mmol) in dichloromethane (160 mL), Grubbs' catalyst (13.0 mg, 0.0158 mmol), and triethylamine (0.5 mL). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 16.0 mg; 0.0713 mmol). The final purification by column chromatography (silica gel, THF/*n*-hexane, 1:15) followed by recrystallization from chloroform/methanol gave the bis[3]catenane **8b** as a colorless, crystalline powder; yield 65.6 mg, 47%. Mp >280 °C (decomposition); ^{1}H NMR (C_6D_6): 10.11 (s, 2H, NH), 10.06 (s, 2H, N*H*), 10.03 (s, 2H, N*H*), 10.00 (s, 2H, N*H*), 8.48 (s, 2H, Ar*H*), 8.40 (d, 2H, *J*=7.8 Hz, Ar*H*), 8.28 (d, 2H, *J*=2.0 Hz, Ar*H*), 8.23 (s, 2H, Ar*H*), 8.16 (s, 2H, Ar*H*), 8.10 (d, 2H, *J*=2.0 Hz, Ar*H*), 8.07 (d, 2H, *J*=1.7 Hz, Ar*H*), 8.06 (d, 2H, *J*=2.4 Hz, Ar*H*), 7.59 (s, 2H, Ar*H*), 7.52 (s, 2H, N*H*), 7.38 (s, 2H, Ar*H*), 7.27 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.22–7.07 (m under the solvent peak, 10H, N*H*, Ar*H*), 7.05 (s, 2H, N*H*), 6.82 (s, 2H, N*H*), 6.71 (d, 2H, *J*=8.2 Hz, Ar*H*), 6.58 (s, 2H, Ar*H*), 6.53 (dd, 2H, *J*=7.8, 1.4 Hz, Ar*H*), 6.48 (s, 2H, Ar*H*), 6.43 (d, 2H, *J*=2.0 Hz, Ar*H*), 6.32 (d, 2H, *J*=2.0 Hz, Ar*H*), 6.27 (d, 2H, *J*=2.4 Hz, Ar*H*), 6.25 (d, 2H, *J*=2.4 Hz, Ar*H*), 4.53 (d, 2H, *J*=11.6 Hz, ArC*H*$_2$Ar), 4.50 (d, 4H, *J*=11.9 Hz, ArC*H*$_2$Ar), 4.40 (d, 2H, *J*=11.6 Hz, ArC*H*$_2$Ar), 4.14–3.49 (m, 40H, OC*H*$_2$), 3.31 (d, 2H, *J*=11.9 Hz, ArC*H*$_2$Ar), 3.29 (d, 2H, *J*=11.9 Hz, ArC*H*$_2$Ar), 3.16 (d, 2H, *J*=11.9 Hz, ArC*H*$_2$Ar), 3.15 (d, 2H, *J*=11.9 Hz, ArC*H*$_2$Ar), 2.11 (m, 4H, C*H*$_2$), 1.97 (m, 12H, C*H*$_2$), 1.81–1.60 (m, 16H, C*H*$_2$), 1.57–1.00 (m, 92H, C*H*$_2$), 0.97 (t, 24H, *J*=7.3 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{212}H_{284}N_{16}O_{28}$ $(MH^{+}+Na^{+}+THF+EtOH)$ 1816.4, observed 1816.1.

4.5.5. *Bis[3]catenane* ***8c***

Approach A: starting with tetraloop compound **5c** (51.6 mg, 0.0240 mmol), tetraalkenyl tetraurea **6c** (40.0 mg, 0.0229 mmol) in dichloromethane (92 mL), Grubbs' catalyst (3.8 mg, 0.0046 mmol), and triethylamine (0.5 mL). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 4.7 mg; 0.021 mmol). The final purification by column chromatography (silica gel, THF/*n*-hexane, 1:20) followed by recrystallization from chloroform/methanol gave the bis[3]catenane **8c** (0.0176 g, 20% yield) as a colorless, crystalline powder.

Approach B: prepared from bisloop compound **7c** (70.0 mg, 0.0413 mmol), octaalkenyl tetraurea **4c** (88.5 mg, 0.0393 mmol) in dichloromethane (160 mL), Grubbs' catalyst (12.9 mg, 0.0157 mmol), and triethylamine (1 mL). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 16.1 mg; 0.0707 mmol). The final purification by column chromatography (silica gel, THF/*n*-hexane, 1:20) followed by recrystallization from chloroform/methanol gave the bis[3]catenane **8c** as a colorless, crystalline powder; yield 72.4 mg, 48%. Mp >300 °C (decomposition); ^{1}H NMR (C_6D_6): 9.99 (s, 2H, N*H*), 9.94 (s, 2H, N*H*), 9.91 (s, 2H, N*H*), 9.87 (s, 2H, N*H*), 8.30–8.19 (m, 8H, Ar*H*), 8.07 (s, 2H, Ar*H*), 8.00 (m, 4H, Ar*H*), 7.90 (d, 2H, *J*=2.2 Hz, Ar*H*), 7.44 (m, 4H, N*H*, Ar*H*), 7.40 (s, 2H, N*H*), 7.35 (m, 2H, Ar*H*), 7.90–7.00 (m under the solvent peak, 12H, N*H*, Ar*H*), 6.62 (dd, 2H, *J*=8.4, 1.7 Hz, Ar*H*), 6.48–6.33 (m, 12H, Ar*H*), 6.30 (d, 2H, *J*=2.2 Hz, Ar*H*), 4.54 (d, 2H, *J*=12.0 Hz, ArC*H*$_2$Ar), 4.48 (d, 2H, *J*=11.7 Hz, ArC*H*$_2$Ar), 4.47 (d, 2H, *J*=11.4 Hz, ArC*H*$_2$Ar), 4.39 (d, 2H, *J*=11.4 Hz, ArC*H*$_2$Ar), 3.96–3.50 (m, 40H, OC*H*$_2$), 3.33 (d, 2H, *J*=12.4 Hz, ArC*H*$_2$Ar), 3.28 (d, 2H, *J*=12.1 Hz, ArC*H*$_2$Ar), 3.21 (d, 2H, *J*=12.4 Hz, ArC*H*$_2$Ar), 3.20 (d, 2H, *J*=11.4 Hz, ArC*H*$_2$Ar), 2.15–1.87 (m, 16H, C*H*$_2$), 1.74–1.02 (m, 160H, C*H*$_2$), 0.98 (t, 12H, *J*=7.3 Hz, C*H*$_3$), 0.97 (t, 12H, *J*=7.3 Hz, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{236}H_{332}N_{16}O_{28}$ $(M+2Na^{+}+CH_3CN)$ 1963.8, observed 1963.8; $(M+2Na^{+}+THF)$ 1979.3, observed 1979.4.

4.5.6. *Bis[3]catenane* ***8d***

Approach A: starting with tetraloop compound **5d** (0.1362 g, 0.0548 mmol), tetraalkenyl tetraurea **6d** (0.10 g, 0.0522 mmol) in dichloromethane (211 mL), Grubbs' catalyst (8.6 mg, 0.0104 mmol), and triethylamine (1 mL). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 10.6 g; 0.0470 mmol). The final purification by column chromatography (silica gel, THF/*n*-hexane, 1:35) followed by recrystallization from chloroform/methanol gave the bis[3]catenane **8d** as a colorless, crystalline powder; yield 0.112 g, 49%.

Approach B: starting with bisloop compound **7d** (75.2 mg, 0.0406 mmol), octaalkenyl tetraurea **4d** (0.10 g, 0.0386 mmol) in dichloromethane (150 mL), Grubbs' catalyst (0.0127 g, 0.0154 mmol), and triethylamine (1 mL). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 15.8 mg; 0.0695 mmol). The final purification by column chromatography (silica gel, THF/*n*-hexane, 1:25) followed by recrystallization from chloroform/methanol gave the bis[3]catenane **8d** as a colorless crystalline powder; yield 56.4 mg, 33%. Mp >130 °C (decomposition); ^{1}H NMR (C_6D_6): 10.03 (s, 8H, N*H*), 8.24 (d, 2H, *J*=2.2 Hz, Ar*H*), 8.20 (d, 2H, *J*=1.9 Hz, Ar*H*), 8.18 (d, 2H, *J*=9.2 Hz, Ar*H*), 8.14 (s, 6H, Ar*H*), 8.06 (s, 2H, Ar*H*), 8.00 (s, 2H, Ar*H*), 7.69 (s, 2H, Ar*H*), 7.61 (d, 2H, *J*=8.0 Hz, Ar*H*), 7.39 (s, 2H, Ar*H*), 7.31 (s, 2H, Ar*H*), 7.30 (s, 2H, N*H*), 7.21 (s, 2H, N*H*), 7.19–7.05 (m under the solvent peak, 8H, Ar*H*, N*H*), 6.60 (dd, 2H, *J*=8.3, 1.9 Hz, Ar*H*), 6.53 (dd, 2H, *J*=8.6,1.6 Hz, Ar*H*), 6.48 (s, 2H, Ar*H*), 6.43 (s, 2H, Ar*H*), 6.38 (s, 4H, Ar*H*), 6.30 (d, 2H, *J*=1.6 Hz, Ar*H*), 6.28 (d, 2H, *J*=2.2 Hz, Ar*H*), 4.62–4.47 (m, 8H, ArC*H*$_2$Ar), 3.97–3.60 (m, 40H, OC*H*$_2$), 3.42 (d, 2H, *J*=11.4 Hz, ArC*H*$_2$Ar), 3.38 (d, 2H, *J*=10.5 Hz, ArC*H*$_2$Ar), 3.34 (d, 2H, *J*=10.8 Hz, ArC*H*$_2$Ar), 3.27 (d, 2H, *J*=11.4 Hz, ArC*H*$_2$Ar), 2.20–1.95 (m, 16H, C*H*$_2$), 1.70–1.08 (m, 232H, C*H*$_2$), 1.05–0.96 (m, 24H, C*H*$_3$); MS (ESI) *m*/*z*: calcd for $C_{272}H_{404}N_{16}O_{28}$ $(M+2H^{+})$ 2174.2, observed 2174.0.

4.5.7. *Bis[3]catenane* ***8e***

Approach B: starting with bisloop compound **7b** (70.0 mg, 0.0442 mmol), octaalkenyl tetraurea **4a** (80.7 mg, 0.0421 mmol) in dichloromethane (170 mL), Grubbs' catalyst (13.8 mg, 0.0168 mmol), and triethylamine (1 mL). Hydrogenation in THF (20 mL) using platinum dioxide (83% Pt, 17.2 g; 0.0758 mmol). The final purification by column chromatography (silica gel, THF/*n*-hexane, 1:9) followed by recrystallization from chloroform/methanol gave the bis[3]catenane **8e** as a colorless, crystalline powder; yield 85.7 mg, 60%. Mp >340 °C (decomposition); ^{1}H NMR (C_6D_6): 10.05 (s, 2H, N*H*), 10.04 (s, 2H, N*H*), 10.03 (s, 2H, N*H*), 9.94 (s, 2H, N*H*), 8.49 (s, 2H, Ar*H*), 8.42 (d, 2H, *J*=8.3 Hz, Ar*H*), 8.20 (s, 2H, Ar*H*), 8.17 (d, 2H, *J*=2.2 Hz, Ar*H*), 8.11 (d, 2H, *J*=2.5 Hz, Ar*H*), 8.10 (s, 2H, Ar*H*), 8.06 (d, 2H, *J*=2.2 Hz, Ar*H*), 7.96 (d, 2H, *J*=2.5 Hz, Ar*H*), 7.58 (s, 2H, Ar*H*), 7.50 (s, 2H, N*H*), 7.42–7.36 (m, 4H, Ar*H*), 7.27 (s, 2H, Ar*H*), 7.20–7.00 (m under the solvent peak, 8H, Ar*H*, N*H*), 6.78 (s, 2H, N*H*), 6.72 (s, 2H, N*H*), 6.66 (dd, 2H, *J*=8.0, 1.9 Hz, Ar*H*), 6.58 (s, 2H, Ar*H*), 6.55–6.50 (m, 4H, Ar*H*), 6.33 (d, 2H, *J*=2.2 Hz, Ar*H*), 6.23 (d, 2H, *J*=1.9 Hz, Ar*H*), 6.05 (d, 2H, *J*=2.2 Hz, Ar*H*), 6.02 (d, 2H, *J*=2.2 Hz, Ar*H*), 4.58–4.46 (m, 8H, ArC*H*$_2$Ar), 4.28–4.16 (m, 8H, OC*H*$_2$), 4.07–3.59 (m, 32H, OCH_2), 3.31 (d, 2H, J=12.1 Hz, ArCH_2Ar), 3.22 (d, 2H, J=11.1 Hz, ArCH_2Ar), 3.19 (d, 2H, J=11.4 Hz, ArCH_2Ar), 3.15 (d, 2H, J=11.8 Hz, ArCH_2Ar), 2.13–2.85 (m, 24H, CH_2), 1.65 (m, 4H, CH_2), 1.58–0.89 (m, 128H, CH_2, CH_3); MS (ESI) m/z: calcd for $C_{204}H_{268}N_{16}O_{28}$ (MH^++Na^++2CH_3CN) 1749.2, observed 1749.0.

4.6. Synthesis of [8]catenanes 9

4.6.1. [8]Catenane **9a**

A solution of tetraloop compound **5b** (50.0 mg, 0.0260 mmol) and tetraurea **4b** (50.2 mg, 0.0248 mmol) in freshly distilled and degassed dichloromethane (100 mL) was stirred at room temperature for 96 h and for 20 h under reflux. Tetrahydrofuran (10 mL) was added to the mixture, which was stirred under reflux for 18 days. The mixture was purged with nitrogen for 30 min and Grubbs' catalyst (8.1 mg, 0.00992 mmol) was added. After 48 h of stirring, the solvent was evaporated from under reduced pressure. The residue was dissolved in chloroform (5 mL), and passed through a column (silica gel, THF/n-hexane, 1:12). The crude product was dissolved in THF (20 mL), platinum dioxide (83% Pt, 5.1 mg, 0.0223 mmol) was added to the solution, and the reaction mixture was stirred vigorously under a hydrogen atmosphere for 6 h at room temperature. The final purification by column chromatography (silica gel, THF/n-hexane, 1:10) followed by recrystallization from chloroform/n-hexane furnished (in addition to 11 mg of the unreacted tetraloop **5b**) the [8]catenane **9a** as colorless, crystalline powder; yield 32.5 mg, 32%. Mp >230 °C (decomposition); ^{1}H NMR (CD_2Cl_2): 9.42 (s, 8H, NH), 7.74 (s, 8H, ArH), 7.72 (s, 8H, ArH), 6.91 (s, 8H, NH), 6.39 (s, 8H, ArH), 6.13 (s, 8H, ArH), 5.68 (s, 8H, ArH), 4.28 (d, 8H, J=11.9 Hz, ArCH_2Ar), 4.14–3.97 (m, 16H, OCH_2), 3.97–3.84 (m, 16H, OCH_2), 3.73 (t, 16H, J=8.0 Hz, OCH_2), 2.86 (d, 8H, J=11.6 Hz, ArCH_2Ar), 1.97 (m, 16H, CH_2), 1.78 (m, 16H, CH_2), 1.50–1.00 (m, 144H, CH_2), 0.96 (t, 24H, J=7.3 Hz, CH_3); MS (ESI) m/z: calcd for $C_{232}H_{320}N_{16}O_{32}$ (M+THF+2Na^+) 1981.7, observed 1981.2.

4.6.2. [8]Catenane **9b**

A solution of tetraloop compound **5c** (50.0 mg, 0.0233 mmol) and tetraurea **4c** (49.9 mg, 0.0222 mmol) in freshly distilled and degassed dichloromethane (90 mL) was stirred at room temperature for 48 h; the complete formation of the heterodimer was verified by ^{1}H NMR. After the signals of the homodimer had disappeared, the mixture was purged with nitrogen for 30 min and Grubbs' catalyst (70 mg, 0.0088 mmol) was added. After 48 h of stirring, triethylamine (0.5 mL) was added and the solution was stirred for 1 h and evaporated. The residue was dissolved in dichloromethane (5 mL) and passed through a column (silica gel, THF/n-hexane, 1:12). The crude product was dissolved in THF (20 mL), platinum dioxide (83% Pt, 0.009 g; 0.0399 mmol) was added to the solution, and the reaction mixture was stirred vigorously under a hydrogen atmosphere for 6 h at room temperature. The final purification by column chromatography (silica gel, THF/hexane, 1:12) followed by recrystallization from chloroform/n-hexane gave the [8]catenane **9b** as a colorless, crystalline powder; yield 39.4 mg, 41%. Mp >285 °C (decomposition); ^{1}H NMR (CD_2Cl_2): 9.45 (s, 8H, NH), 7.74 (s, 8H, ArH), 7.64 (s, 8H, ArH), 6.68 (br s, 16H, ArH, NH), 6.13 (s, 8H, ArH), 5.89 (s, 8H, ArH), 4.28 (d, 8H, J=11.7 Hz, ArCH_2Ar), 4.06–3.63 (m, 48H, OCH_2), 2.88 (d, 8H, J=11.7 Hz, ArCH_2Ar), 1.96 (m, 16H, CH_2), 1.74 (m, 16H, CH_2), 1.70–1.00 (m, 208H, CH_2), 0.95 (t, 24H, J=7.2 Hz, CH_3); MS (ESI) m/z: calcd for $C_{264}H_{384}N_{16}O_{32}$ (M+THF+2Na^+) 2206.8, observed 2206.1.

4.6.3. [8]Catenane **9c**

Tetraloop compound **5d** (0.0193 g, 0.00777 mmol), tetraurea **4d** (0.01915 g, 0.00740 mmol), Grubbs' catalyst (0.0024 g, 0.00296 mmol) in dichloromethane (30 mL), and triethylamine (0.5 mL) were reacted as described for **9b**. The residue formed after evaporation of the reaction mixture was passed through a column (silica gel, THF/n-hexane, 1:14). The crude product was dissolved in THF (20 mL), platinum dioxide (83% Pt, 30.2 mg, 0.0133 mmol) was added to the solution, and the reaction mixture was stirred vigorously under a hydrogen atmosphere for 6 h at room temperature. The final purification by column chromatography (silica gel, THF/n-hexane, 1:14) followed by recrystallization from chloroform/n-hexane gave the [8]catenane **9c** as a colorless, crystalline powder; yield 14.7 mg, 40%. Mp 120 °C; ^{1}H NMR (CD_2Cl_2): 9.38 (s, 8H, NH), 7.76 (s, 8H, ArH), 7.50 (s, 8H, ArH), 6.90 (s, 8H, NH), 6.41 (br s, 8H, ArH), 6.13 (s, 8H, ArH), 5.75 (s, 8H, ArH), 4.27 (d, 8H, J=11.7 Hz, ArCH_2Ar), 4.05–3.63 (m, 48H, OCH_2), 2.94 (d, 8H, J=11.7 Hz, ArCH_2Ar), 1.97 (m, 16H, CH_2), 1.74 (m, 16H, CH_2), 1.63 (m, 16H, CH_2), 1.50–1.00 (m, 288H, CH_2), 0.97 (t, 24H, J=7.2 Hz, CH_3); MS (ESI) m/z: calcd for $C_{312}H_{480}N_{16}O_{32}$ (M+THF+2Na^+) 2542.8, observed 2542.4.

4.7. X-ray crystallography

X-ray diffraction measurements were performed on a Stoe-IPDS-II diffractometer. An absorption correction was carried out with the MULABS[43] option in PLATON.[44] Crystal data and refinement details are given in Table 3. The structures were solved by SHELXD[45] and refined by full-matrix least-squares techniques using SHELXL.[45] The methylene chain C atoms were only refined isotropically. All hydrogen atoms were inserted in calculated positions and refined using a riding model. Restraints had to be applied to keep the geometric parameters in a reasonable range.

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