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Calix[4]arene-Based Bis[2]catenanes: Synthesis and Chiral Resolution

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Abstract: The exclusive formation of hydrogen-bonded dimers between tetraaryl and tetratosylurea calix[4]arenes has been used to prepare a series of ten "bisloop" tetraurea calix[4]arenes **3**, in which adjacent phenylurea groups are covalently linked through α,ω-dioxyalkane chains. This dimerization with tetratosylurea **2** as template preorganizes the alkenyl residues of tetra(*m*-alkenyloxyphenyl) ureas **1** and enables their selective connection in high yield (up to 95 %) by olefin metathesis followed by hydrogenation. The "bisloop" calixarenes **3** also exclusively form heterodimers with **1**. Thus, in a separated metathesis/hydrogenation sequence, a series of 14 cyclic bis[2]catenanes **4**, in which two calix[4]arenes are connected through their wide rims by two pairs of interlocked rings (total size 29 to 41 atoms), were prepared in yields of up to 97 %. Optical resolution of these chiral bis[2]catenanes was studied by HPLC on chiral stationary phases. The single-crystal X-ray structure of one example (**4(P,10)**) confirmed the interlocking rings and revealed that the hydrogen-bonded dimeric capsule of the calix[4]arene can be "completely" opened.

Keywords: calixarenes • catenanes • chiral resolution • metathesis • template synthesis

Introduction

Catenanes are compounds in which (covalently linked) macrocyclic molecules are (mechanically) connected as the rings of a chain (latin: catena).[1,2] And similarly to the (traditional) preparation of a macroscopic chain, the synthesis of catenanes requires macrocyclic rings to be closed while penetrating other rings. Evidently an efficient synthesis needs appropriate preorganization in both cases, although the first catenanes, unlike their macroscopic analogues, were synthesized on a statistical basis.[3] Preorganization on a molecular level was first achieved through the use of covalent bonds in a carefully designed multistep reaction.[4] Although the principle of "covalent preorganization" has recently again been used for the "large-scale" synthesis of [2]catenanes made up of very large rings,[5] the breakthrough in catenane synthesis came when the (reversible) coordination of suitable building blocks to a metal cation was used for their appropriate preorganization in space.[6] The rapidly developing field of "supramolecular chemistry" gave rise to numerous further examples of the preorganization of reactive precursors through reversible, noncovalent links. In addition to metal coordination,[7] the use of coordination to anions,[8] apolar forces,[9] (charge transfer complexes) or hydrogen bonds[10] should also be mentioned, and often there is a combination of several factors.

Calix[4]arenes substituted on their wide rims by four urea functions form hydrogen-bonded dimeric capsules in aprotic, apolar solvents. This well known dimerization also brings residues attached to the urea groups into unique positions relative to each other. According to calculations (and consistently with several X-ray structures[11]) the eight (two × four) *p*-methyl groups in a dimer of tetratolyl urea occupy the corners of two regular squares with a common side length of 13.4 Å (Figure 1. Both planes are close to the reference plane (of the methylene bridges) of the other calixarene (distance 0.2 Å), while they are 9.9 Å apart from each

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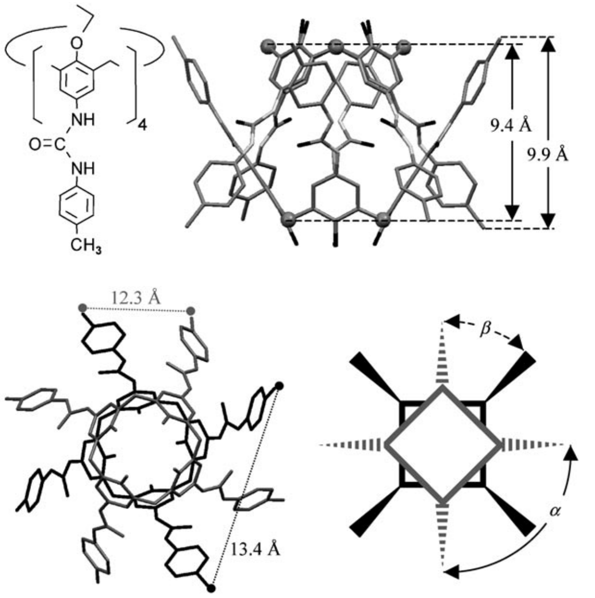


Figure 1. Hydrogen-bonded dimer of tetraurea calix[4]arene seen from different directions (relevant distances are indicated) and short representation of a dimer, illustrating potential covalent connection points.

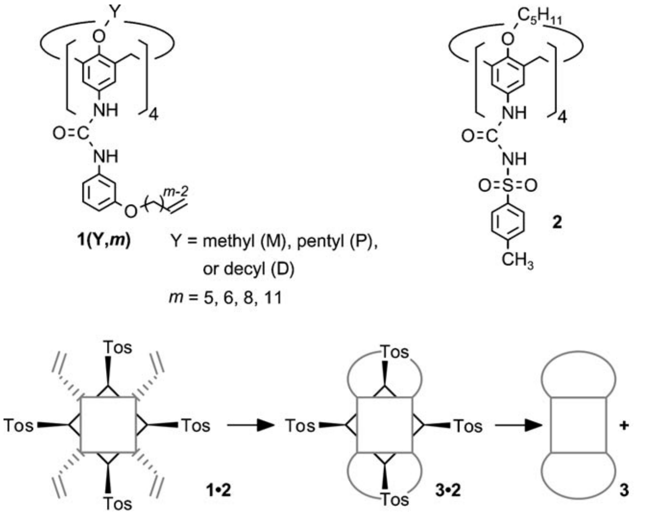


Figure 2. Schematic representation of the synthesis of bisloop compounds **3(Y,*n*)** by metathesis of **1(Y,*m*)** through the use of tetratosylurea **2** as template. Compounds are characterized by the number **1** or **3**, followed (in brackets) by the ether residue Y (M = methyl, P = pentyl, D = decyl), and the number of carbon atoms in the alkenyl residue (*m*) or in the connecting chain (*n* = 2*m*-2).

other. Thus, the distance between adjacent *p*-methyl groups belonging to different calixarenes is only slightly shorter (1.1 Å) than the distance to the adjacent group in the same calixarene. This unique arrangement in space[12] inspired the idea that covalent connection between functional groups attached to the urea groups of a calix[4]arene should give rise to novel and interesting catenanes.

Syntheses

For the covalent linkage of urea residues we chose metathesis reactions between alkenyl ether groups, with subsequent hydrogenation of the olefinic double bonds to avoid stereochemical complications. This reaction has often been used to establish similar connections within larger molecules (e.g., dendrimers[13]) or molecular assemblies[14]. The required tetraurea calixarenes **1** are easily prepared by acylation of the corresponding tetraaminocalix[4]arene with the activated urethanes, which in turn are obtained from *m*-hydroxyacetanilide by *O*-alkylation, hydrolysis of the amide group, and acylation with *p*-nitrochloroformate.[15]

An early attempt, direct metathesis with the dimer **1(P,8)·1(P,8)** (Figure 2), provided a mixture of three isomeric compounds:[16] the desired bis[2]catenane **4(P,14)**, in which two α-connections were present, a tetrabridged capsule (two β-connections), and a doubly bridged [2]catenane (α- and β-connections).

The difficult separation of these isomeric compounds could be avoided by starting with tetraurea calix[4]arene **3**, in which adjacent urea residues are already covalently linked. Such prefabricated bisloop compounds **3** can be prepared by conventional acylation of a tetramino-substituted calix[4]arene with an activated bisurethane or a diisocyanate under high-dilution conditions. A better strategy, however, is again based on the metathesis of tetraalkenylureas **1** in heterodimers **1·2** with tetratosylurea **2** as template (Figure 2).[17]

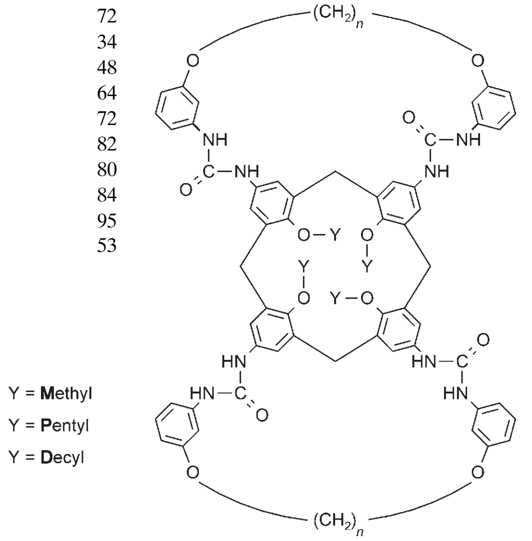
This heterodimerization prevents undesired transcavity connections and, in the case of the tetramethyl ethers **1(M,*m*)**, forces the molecules to assume the required cone conformation.[18] Metathesis occurs smoothly in benzene or toluene in the presence of the first generation of Grubbs' catalyst. To suppress reactions between heterodimers the concentration was kept around 0.5 mM. After the reaction, the heterodimer is easily split by use of hydrogen bond-breaking solvents, usually THF. After hydrogenation of the double bonds, to avoid stereochemical complications due to *cis*/*trans* isomerism, the bisloop compounds **3** were isolated in yields of up to 95 % (see Table 1).

Bisloop compounds **3** do not form homodimers; obviously this would result in unfavorable overlap of the chains connecting adjacent urea residues. The tendency to dimerize in apolar solvents thus results in the exclusive formation of heterodimers in a stoichiometric mixture of **3** with **1**, since this is the only way to get all urea groups incorporated in the favorable hydrogen-bonded belt. This dimerization can be easily monitored by ^{1}H NMR. Again, in such a dimer **1·3** only adjacent alkenyl residues can be connected (see Figure 3). Thus, under the conditions of the metathesis reaction described above, the formation of a bis[2]catenane is more or less quantitative. Consequently, after hydrogenation, the bis[2]catenanes **4** were isolated in yields of up to 97 % (see Table 2).

It should be mentioned that the sizes of the interlocking residues can be easily made different, if the alkenyl groups

Table 1. Survey on bisloop compounds **3**, prepared by template synthesis as shown in Figure 2.

Compound	Yield [%]
3(M,8)	72
3(M,10)	34
3(M,14)	48
3(M,20)	64
3(P,8)	72
3(P,10)	82
3(P,14)	80
3(P,20)	84
3(D,10)	95
3(D,14)	53



of the tetraureas **1** used for the synthesis of the bisloop compound **3** in the first step and for the catenane **4** in the second step are different, as demonstrated by the examples **5(P,8/14)** and **5(P,8/20)**.[19] Structural differences due to different ether groups Y, or different connecting chains[20] can also be achieved.

While the pairs of interlocking rings are different in size (*n*/*n*′), the pairs belonging to one calixarene are identical (either n_I or n_II) in the examples described above. There is another isomeric possibility in which the two calixarenes are identical but carry rings of different size *n*/*n*′. Bis[2]catenanes of this type are available, through the use of analogous principles for the self-assembly.

Monoloop bisalkenyl ureas **6** are easily prepared in three steps from a bis-Boc-protected tetraamino-substituted calix[4]arene[21] by cyclization with an activated bisurethane, deprotection and acylation with the activated urethane. In apolar solvents they readily dimerize. Of the two potentially possible regioisomers exclusively one is formed,[22] in which the two loops do not overlap. For a metathesis reaction restricted to dimers **6•6** the number of wrong connections is reduced in comparison to dimers **1•1**. At first glance there should be only one β-connection between the two calix[4]arenes, but after a first α-connection, the second connection must again be α.

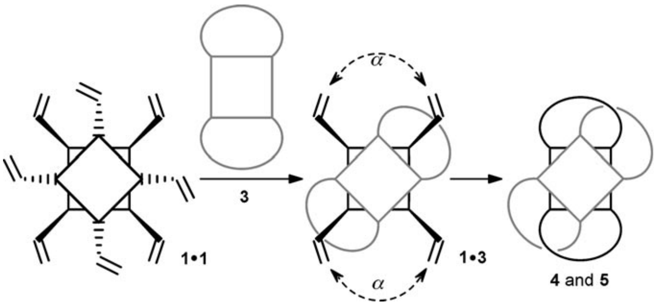


Figure 3. Schematic representation of the synthesis of bis[2]catenanes **4(Y,$n_\mathrm{I}=n_\mathrm{II}$)** and **5(Y,$n_\mathrm{I}\neq n_\mathrm{II}$)** through the use of heterodimers between tetraalkenyl derivatives **1** and bisloop compounds **3**. The characterization of the compounds follows the rules described above. Ether residues (Y_I/Y_II) and loop sizes (n_I/n_II) can be different for both calixarenes. A single letter/number indicates that they are identical.

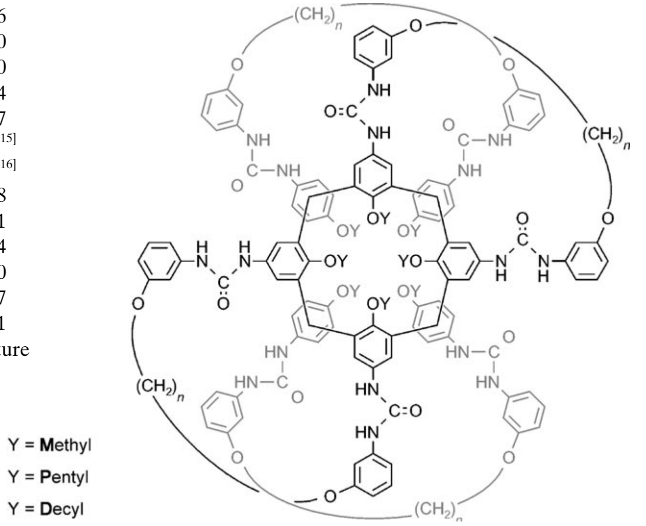
As shown in Figure 4, the bis[2]catenane **7(P,8+14)** was prepared in 41 % yield, while in the case of **7(P,8+20)** no pure product could be separated from a mixture of similar or isomeric compounds.[24] The pathway via homodimers of monoloop compounds **6** thus offers an interesting and complementary possibility, but the reaction of heterodimers between tetraalkenyl compounds **1** and bisloop compounds **3** is the method of choice for the preparation of bis[2]catenanes of type **4**.

Characterization

NMR Spectroscopy: In apolar solvents, bisloop compounds **3** show broad spectra due to "irregular" association, but in

Table 2. Survey of bis[2]catenanes **4** and **5**, prepared by template synthesis as shown in Figure 3, and bis[2]catenanes **7**, prepared as shown in Figure 4.

Compound	Yield [%]
4(M,8)[a]	66
4(M,10)	50
4(M,14)	70
4(M,20)	64
4(P,8)	67
4(P,10)	70[15]
4(P,14)	78[16]
4(P,20)	88
5(P,8/14)[b]	81
5(P,8/20)	64
4(D,10)	50
4(D,14)	97
7(P,8+14)[c]	41
7(P,8+20)	mixture



[a] One number means that all loops have the same size (e.g., eight CH_2 groups). [b] Two numbers separated by "/" means different loops but identical within each calixarene (e.g., eight in one calixarene and 14 in the second). [c] Two numbers separated by "+" means identical calixarenes with different loops (e.g., eight and 14 CH_2 groups).

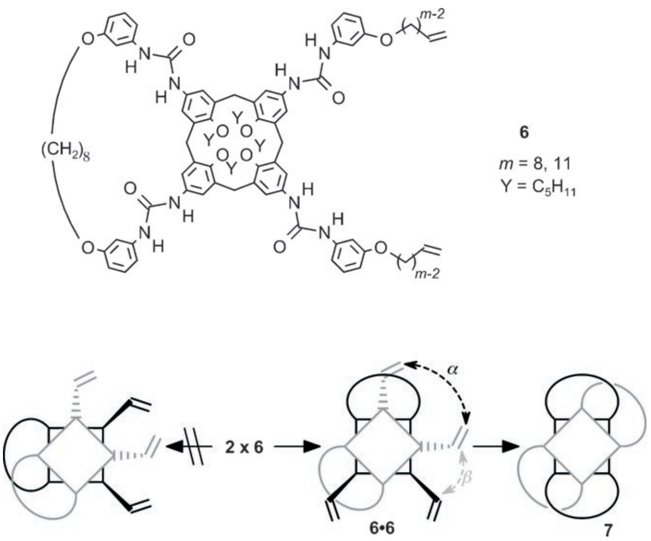


Figure 4. Schematic representation of the synthesis of bis[2]catenanes **7(Y,*n*+*n*′)** by use of homodimers of monoloop bisalkenyl derivatives **6(Y,*m*+*n*′)**. The characterization of the compounds follows the rules described above. Loop sizes (*n*/*n*′) are different within both (identical) calixarenes but identical for the interlocking pairs.[23]

polar, hydrogen bond-breaking solvents ([D$_8$]THF, [D$_6$]DMSO, [D$_5$]Pyr) the ^{1}H NMR spectra reflect the expected C_{2v} symmetry with two symmetry planes intersecting opposite methylene bridges. Typically one pair of *m*-coupled doublets for the aromatic protons of the calixarene part (in the 7.2–6.5 ppm region) and two pairs of doublets (geminal coupling) for the methylene bridges (4.6–4.2 ppm for the axial and 3.2–3.0 ppm for the equatorial protons) are found. Sometimes just one doublet appears for the axial protons but two doublets for the equatorial ones, and the pentyl or decyl ethers with larger loops ($n = 14$, 20) show only one pair of doublets (sometimes broad) for axial and equatorial protons in the expected area (Table 3). As in the starting **1**, the aryl protons of the urea residues appear as two “doublets of doublets” and two “triplets” reflecting the *ortho* coupling and the *meta* coupling (not always well resolved).

The tetramethyl ethers of **3** are held in the cone conformation, as attested to by the signals of the methylene bridges. A remarkable exception, though, is the derivative **3(M,20)**, the spectrum of which in [D$_8$]THF at 25 °C shows the “normal” pattern with one doublet for the axial protons and two doublets for the equatorial ones (Table 3, line 6), while in [D$_6$]DMSO at 25 °C just two very broad signals appear at δ 4.23 and 3.18 ppm. With increasing temperature the two signals became broader and broader and around 100 °C their coalescence temperature is reached, which indicates a cone-to-cone inversion. The spectrum in pyridine is even more complicated (see Figure 5). The number of the signals marked suggests that the molecule adopts more then one conformation.

Before we discuss the ^{1}H NMR spectra of bis[2]catenanes, it is reasonable to deal with their symmetry properties. Bis[2]catenanes **4(Y,*n*)** with four identical loops (composed of two identical C_{2v}-symmetrical calixarenes) have D_2 symmetry, which is reduced to C_2 symmetry by the directionality of the hydrogen-bonded belt, which is kinetically stable. This is expressed by four NH signals at low field (9.7–10 ppm) for the strong hydrogen bonds of the α-NH groups and four signals (7.3–6.9 ppm) for the β-NH groups,[22] which are often overlapped by the signal of the solvent (CHCl$_3$, C$_6$H$_6$). The 16 aromatic protons of the calixarene skeletons appear as eight *m*-coupled doublets, which are usually well resolved ($n = 8$, 10). Four singlets for methoxy groups are found around 3.5 ppm for compounds **4(M,*n*)**. Four pairs of doublets with geminal coupling for the eight methylene bridges also appear in the same region (4.5–3.0 ppm).

Table 3. NMR data for bisloop compounds. Each signal is one doublet.

	Solvent	Signals of the methylene bridges (ppm) axial	equatorial
3(M,8)	DMSO	4.26; 4.24	3.19; 3.16
	Pyr	4.42; 4.36	3.27; 3.04
3(M,10)	THF	4.33	3.14; 3.11
	DMSO	4.26; 4.24	3.19; 3.17
3(M,14)	THF	4.33; 4.32	3.12; 3.06
3(M,20)	THF	4.34	3.12; 3.11
	DMSO	4.23 (br)	3.18 (br)
3(P,8)	DMSO	4.34; 4.33	3.12; 3.11
3(P,10)	THF	4.44	3.08; 3.06
3(P,14)	THF	4.45; 4.44	3.08; 3.07
3(P,20)	THF	4.43	3.08
	DMSO	4.33	3.11
3(D,10)	THF	4.44	3.08; 3.06
3(D,14)	DMSO	4.32	3.10

Bis[2]catenanes **5(Y,*n*$_\mathrm{I}$/*n*$_\mathrm{II}$)**, composed of two different (C_{2v}-symmetrical) calix[4]arenes with identical loops, have C_2 symmetry. The C_2 axis is identical with the molecular axis of the calixarenes, and the symmetry is retained for kinetically stable hydrogen bonds. However, the directionality of the H-bonded belt adds an independent element of chirality in heterodimers (the two calixarenes are different!) and so we observe two diastereomeric pairs of enantiomers (see Figure 6).[25] This becomes evident through, for instance, (4+4) NH signals at low field and partly overlapping in Figure 7 (six signals, of which two have double intensity).

The situation is different again in **7(P,8+14)**, made up of two identical, C_s-symmetrical calixarenes bearing different loops. Bis[2]catenanes of this type have C_2 symmetry, but the twofold axis is perpendicular (!) to the molecular axis of the two calixarenes. In other words, the two calixarenes are symmetry-related by this C_2 axis. The directionality of H-bonds therefore reduces the symmetry to C_1, but it is not an independent element of chirality (we are dealing with a homodimer!). As illustrated in Figure 7, one pair of enantiomers exists, though there is no symmetry element, which is expressed by, for instance, eight low-field NH signals.

A polar solvent such as [D$_6$]DMSO disrupts the hydrogen bonding between the urea groups and destroys the capsule (see Figure 8). Even with the smallest loop size the ^{1}H NMR spectrum resembles the spectrum of a C_{2v}-symmetrical tetraurea.

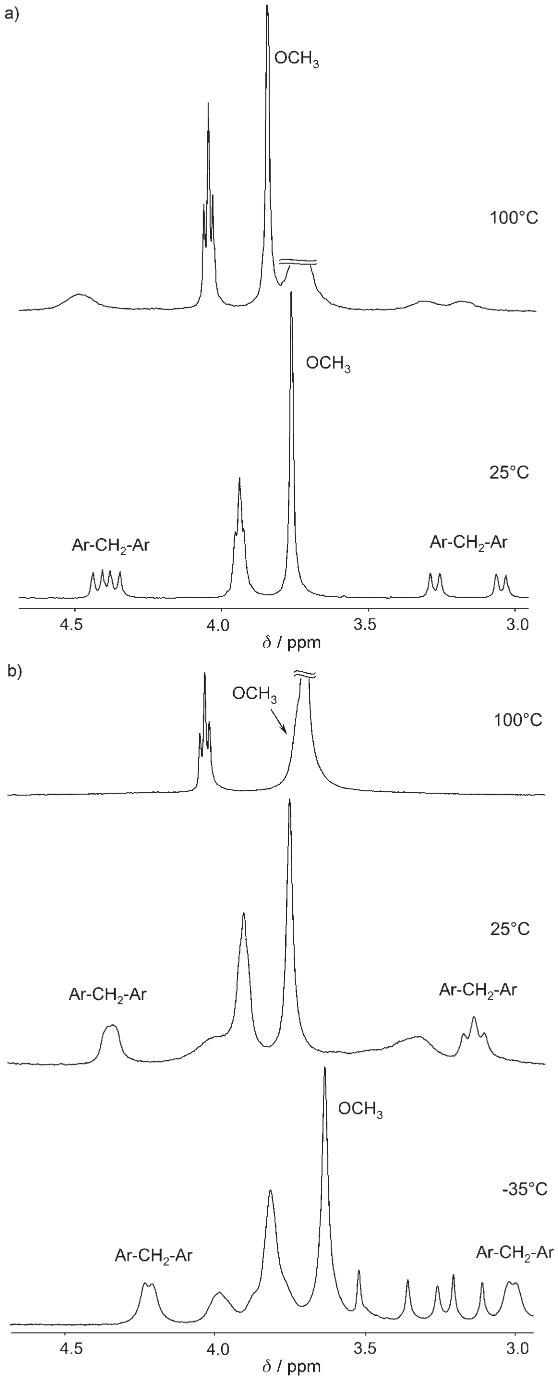


Figure 5. Sections of the ^{1}H NMR spectra ([D$_5$]Pyr at different temperatures) of a) **3(M,8)** and b) **3(M,20)**. Protons of the methylene bridges and of the methoxy groups are indicated.

X-ray analysis: A good-quality crystal of the compound **4(P,10)** was obtained from a chloroform/methanol mixture (1:1). Its structure could be completely solved; Figure 8 shows the molecular structure of the catenane from two perspectives.

Unlike in an earlier attempt,[16] all atoms of the four loops were found and so their catenation/intertwining could be established unambiguously. The "gray" loop between A1 and A2 penetrates the "black" loop between B7 and B8, while the loop connecting A3 and A4 passes through the one connecting B5 and B6.

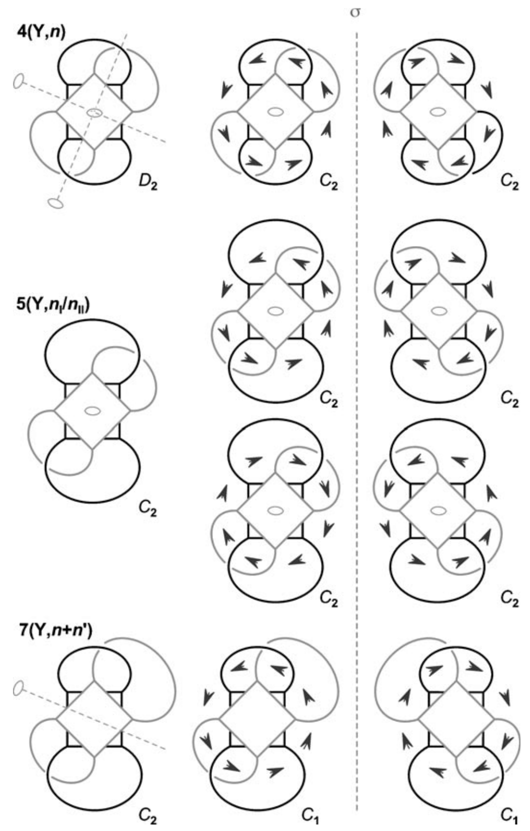


Figure 6. Schematic representation of the symmetry properties of the catenanes **4(Y,*n*)**, **5(Y,*n*$_I$/*n*$_{II}$)**, and **7(Y,*n*+*n*′)**. The C_2 symmetry axis, the directionality of the hydrogen-bonded belt, and the mirror plane are indicated.

Evidently the two calixarenes do not form a hydrogen-bonded capsule any longer, the whole structure being opened but held together by the catenated loops. The reference planes of the two calixarenes, defined by the carbon atoms of the methylene bridges, which are (more or less) parallel in a dimer, include an angle of 70.50°. The distance between the centers of the reference planes is 12.67 Å, while in a hydrogen-bonded dimer it should be ≈9.4–9.5 Å.

The two calixarenes each assume a *pinched-cone* conformation in which two opposite aromatic units are almost parallel (units A2/A4, B6/B8). In fact, the angles between the reference planes and the aromatic units are slightly less than 90° ($\delta = 87$–$89°$), with the exception of unit A2, which is oriented more inside ($\delta = 79°$; see Table 4). Consequently the four other phenolic units are bent outwards, forming angles of $\delta = 141$–$143°$ with the reference plane; again there is one exception (unit B5, with $\delta = 133°$).

The pinched-cone conformation may also be characterized by the distances of the carbon atoms in the *p*-positions, of A2/A4 = 4.778 Å and A1/A3 = 9.843 Å in the calixarene A and B6/B8 = 5.55 Å and B5/B7 = 9.56 Å in the calixare-

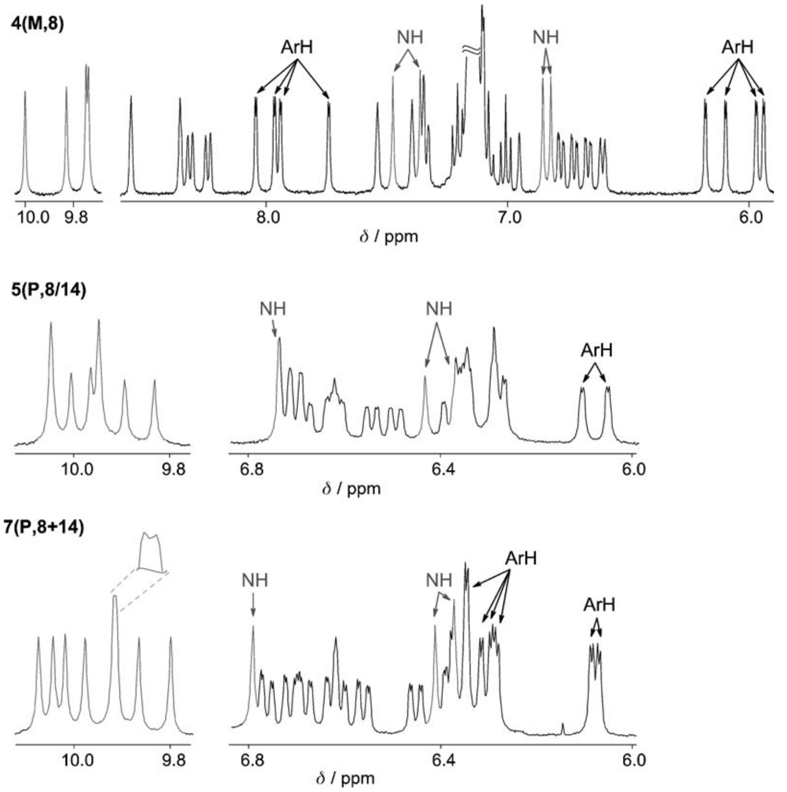


Figure 7. Sections of the ^1H NMR spectra (C_6D_6, 25 °C) of **4(M,8)**, **5(P,8/14)**, and **7(P,8+14)**. NH protons are marked with NH, protons of the calixarene skeletons with ArH. All the protons with ppm value higher than 9.7 are NH protons with stronger hydrogen bonds.

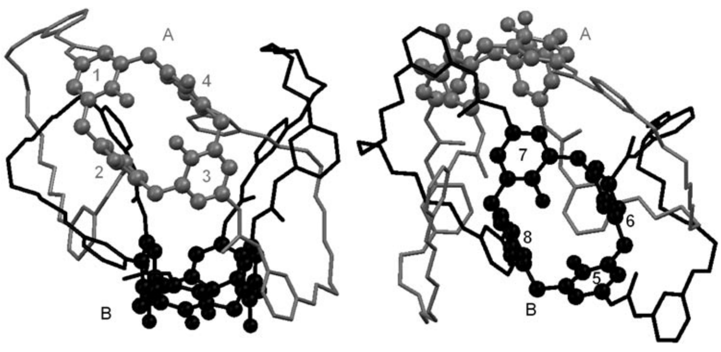


Figure 8. Two different views of the X-ray structure of the compound **4-(P,10)**. The two calixarene are colored in grey and black. Each aromatic unit is numbered.

ne B. This means that the calixarene A is more strongly pinched then B.

Optical resolution: The chiral resolution of the bis[2]catenanes **4**, **5**, and **7** was studied by chromatography on the chiral stationary phases Chiralpak AD-H (silica-bound amylose with 3,5-dimethylphenylcarbamate units) and Chiralpak OD (silica-bound cellulose with 3,5-dimethylphenylcarbamate units)[26] with mixtures of hexane and ethanol as eluents. These stationary phases have been successfully used for the resolution of various topologically chiral compounds such as [2]catenanes,[27] [2]rotaxanes,[27b] pretzelanes,[27b] knots,[28] and knotaxanes,[29] and also for one example (**4(P,10)**) of a bis[2]catenane.[30] Figure 9 shows a typical example of a successful separation.

Since the first examples of compounds **4** suggested some general trends for the separation factors with respect to the ether residues Y and the loop size *n*, we decided to study all the catenanes under the same standard conditions (Table 5). These trends were not confirmed for the whole series, however, and unfortunately a satisfactory separation was not even possible in all cases. In the series of compounds with the $(CH_2)_{10}$ bridges/loops, for example, α is approximately the same for the catenanes with methyl (1.48, entry 2) or pentyl (1.52, entry 7) ether groups, while it drops down to "≈1" for the decyl ether (entry 15). In the series of compounds possessing $(CH_2)_{14}$ loops, α increases steadily from 1.39 (entry 3) through 1.92 (entry 9) to 2.36 (entry 16). For the compounds with $(CH_2)_8$ and $(CH_2)_{20}$ loops, α is higher for the methyl ethers (entries 1, 4) than for the pentyl ethers (entries 5 and 10). Entries 11, 12, and 14 suggest that the chiral resolution of catenanes containing different loops (including the isomeric pair **5(P,8/14)** and **7(P,8+14)**), is more difficult (at least under the "standard" conditions A), although it was possible in one case through application of a less polar eluent (entry 13).

Table 4. Selected crystallographic data: I) Distances [Å] between carbon atoms of the methylene bridges within one calixarene. II) Angles [°] between the planes of the aromatic units and the reference plane of the calixarene.

First calixarene		Second calixarene	
	I) reference planes		
C1–C2	5.007	C5–C6	5.029
C2–C3	5.105	C6–C7	5.121
C3–C4	5.038	C7–C8	5.013
C1–C4	5.046	C5–C8	5.100
C1–C3	7.153	C5–C7	7.268
C2–C4	7.124	C6–C4	7.058
	II) inclination of the aromatic units		
1	140.79	5	133.13
2	79.39	6	87.13
3	143.2	7	141.61
4	88.94	8	88.27

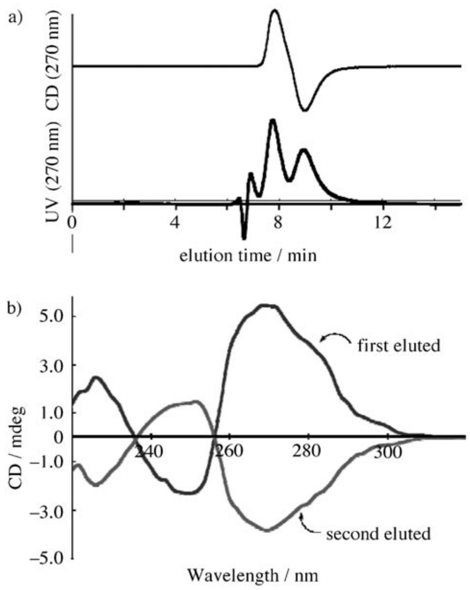


Figure 9. Separation of the compound **4(P,14)**. a) Column Chiralpak AD-H, hexane/ethanol 9:1; b) CD spectra of both fractions: hexane/ethanol 9:1, cell length: 25 mm.

Table 5. Resolution of enantiomers of bis[2]catenanes **4**, **5**, and **7**.

Entry	Conditions[a]	t_0 [min]	t_1 [min]	t_2 [min]	k'_1[b]	k'_2[b]	α[c]	
1	**4(M,8)**	A	6.47	22.57	31.49	2.49	3.87	1.55
2	**4(M,10)**	A	6.77	32.17	44.35	3.75	5.55	1.48
3	**4(M,14)**	A	6.47	17.55	21.79	1.71	2.37	1.39
4	**4(M,20)**	A	6.77	10.08	11.79	0.49	0.74	1.51
5	**4(P,8)**	A	6.77	8.38	≈8.38	0.24	≈0.24	≈1
6	**4(P,8)**	B	6.83	12.03	12.73	0.76	0.86	1.13
7	**4(P,10)**	A	6.77	9.13	10.38	0.35	0.53	1.52
8	**4(P,10)**[15]	C	5.77	14.13	22.99	1.45	2.98	2.06
9	**4(P,14)**[16]	A	6.47	7.76	8.95	0.20	0.38	1.92
10	**4(P,20)**	A	6.77	7.59	8.11	0.12	0.20	1.67
11	**5(P,8/14)**	A	6.77	7.73	≈7.73	0.14	≈0.14	≈1
12	**5(P,8/20)**	A	6.77	7.27	≈7.27	0.07	≈0.07	≈1
13	**5(P,8/20)**	D	7.08	14.93	17.52	1.11	1.47	1.33
14	**7(P,8+14)**	A	6.97	8.28	≈8.28	0.19	≈0.19	≈1
15	**4(D,10)**	A	6.97	7.99	≈7.99	0.15	≈0.15	≈1
16	**4(D,14)**	A	6.88	7.32	7.91	0.063	0.14	2.36

[a] A: Column Chiralpak AD-H, hexane/ethanol 9:1, flow rate 0.5 mL min^{-1}; B: column Chiralpak OD, hexane/ethanol 100:1, flow rate 0.5 mL min^{-1}; C: column Chiracel OD, hexane/ethanol 9:1, flow rate 0.5 mL min^{-1}; D: column Chiralpak AD-H, hexane/ethanol 1000:1, flow rate 0.5 mL min^{-1}. [b] $k'_1=(t_1-t_0)/t_0$; $k'_2=(t_2-t_0)/t_0$. [c] $\alpha=k'_2/k'_1$.

It is not easy to give a rational explanation for the resolution data. Of course, without retention a compound cannot be resolved or recognized, and so a compound (a large molecule) that is strongly retained is often better resolved than a compound (a small molecule) that is weakly retained. Unfortunately this is not always true. In general, the retention times for compounds **4** decrease in the order methyl ≫ pentyl > decyl ether, while no clear order is seen for the loop size (the retention time shows a maximum for $(CH_2)_{10}$). However, **4(D,14)** with the lowest k'_1 has the highest α value of all bis[2]catenanes studies (entry 16).

The interactions between a chiral stationary phase and a racemate may be roughly separated into two categories: interaction involving enantioselectivity and nonstereoselective interaction. Thus, if by changing the structure of a racemate the nonstereoselective interaction is relatively reduced, the resolution should be enhanced. If, however, the enantioselective interaction is relatively reduced by a structural change, the resolution should be decreased. In the case of the catenanes, it is probable that both interactions are influenced more or less similarly by changing of the ether chains and/or the loops, so no clear effect on the chiral separation has been observed. For a practical separation the optimum conditions will obviously have to be elaborated individually for each example.

Conclusions and Outlook

Through the use of a tetratosylurea (e.g., **2**) as template, it is possible to convert the tetraalkenyl calix[4]arenes **1** by olefin metathesis into the corresponding bisloop derivatives **3**, sometimes in excellent yields, which have not even been optimized yet for the special examples. While the results reported here were obtained under high-dilution conditions ($c=0.5$ mM), first results at higher concentrations show no drop in the yields. This suggests that even larger quantities should be available in a single experiment. The fact that bisloop compounds **3** cannot form homodimers can be used to convert their heterodimers with **1** into bis[2]catenanes **4** under similar reaction conditions, again in excellent yields. This opens a preparatively useful pathway to a variety of such chiral capsular compounds, in which the rate of guest exchange might be controllable through the lengths and the structures of these intertwining rings. Bis[2]catenanes **4** are chiral. How this chirality can be used for the discrimination of chiral guests (kinetically or thermodynamically) is one of the open questions awaiting answer by future studies.

Experimental Section

General procedure for the synthesis of tetraureacalix[4]arenes 1: A solution of tetraaminocalix[4]arene[31] (1 mmol), active urethane (5 mmol), and triethylamine (5 mmol) in DMF (50 mL) was stirred for two days at room temperature. The solution was then diluted with dichloromethane (400 mL), a solution of K_2CO_3 (1 M, 300 mL) was added, the biphasic mixture was stirred for 1 hour at room temperature, and the organic layer was washed with a solution of K_2CO_3 (0.3 M, 3×300 mL). After drying over $MgSO_4$, the solvent was evaporated and the desired tetraurea was purified by column chromatography on silica gel.

An alternative procedure, starting from the active urethane of calix[4]arene and the corresponding aniline,[32] was also used and has been described previously.[16]

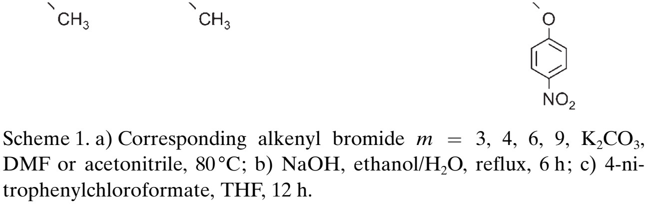
General procedure for the synthesis of bisloop derivatives 3: A mixture of the tetratosyl urea **2** (1.15 mmol) and an open chain tetraalkenyl urea **1(Y,*m*)** (1 mmol) in benzene (500 mL) was heated at reflux for 2–3 minutes. During this period a clear solution was usually formed. The reaction mixture was allowed to cool to room temperature and the complete formation of the heterodimer was checked with an evaporated sample ($\approx$2 mL) by ^{1}H NMR ([D$_6$]C_6H_6). The reaction mixture was purged with nitrogen for 30 minutes and a solution of the Grubbs' catalyst (0.2 mmol) in benzene (3 mL) was added in one portion. After the mixture had been stirred at 20 °C for two days, triethylamine (1.5 mL) was added and the reaction mixture was stirred for 1 hour, the solvent was then evaporated, and the residue was dissolved in THF (50 mL), heated to reflux, and allowed to cool to room temperature. After evaporation under reduced pressure, hydrogenation of the crude product was carried out in THF (20 mL) at normal pressure in the presence of platinum dioxide (83 %, 0.9 mmol). The desired product was purified by column chromatography (silica gel, THF/hexane 2:3). The pure product was finally crystallized from THF/methanol.

General procedure for the synthesis of bis[2]catenanes 4: A mixture of a tetraalkenyl urea **1** (1 mmol) and the corresponding bisloop **3** (1.05 mmol) in benzene (200 mL) was heated at reflux until a clear solution had been formed, which usually requires 10 to 60 minutes. After the mixture had cooled to room temperature the formation of the heterodimer was checked by ^{1}H NMR (C_6D_6). The reaction mixture was then purged with nitrogen for 30 minutes and a solution of the Grubbs' catalyst (0.2 mmol) in benzene (5 mL) was added in one portion. After the system had been stirred at 20 °C for two days, triethylamine (1 mL) was added, the reaction mixture was stirred for a further hour, and the solvent was evaporated. The crude product was purified by column chromatography (silica gel) and then dissolved in THF (50 mL) and hydrogenated (1 atm) in the presence of platinum dioxide (83 %, 0.9 mmol). After filtration and evaporation, the product was finally crystallized from THF/methanol.

The bis[2]catenane **6** was synthesized from the monoloop derivatives **5** (2 mmol) by the procedure for bis[2]catenanes **4**.

Syntheses and characterization: The ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance DRX 400 (400 MHz) and Bruker 300 (300 MHz) spectrometers with use of the solvent signals as internal reference. FD mass spectra were recorded with a Finnigan MAT 90 (5 kV/10 mA min^{-1}) machine. ESI-MS spectra were obtained on a Q-TOF Ultima3 (Micromass) instrument. Melting points were determined with a MEL TEMP 2 capillary melting point apparatus and are uncorrected. Acetanilides and anilines were obtained by a described procedure.[32] For acetanilide, aniline $m=5$ and acetanilide, aniline, urethane $m=6$ see refs. [32] and [15].

3-(Undec-10′-enyloxy)acetanilide (see Scheme 1): Yield 83 %; m.p. 53.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta=7.20$ (overlapped with solvent signal, br t, 1 H; CH), 7.16 (br s, 1 H; NH), 7.17 (t, $^{3}J=8.2$ Hz, 1 H; CH), 6.92 (br d, $^{3}J=7.8$ Hz, 1 H; CH), 6.63 (dd, $^{3}J=8.2$, $^{4}J=1.7$ Hz, 1 H; CH), 6.92 (m, 1 H; -CH=CH$_2$), 4.99 (ddd, $^{2}J=1.7$, $^{3}J=17.0$, $^{4}J=1.7$ Hz, 1 H; -CH=CH$_2$), 4.92 (ddd, $^{2}J=1.7$, $^{3}J=10.2$, $^{4}J=1.0$ Hz, 1 H; -CH=CH$_2$), 3.93 (t, $^{3}J=6.5$ Hz, 2 H; OCH$_2$), 2.15 (s, 3 H; C(O)CH$_3$), 2.03 (m, 2 H; -CH$_2$CH=CH$_2$), 1.75 (m, 2 H; -CH$_2$-), 1.50–1.20 (m, 12 H; -CH$_2$-); elemental analysis (%) calcd for $C_{19}H_{29}NO_2$: C 75.21, H 9.63, N 4.62; found: C 75.14, H 9.50, N 4.72.



Scheme 1. a) Corresponding alkenyl bromide m = 3, 4, 6, 9, K_2CO_3, DMF or acetonitrile, 80 °C; b) NaOH, ethanol/H_2O, reflux, 6 h; c) 4-nitrophenylchloroformate, THF, 12 h.

3-(Oct-7′-enyloxy)acetanilide: Yield 81 %; m.p. 70 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta=7.70$ (s, 1 H; NH), 7.26 (overlapped with solvent signal, br t, 1 H; CH), 7.15 (t, $^{3}J=8.2$ Hz, 1 H; CH), 6.95 (br dd, $^{3}J=7.9$ Hz, 1 H; CH), 6.62, 6.60 (dd, $^{3}J=8.2$, $^{4}J=1.7$ Hz, 1 H; CH), 5.82–5.74 (m, 1 H; -CH=CH$_2$), 4.99 (m, 1 H; -CH=CH$_2$), 3.90 (t, $^{3}J=6.5$ Hz, 2 H; OCH$_2$), 2.13 (s, 3 H; C(O)CH$_3$), 2.06 (m, 2 H; -CH$_2$CH=CH$_2$), 1.75 (m, 2 H; -CH$_2$-), 1.45–1.32 ppm (m, 6 H; -CH$_2$-); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta=168.56$, 159.61, 139.14, 138.97, 129.48, 114.21, 111.81, 110.53, 106.23, 67.91, 33.64, 29.12, 28.78, 25.81, 24.55 ppm; FD-MS: m/z: calcd for $C_{16}H_{23}N_1O_2$: 261.3; found: 261.6 $[M]^+$.

3-(Undec-10′-enyloxy)aniline: Yield 99 %; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta=7.04$ (t, $^{3}J=8.2$ Hz, 1 H; CH), 6.33 (dd, $^{3}J=8.2$, $^{4}J=2.4$ Hz, 1 H; CH), 6.28 (dd, $^{3}J=7.8$, $^{4}J=2.0$ Hz, 1 H; CH), 6.25 (t, $^{4}J=2.0$ Hz, 1 H; CH), 5.81 (m, 1 H; -CH=CH$_2$), 4.99 (m, 2 H; -CH=CH$_2$), 3.90 (t, $^{3}J=6.8$ Hz, 2 H; OCH$_2$-), 3.90–3.60 (br s, 2 H; -NH$_2$), 2.04 (m, 2 H; -CH$_2$-CH=CH$_2$), 1.74 (m, 2 H; -OCH$_2$CH$_2$-), 1.50–1.20 (m, 12 H; -CH$_2$-); elemental analysis (%) calcd for $C_{12}H_{27}NO$: 78.11, H 10.41, N 5.36; found: C 78.06, H 9.97, N 5.31.

3-(Oct-7′-enyloxy)aniline: Yield 95 %; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta=7.04$ (t, $^{3}J=8.2$ Hz, 1 H; CH), 6.31 (dd, $^{3}J=8.2$, $^{4}J=1.5$ Hz, 1 H; CH), 6.27 (dd, $^{3}J=7.8$, $^{4}J\approx1.0$ Hz, 1 H; CH), 6.25 (br t, 1 H; CH), 5.85–5.75 (m, 1 H; -CH=CH$_2$), 5.01–4.91 (m, 2 H; -CH=CH$_2$), 3.90 (t, $^{3}J=6.6$ Hz, 2 H; OCH$_2$-), 3.62 (br s, 2 H; -NH$_2$), 2.04 (m, 2 H; -CH$_2$-CH=CH$_2$), 1.74 (m, 2 H; -CH$_2$-), 1.44–1.38 ppm (m, 6 H; -CH$_2$-).

General procedure for the synthesis of urethanes from the corresponding anilines (Scheme 1): A solution of the aniline (13.3 mmol) and 4-nitrophenyl chloroformate (14 mmol) in a mixture of chloroform (30 mL) and tetrahydrofuran (20 mL) was heated at reflux for 12 h. The solvents were evaporated and the residue was dissolved in chloroform and precipitated with diethyl ether. The pure compound was recrystallized from acetonitrile as white to yellowish crystals.

4-Nitrophenyl-*N*-[3′-(undec-10″-enyloxy)phenyl]carbamate: Yield 51 %; m.p. 104.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta=8.28$ (d, $^{3}J=9.0$ Hz, 2 H; CH), 7.38 (d, $^{3}J=9.0$ Hz, 2 H; CH), 7.23 (t, $^{3}J=8.2$ Hz, 1 H; CH), 7.15 (br s, 1 H; CH), 6.95 (br s, 1 H; NH), 6.90 (dd, $^{3}J=7.8$, $^{4}J=1.7$ Hz, 1 H; CH), 6.68 (dd, $^{3}J=8.2$, $^{4}J=2.0$ Hz, 1 H; CH), 5.80 (m, 1 H; -CH=CH$_2$), 4.98–4.92 (m, 1 H; -CH=CH$_2$), 3.95 (t, $^{3}J=6.5$ Hz, 2 H; OCH$_2$), 2.03 (m, 2 H; -CH$_2$-CH=CH$_2$), 1.76 (m, 2 H; -CH$_2$-), 1.43 (m, 2 H; -CH$_2$-), 1.40–1.20 ppm (m, 10 H; -CH$_2$-).

4-Nitrophenyl-*N*-[3′-(oct-7″-enyloxy)phenyl]carbamate: Yield 90 %. m.p. 101–102 °C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta=8.26$ (d, $^{3}J=9.1$ Hz, 2 H; CH), 7.37 (d, $^{3}J=9.1$ Hz, 2 H; CH), 7.22 (t, $^{3}J=8.2$ Hz, 1 H; CH), 7.14 (br s, 1 H; CH), 7.03 (br s, 1 H; NH), 6.89 (dd, $^{3}J=7.9$, $^{4}J=1.5$ Hz, 1 H; CH), 6.67 (dd, $^{3}J=8.2$, $^{4}J=2.1$ Hz, 1 H; CH), 5.80 (m, 1 H; -CH=CH$_2$), 5.01–4.91 (m, 2 H; -CH=CH$_2$), 3.94 (t, $^{3}J=6.6$ Hz, 2 H; OCH$_2$), 2.05 (m, 2 H; -CH$_2$-CH=CH$_2$), 1.77 (m, 2 H; -CH$_2$-), 1.48–1.10 ppm (m, 6 H; -CH$_2$-); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta=159.95$, 155.31, 150.01, 145.06, 138.97, 137.75, 129.93, 125.19, 122.12, 114.27, 110.9, 110.80, 105.30, 68.04, 33.66, 29.11, 28.79, 28.78, 25.84 ppm; FD-MS: m/z: calcd for $C_{21}H_{24}N_2O_5$: 384.4; found: 384.8 $[M]^+$; elemental analysis (%) calcd for $C_{21}H_{24}N_2O_5$: C 65.61, H 6.29, N 7.29; found: C 65.26, H 6.17, N 7.25.

4-Nitrophenyl-*N*-[3′-(pent-4″-enyloxy)phenyl]carbamate: Yield 85 %; m.p. 106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta=8.27$ (d, $^{3}J=8.8$ Hz, 2 H; CH), 7.37 (d, $^{3}J=8.8$ Hz, 2 H; CH), 7.23 (t, $^{3}J=8.8$ Hz, 1 H; CH), 7.15 (br s, 1 H; CH), 7.01 (br s, 1 H; NH), 6.90 (dd, $^{3}J=7.8$, $^{4}J=1.7$ Hz, 1 H; CH), 6.68 (dd, $^{3}J=7.8$, $^{4}J=2.0$ Hz, 1 H; CH), 5.84 (m, 1 H; -CH=CH$_2$), 5.05–4.99 (m, 2 H; -CH=CH$_2$), 3.96 (t, $^{3}J=6.4$ Hz, 2 H; OCH$_2$-), 2.22 (m, 2 H; -CH$_2$-CH=CH$_2$), 1.87 ppm (m, 2 H; -CH$_2$-); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta=159.89$, 155.32, 150.02, 145.08, 137.77, 137.70, 129.96, 125.20, 122.12, 115.23, 110.99, 110.79, 105.36, 67.27, 30.03, 28.34 ppm; elemental analysis (%) calcd for $C_{18}H_{18}N_2O_5$: C 63.15, H 5.30, N 8.18; found: C 63.05, H 5.25, N 8.17.

Tetraurea 1(M,5): Yield 76%; m.p. 145–150 (phase transition), 170–173°C; ^{1}H NMR (C_6D_6, 400 MHz, 25°C): $\delta=9.78$ (s, 8H; NH), 8.00 (br t, 8H; Ar-H), 7.99 (d, $^{4}J=2.6$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.66 (dd, $^{3}J=8.2$, $^{4}J=0.9$ Hz, 8H; Ar-H), 7.28 (s, 8H; NH), 7.10 (t, $^{3}J=8.2$ Hz, 8H; Ar-H), 6.56 (dd, $^{3}J=8.2$, $^{4}J=2.1$ Hz, 8H; Ar-H), 6.14 (d, $^{4}J=2.6$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.61 (m, 8H; -CH=CH$_2$), 4.95–4.85 (m, 16H; -CH=CH$_2$), 4.24 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.85–3.60 (m, 16H; -OCH$_2$-), 3.57 (s, 24H; -OCH$_3$), 3.16 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 1.96 (m, 16H; -CH$_2$-CH=CH$_2$), 1.58 ppm (m, 16H; -CH$_2$-); ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.25$ (s, 8H; NH), 7.63 (d, $^{4}J=1.8$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.50 (br t, 8H; Ar-H), 7.37 (br dd, $^{3}J=8.2$ Hz, 8H; Ar-H), 7.24 (t, $^{3}J=8.2$ Hz, 8H; Ar-H), 7.08 (s, 8H; NH), 6.58 (dd, $^{3}J=8.2$, $^{4}J=1.8$ Hz, 8H; Ar-H), 5.80 (d, $^{4}J=1.8$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.75 (m, 8H; -CH=CH$_2$), 4.96–4.91 (m, 16H; -CH=CH$_2$), 4.07 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 4.00–3.80 (m, 16H; -OCH$_2$-), 3.72 (s, 24H; -OCH$_3$), 2.83 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 2.10 (m, 16H; -CH$_2$-CH=CH$_2$), 1.79 ppm (m, 16H; -CH$_2$-); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.18$, 154.19, 152.51, 140.64, 137.76, 134.83, 134.45, 133.39, 130.48, 117.64, 116.24, 115.01, 110.00, 109.56, 103.98, 67.14, 60.98, 30.82, 29.97, 28.34 ppm; ESI-MS: m/z (%): calcd for $C_{80}H_{88}N_8O_{12}$: 1352.65; found: 1375.68 (100) $[M+\text{Na}]^+$.

Tetraurea 1(M,6): Yield 72%; m.p. 173–175°; ^{1}H NMR (C_6D_6, 400 MHz, 25°C): $\delta=9.79$ (s, 8H; NH), 8.03 (br t, 8H; Ar-H), 8.00 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.66 (br dd, $^{3}J=8.2$ Hz, 8H; Ar-H), 7.29 (s, 8H; NH), 7.12 (t, $^{3}J=8.2$ Hz, 8H; Ar-H), 6.58 (dd, $^{3}J=8.2$, $^{4}J=1.8$ Hz, 8H; Ar-H), 6.15 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.60 (m, 8H; -CH=CH$_2$), 4.95–4.85 (m, 16H; -CH=CH$_2$), 4.24 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.85–3.65 (m, 16H; -OCH$_2$-), 3.57 (s, 24H; -OCH$_3$), 3.15 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 1.84 (m, 16H; -CH$_2$-CH=CH$_2$), 1.51 (m, 8H; -CH$_2$-), 1.29 ppm (m, 16H; -CH$_2$-); ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.26$ (s, 8H; NH), 7.64 (d, $^{4}J=2.0$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.52 (br t, 8H; Ar-H), 7.37 (br dd, $^{3}J=7.6$ Hz, 8H; Ar-H), 7.24 (t, $^{3}J=8.1$ Hz, 8H; Ar-H), 7.07 (s, 8H; NH), 6.58 (dd, $^{3}J=6.8$, $^{4}J=1.5$ Hz, 8H; Ar-H), 5.81 (d, $^{4}J=2.0$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.75 (m, 8H; -CH=CH$_2$), 4.96–4.92 (m, 16H; -CH=CH$_2$), 4.07 (d, $^{2}J=12.0$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 4.00–3.80 (m, 16H; -OCH$_2$-), 3.72 (s, 24H; -OCH$_3$), 2.84 (d, $^{2}J=12.0$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 2.02 (m, 16H; -CH$_2$-CH=CH$_2$), 1.72 (m, 8H; -CH$_2$-), 1.43 ppm (m, 16H; -CH$_2$-); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.21$, 154.18, 152.49, 140.63, 138.50, 134.83, 134.45, 133.39, 130.47, 117.63, 116.24, 114.57, 109.91, 109.63, 103.84, 67.72, 60.99, 33.34, 30.81, 28.60, 25.17 ppm; ESI-MS: m/z (%): calcd for $C_{84}H_{96}N_8O_{12}$: 1408.71; found: 1431.73 (100) $[M+\text{Na}]^+$.

Tetraurea 1(M,8): Yield 79%; m.p. 125°C (phase transition), 158–160°C; ^{1}H NMR (C_6D_6, 400 MHz, 25°C): $\delta=9.83$ (s, 8H; NH), 8.11 (br t, 8H; Ar-H), 8.04 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.67 (br dd, $^{3}J=8.2$ Hz, 8H; Ar-H), 7.33 (s, 8H; NH), 7.12 (t, $^{3}J=8.2$ Hz, 8H; Ar-H), 6.65 (dd, $^{3}J=8.5$, $^{4}J=1.8$ Hz, 8H; Ar-H), 6.19 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.81 (m, 8H; -CH=CH$_2$), 5.07–5.03 (m, 16H; -CH=CH$_2$), 4.28 (d, $^{2}J=11.4$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.85–3.65 (m, 16H; -OCH$_2$-), 3.60 (s, 24H; -OCH$_3$), 3.20 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 1.97 (m, 16H; -CH$_2$-CH=CH$_2$), 1.60 (m, 16H; -CH$_2$-), 1.40–1.10 ppm (m, 48H; -CH$_2$-); ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.25$ (s, 8H; NH), 7.63 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.52 (br t, 8H; Ar-H), 7.34 (br dd, $^{3}J=7.9$ Hz, 8H; Ar-H), 7.23 (t, $^{3}J=8.1$ Hz, 8H; Ar-H), 7.06 (s, 8H; NH), 6.56 (dd, $^{3}J=8.2$, $^{4}J=1.8$ Hz, 8H; Ar-H), 5.81 (d, $^{4}J=2.0$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.75 (m, 8H; -CH=CH$_2$), 4.96–4.90 (m, 16H; -CH=CH$_2$), 4.06 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 4.00–3.80 (m, 16H; -OCH$_2$-), 3.71 (s, 24H; -OCH$_3$), 2.83 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 1.98 (m, 16H; -CH$_2$-CH=CH$_2$), 1.68 (m, 16H; -CH$_2$-), 1.40–1.10 ppm (m, 48H; -CH$_2$-); ESI-MS: m/z (%): calcd for $C_{92}H_{112}N_8O_{12}$: 1520.83; found: 1544.87 (100) $[M+\text{Na}]^+$.

Tetraurea 1(M,11): Yield 69%; m.p. 169–173°C; ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.25$ (s, 8H; NH), 7.63 (d, $^{4}J=1.7$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.51 (br t, 8H; Ar-H), 7.35 (br dd, $^{3}J=7.4$ Hz, 8H; Ar-H), 7.23 (t, $^{3}J=7.2$ Hz, 8H; Ar-H), 7.06 (s, 8H; NH), 6.56 (dd, $^{3}J=8.2$, $^{4}J=1.70$ Hz, 8H; Ar-H), 5.79 (d, $^{4}J=1.70$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.79 (m, 8H; -CH=CH$_2$), 4.98–4.91 (m, 16H; -CH=CH$_2$), 4.06 (d, $^{2}J=11.9$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.88 (m, 16H; -OCH$_2$-), 3.71 (s, 24H; -OCH$_3$), 2.83 (d, $^{2}J=11.9$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 2.02 (m, 16H; -CH$_2$-CH=CH$_2$), 1.68 (m, 16H; -CH$_2$-), 1.40–1.10 ppm (m, 48H; -CH$_2$-); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.57$, 154.19, 152.47, 140.63, 139.19, 134.83, 134.44, 133.41, 130.43, 117.62, 116.24, 114.09, 109.84, 109.69, 103.78, 67.98, 60.96, 33.80, 30.83, 29.48, 29.42, 29.36, 29.21, 29.12, 28.92, 25.91 ppm; ESI-MS: m/z (%): calcd for $C_{104}H_{136}N_8O_{12}$: 1689.02; found: 1713.03 (100) $[M+\text{Na}]^+$.

Tetraurea 1(P,5): Yield 73%; m.p. 225–227°C; ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.43$ (s, 8H; NH), 7.67 (d, $^{4}J=2.2$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.55 (br t, 8H; Ar-H), 7.38 (br dd, $^{3}J=7.6$ Hz, 8H; Ar-H), 7.24 (t, $^{3}J=8.2$ Hz, 8H; Ar-H), 6.90 (s, 8H; NH), 6.57 (dd, $^{3}J=8.2$, $^{4}J=1.8$ Hz, 8H; Ar-H), 5.86 (d, $^{4}J=2.2$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.73 (m, 8H; -CH=CH$_2$), 4.94–4.90 (m, 16H; -CH=CH$_2$), 4.22 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.95–3.75 (m, 16H; OCH$_2$), 3.70–3.55 (m, 16H; OCH$_2$), 2.85 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 2.08 (m, 16H; -CH$_2$-CH=CH$_2$), 1.92 (m, 16H; -CH$_2$-), 1.77 (m, 16H; -CH$_2$-), 1.37 (m, 16H; -CH$_2$-), 1.27 (m, 16H; -CH$_2$-), 0.94 ppm (t, $^{3}J=7.0$ Hz, 24H; -CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.17$, 154.24, 151.30, 140.64, 137.73, 135.23, 134.77, 133.04, 130.48, 117.61, 116.43, 114.98, 109.91, 109.59, 103.81, 75.63, 67.12, 30.35, 29.96, 29.80, 28.36, 28.11, 22.80, 14.17 ppm; ESI-MS: m/z (%): calcd for $C_{96}H_{120}N_8O_{12}$: 1576.90; found: 1600.91 (100) $[M+\text{Na}]^+$.

Tetraurea 1(P,11): Yield 68%; m.p. 150–152°C; ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.43$ (s, 8H; NH), 7.67 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.59 (br t, 8H; Ar-H), 7.35 (br dd, $^{3}J=7.9$ Hz, 8H; Ar-H), 7.23 (t, $^{3}J=8.2$ Hz, 8H; Ar-H), 6.90 (s, 8H; NH), 6.56 (dd, $^{3}J=7.9$, $^{4}J=1.8$ Hz, 8H; Ar-H), 5.86 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.56 (m, 8H; -CH=CH$_2$), 4.98–4.92 (m, 16H; -CH=CH$_2$), 4.22 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.95–3.75 (m, 16H; OCH$_2$), 3.70–3.55 (m, 16H; OCH$_2$), 2.85 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 2.02 (m, 16H; -CH$_2$-CH=CH$_2$), 1.93 (m, 16H; -CH$_2$-), 1.67 (m, 16H; -CH$_2$-), 1.50–1.05 (m, 128H; -CH$_2$-), 0.95 ppm (t, $^{3}J=7.3$ Hz, 24H; -CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.27$, 154.25, 151.28, 140.64, 139.18, 135.24, 134.76, 133.06, 130.40, 117.60, 116.44, 114.09, 109.83, 109.76, 103.53, 75.59, 67.99, 33.81, 30.36, 29.81, 29.45, 29.39, 29.21, 29.14, 28.94, 28.15, 25.86, 22.82, 14.18 ppm; ESI-MS: m/z (%): calcd for $C_{120}H_{168}N_8O_{12}$: 1913.27; found: 1937.30 (100) $[M+\text{Na}]^+$.

Tetraurea 1(D,6): Yield 85%; m.p. 207–209°C; ^{1}H NMR (C_6D_6, 400 MHz, 25°C): $\delta=10.00$ (s, 8H; NH), 8.13 (d, $^{4}J=1.9$ Hz, 8H; Ar$_{\text{calix}}$-H), 8.09 (br t, 8H; Ar-H), 7.70 (br dd, $^{3}J=7.8$ Hz, 8H; Ar-H), 7.21 (s, 8H; NH), 7.12 (t, $^{3}J=8.2$ Hz, 8H; Ar-H), 6.59 (dd, $^{3}J=8.6$, $^{4}J=2.0$ Hz, 8H; Ar-H), 6.31 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.75 (m, 8H; -CH=CH$_2$), 5.05–4.90 (m, 16H; -CH=CH$_2$), 4.60 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.90–3.60 (m, 32H; OCH$_2$), 3.30 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 2.14 (m, 16H; -CH$_2$-), 1.86 (m, 16H; -CH$_2$-CH=CH$_2$), 1.55–1.10 (m, 144H; -CH$_2$-), 0.96 ppm (t, $^{3}J=6.7$ Hz, 24H; -CH$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.43$ (s, 8H; NH), 7.66 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 7.58 (br t, 8H; Ar-H), 7.35 (br dd, $^{3}J=7.9$ Hz, 8H; Ar-H), 7.23 (t, $^{3}J=7.9$ Hz, 8H; Ar-H), 6.90 (s, 8H; NH), 6.55 (dd, $^{3}J=8.2$, $^{4}J=1.8$ Hz, 8H; Ar-H), 5.85 (d, $^{4}J=2.4$ Hz, 8H; Ar$_{\text{calix}}$-H), 5.72 (m, 8H; -CH=CH$_2$), 4.94–4.91 (m, 16H; -CH=CH$_2$), 4.21 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.95–3.75 (m, 16H; OCH$_2$), 3.70–3.55 (m, 16H; OCH$_2$), 2.84 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 2.00 (m, 16H; -CH$_2$-CH=CH$_2$), 1.91 (m, 16H; -CH$_2$-), 1.69 (m, 16H; -CH$_2$-), 1.40 (m, 16H; -CH$_2$-), 1.29 (m, 112H; -CH$_2$-), 0.89 ppm (t, $^{3}J=6.8$ Hz, 24H; -CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.22$, 154.25, 151.32, 140.64, 138.46, 135.24, 134.76, 133.04, 130.45, 117.62, 116.45, 114.60, 109.83, 109.79, 103.59, 75.67, 67.70, 33.35, 32.00, 30.35, 30.26, 30.05, 30.02, 29.81, 29.47, 28.59, 26.12, 25.12, 22.72, 14.12 ppm; ESI-MS: m/z (%): calcd for $C_{120}H_{168}N_8O_{12}$: 1913.27; found: 1937.28 (100) $[M+\text{Na}]^+$.

Tetraurea 1(D,8): Yield 80%; m.p. 205–207°C; ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): $\delta=9.43$ (s, 8H; NH), 7.66 (br d, 8H; Ar$_{\text{calix}}$-H), 7.60 (br t, 8H; Ar-H), 7.32 (br dd, $^{3}J=8.0$ Hz, 8H; Ar-H), 7.22 (t, $^{3}J=8.1$ Hz, 8H; Ar-H), 6.89 (s, 8H; NH), 6.55 (br dd, $^{3}J=7.9$ Hz, 8H; Ar-H), 5.85 (br d, 8H; Ar$_{\text{calix}}$-H), 5.76 (m, 8H; -CH=CH$_2$), 4.96–4.90 (m, 16H; -CH=CH$_2$), 4.20 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{ax}}$), 3.95–3.75 (2×m, 16H; -OCH$_2$-), 2.84 (d, $^{2}J=11.7$ Hz, 8H; ArCH$_2$Ar$_{\text{eq}}$), 1.98 (m, 16H; -CH$_2$-CH=CH$_2$), 1.95–1.70 (m, 32H; -CH$_2$-), 1.66 (m, 16H; -CH$_2$-), 1.50–1.20 (m, 160H; -CH$_2$-), 0.89 ppm (t, $^{3}J=6.9$ Hz, 24H; -CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.26$, 154.24, 151.31, 140.64, 138.98, 135.24, 134.76, 133.04, 130.40, 117.60, 116.44, 114.20, 109.86, 109.77, 103.46, 75.65, 67.92, 33.68, 32.00, 30.35, 30.25, 30.06, 30.02, 29.82, 29.48, 29.13, 28.83, 28.74, 26.14, 25.69, 22.72, 14.12 ppm; ESI-MS: *m*/*z* (%): calcd for $C_{128}H_{184}N_8O_{12}$: 2025.40; found: 2049.44 (100) $[M+\text{Na}]^+$.

Bisloops and bis[2]catenanes

Bisloop 3(M,8): Yield 72%; m.p. >285°C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25°C): $\delta=8.37$ (s, 4H; NH), 8.25 (s, 4H; NH), 7.25 (br t, $^4J\approx1$ Hz, 4H; Ar$_{\text{meta}}$-H), 7.17 (d, $^4J=2.1$ Hz, 4H; Ar$_{\text{calix}}$-H), 7.09 (t, $^3J=8.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.64 (d, $^4J=2.1$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.60 (br dd, $^3J=8.5$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.48 (dd, $^3J=8.2$, $^4J=2.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.26 (d, $^2J=12.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 4.24 (d, $^2J=12.0$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.90 (t, $^3J=6.2$ Hz, 8H; OCH$_2$-), 3.78 (s, 12H; OCH$_3$), 3.19 (d, $^2J=12.0$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.16 (d, $^2J=12.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.68 (m, 8H; -CH$_2$-), 1.40 (m, 8H; -CH$_2$-), 1.33 ppm (m, 8H; -CH$_2$-); ESI-MS: *m*/*z* (%): calcd for $C_{76}H_{84}N_8O_{12}$: 1300.62; found: 1323.71 (100) $[M+\text{Na}]^+$.

Bisloop 3(M,10): Yield 57%; m.p. >245°C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25°C): $\delta=8.34$ (s, 4H; NH), 8.26 (s, 4H; NH), 7.15–7.00 (m, 12H; Ar$_{\text{meta}}$-H, Ar$_{\text{calix}}$-H), 6.80–6.70 (m, 8H; Ar$_{\text{meta}}$-H, Ar$_{\text{calix}}$-H), 6.48 (dd, $^3J=8.2$, $^4J=1.8$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.26 (d, $^2J=11.7$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 4.24 (d, $^2J=12.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.90 (t, $^3J=6.2$ Hz, 8H; OCH$_2$-), 3.78 (s, 12H; OCH$_3$), 3.19 (d, $^2J=12.0$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.17 (d, $^2J=12.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.67 (m, 8H; -CH$_2$-), 1.39 (m, 8H; -CH$_2$-), 1.28 ppm (m, 16H; -CH$_2$-); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.66$ (s, 4H; NH), 7.62 (s, 4H; NH), 7.14 (br t, 4H; Ar$_{\text{meta}}$-H), 7.02 (br d, 4H; Ar$_{\text{calix}}$-H), 6.99 (t, $^3J=8.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.78 (br d, 4H; Ar$_{\text{calix}}$-H), 6.76 (br dd, $^3J\approx8.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.41 (dd, $^3J=8.2$, $^4J=2.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.33 (d, $^2J=13.1$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.89 (t, $^3J=6.2$ Hz, 8H; OCH$_2$-), 3.78 (s, 12H; OCH$_3$), 3.14 (d, $^2J=12.5$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.11 (d, $^2J=12.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.45 (m, 8H; -CH$_2$-), 1.40–1.20 ppm (m, 24H; -CH$_2$-); ESI-MS: *m*/*z* (%): calcd for $C_{80}H_{92}N_8O_{12}$: 1356.68; found: 1379.70 (100) $[M+\text{Na}]^+$.

Bisloop 3(M,14): Yield 48%; m.p. >250°C (decomp); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.56$ (s, 4H; NH), 7.45 (s, 4H; NH), 7.11 (br t, 4H; Ar$_{\text{meta}}$-H), 7.00 (t, $^3J=8.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.95 (d, $^4J=1.7$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.82 (br dd, $^3J\approx8.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.817 (br d, 4H; Ar$_{\text{calix}}$-H), 6.43 (dd, $^3J=8.0$, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 4. 33 (d, $^2J=12.6$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 4.32 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.89 (t, $^3J=6.2$ Hz, 8H; OCH$_2$-), 3.78 (s, 12H; OCH$_3$), 3.12 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.06 (d, $^2J=13.0$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.46 (m, 8H; -CH$_2$-), 1.40–1.20 ppm (m, 40H; -CH$_2$-); ESI-MS: *m*/*z* (%): calcd for $C_{88}H_{108}N_8O_{12}$: 1468.80; found: 1492.82 (100) $[M+\text{Na}]^+$.

Bisloop 3(M,20): Yield 64%; m.p. >260°C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25°C): $\delta=8.31$ (s, 4H; NH), 8.28 (s, 4H; NH), 7.09 (t, $^3J=7.9$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.97, 6.87 (2×br m, 16H; Ar$_{\text{meta}}$-H, Ar$_{\text{calix}}$-H), 6.47 (dd, $^3J=8.5$, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.23 (very broad signal, 4H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.90 (t, $^3J=5.9$ Hz, 8H; OCH$_2$-), 3.78 (br s, 12H; OCH$_3$), 3.18 (very broad signal, 4H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.66 (m, 8H; -CH$_2$-), 1.37 (m, 8H; -CH$_2$-), 1.21 ppm (m, 56H; -CH$_2$-); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.58$ (s, 4H; NH), 7.45 (s, 4H; NH), 7.12 (br t, 4H; Ar$_{\text{meta}}$-H), 7.00 (t, $^3J=8.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.93 (br d, 4H; Ar$_{\text{calix}}$-H), 6.85 (br d, 4H; Ar$_{\text{calix}}$-H), 6.81 (br dd, $^3J\approx7.9$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.43 (br dd, $^3J=8.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.34 (d, $^2J=12.8$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.87 (t, $^3J=6.2$ Hz, 8H; OCH$_2$-), 3.78 (s, 12H; OCH$_3$), 3.11 (d, $^2J=12.6$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.11 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.65 (m, 8H; -CH$_2$-), 1.37–1.21 (m, 64H; -CH$_2$-) ppm; ESI-MS: *m*/*z* (%): calcd for $C_{100}H_{132}N_8O_{12}$: 1636.99; found: 1660.99 (100) $[M+\text{Na}]^+$.

Bisloop 3(P,8): Yield 72%; m.p. >250°C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25°C): $\delta=8.37$ (s, 4H; NH), 8.14 (s, 4H; NH), 7.29 (t, $^4J=2.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 7.09 (d, $^4J=2.6$ Hz, 4H; Ar$_{\text{calix}}$-H), 7.06 (t, $^3J=8.2$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.53 (dd, $^3J=8.2$, $^4J=1.2$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.49 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.47 (dd, $^3J=8.2$, $^4J=2.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.34 (d, $^2J=12.6$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 4.33 (d, $^2J=12.6$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.90 (t, $^3J=6.0$ Hz, 8H; OCH$_2$-), 3.85–3.75 (m, 8H; OCH$_2$-), 3.12 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.11 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.89 (m, 8H; -CH$_2$-), 1.68 (m, 8H; -CH$_2$-), 1.50–1.20 (m, 32H; -CH$_2$-), 0.93 ppm (t, $^3J=6.9$ Hz, 12H; -CH$_3$); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.64$ (s, 4H; NH), 7.63 (s, 4H; NH), 7.19 (t, $^4J=2.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.99 (d, $^4J=2.6$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.95 (t, $^3J=8.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.64 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.62 (dd, $^3J=8.0$, $^4J\approx1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.41 (dd, $^3J=8.0$, $^4J=2.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.43 (d, $^2J=13.1$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 4.42 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.93–3.80 (m, 16H; OCH$_2$-), 3.09 (d, $^2J=13.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.05 (d, $^2J=13.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.94 (m, 8H; -CH$_2$-), 1.50–1.25 (m, 40H; -CH$_2$-), 0.96 ppm (t, $^3J=7.0$ Hz, 12H; -CH$_3$); ESI-MS (THF+MeOH+HCO$_2$H 90:7:2): *m*/*z* (%): calcd for $C_{92}H_{116}N_8O_{12}$: 1525.87; found: 1526.97 (100) $[M+\text{H}]^+$, 1548.95 (73) $[M+\text{Na}]^+$.

Bisloop 3(P,14): Yield 80%; m.p. >250°C (decomp); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.53$ (s, 4H; NH), 7.48 (s, 4H; NH), 7.10 (t, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.98 (t, $^3J=8.2$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.87 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.81 (dd, $^3J=6.76$, $^4J=1.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.76 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.41 (dd, $^3J=8.2$, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.444 (d, $^2J=13.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 4.440 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.89–3.86 (m, 16H; OCH$_2$-), 3.08 (d, $^2J=13.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.07 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.95 (m, 8H; -CH$_2$-), 1.50–1.25 (m, 64H; -CH$_2$-), 0.96 (t, $^3J=6.9$ Hz, 12H; -CH$_3$) ppm; ESI-MS: *m*/*z* (%): calcd for $C_{104}H_{140}N_8O_{12}$: 1693.06; found: 1717.14 (100) $[M+\text{Na}]^+$.

Bisloop 3(P,20): Yield 84%; m.p. >245°C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25°C): $\delta=8.31$ (s, 4H; NH), 8.16 (s, 4H; NH), 7.07 (t, $^3J=7.9$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.95 (br t, $^4J\approx2$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.90–6.80 (m, 8H; Ar$_{\text{meta}}$-H, Ar$_{\text{calix}}$-H), 6.75 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.46 (dd, $^3J=8.2$, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.33 (d, $^2J=12.3$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.85 (t, $^3J=6.6$ Hz, 8H; OCH$_2$-), 3.82 (t, $^3J=7.5$ Hz, 8H; OCH$_2$-), 3.11 (d, $^2J=12.0$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.91 (m, 8H; -CH$_2$-), 1.66 (m, 8H; -CH$_2$-), 1.50–1.10 (m, 80H; -CH$_2$-), 0.94 ppm (t, $^3J=6.9$ Hz, 12H; -CH$_3$); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.69$ (s, 4H; NH), 7.66 (s, 4H; NH), 7.08 (t, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.98 (t, $^3J=8.1$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.86 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.82 (dd, $^3J=8.2$ Hz, 4H; $^4J=1.0$ Hz, Ar$_{\text{meta}}$-H), 6.79 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.41 (dd, $^3J=8.1$, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.43 (d, $^2J=13.1$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.87 (t, $^3J=6.2$ Hz, 8H; OCH$_2$-), 3.85 (t, $^3J=6.2$ Hz, 8H; OCH$_2$-), 3.08 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.07 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.94 (m, 8H; -CH$_2$-), ≈1.70 (m, under the solv. signal; -CH$_2$-), 1.50–1.25 (2×m, 80H; -CH$_2$-), 0.96 ppm (t, $^3J=7.1$ Hz, 12H; -CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): $\delta=160.70$, 153.31, 152.67, 142.49, 135.83, 134.91, 129.76, 119.44, 119.38, 111.03, 108.31, 105.24, 75.91, 67.97, 32.12, 30.89, 30.20, 30.07, 29.98, 29.50, 26.86, 23.77, 14.60 ppm.

Bisloop 3(D,10): Yield 95%; m.p. >250°C (decomp); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.49$ (s, 4H; NH), 7.47 (s, 4H; NH), 7.10 (t, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.98 (t, $^3J=8.2$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.91 (d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.78 (dd, $^3J=8.2$, $^4J=1.2$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.74 (br d, $^4J=2.4$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.41 (dd, $^3J=8.2$, $^4J=2.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.44 (d, $^2J=12.9$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.86 (m, 16H; OCH$_2$-), 3.08 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.06 (d, $^2J=13.3$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.95 (m, 8H; -CH$_2$-), 1.50–1.10 (2×m, 88H; -CH$_2$-), 0.89 ppm (t, $^3J=7.0$ Hz, 12H; -CH$_3$); ESI-MS: *m*/*z* (%): calcd for $C_{116}H_{164}N_8O_{12}$: 1861.25; found: 1863.33 (100) $[M+\text{H}]^+$, 1885.30 (43) $[M+\text{Na}]^+$.

Bisloop 3(D,14): Yield 53%; m.p. >260°C (decomp); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25°C): $\delta=8.24$ (s, 4H; NH), 8.08 (s, 4H; NH), 7.06 (t, $^3J=8.0$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.97 (br t, unresolved coupling, 4H; Ar$_{\text{meta}}$-H), 6.89 (d, $^4J=2.0$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.85 (br dd, $^3J=6.8$ Hz, unresolved coupling, 4H; Ar$_{\text{meta}}$-H), 6.69 (br d, $^4J=2.0$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.46 (dd, $^3J=7.9$, $^4J=1.7$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.34 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 4.33 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.88 (t, $^3J=6.3$ Hz, 8H; OCH$_2$-), 3.82 (t, $^3J=6.6$ Hz, 8H; OCH$_2$-), 3.20–3.15 (overlap with the solvent signal, 4H; Ar-CH$_2$-Ar$_{\text{eq}}$), 3.10 (d, $^2J=12.3$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{eq}}$), 1.90 (m, 8H; -CH$_2$-), 1.66 (m, 8H; -CH$_2$-), 1.50–1.10 (m, 96H; -CH$_2$-), 0.85 ppm (t, $^3J=6.9$ Hz, 12H; -CH$_3$); ^{1}H NMR ([D$_8$]THF, 400 MHz, 25°C): $\delta=7.52$ (s, 4H; NH), 7.46 (s, 4H; NH), 7.10 (br t, $^4J\approx2$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.99 (t, $^3J=7.8$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.88 (br d, $^4J\approx2$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.81 (br dd, $^3J=7.8$ Hz, 4H; Ar$_{\text{meta}}$-H), 6.76 (br d, $^4J\approx2$ Hz, 4H; Ar$_{\text{calix}}$-H), 6.42 (br dd, $^3J=7.2$ Hz, 4H; Ar$_{\text{meta}}$-H), 4.44 (d, $^2J=12.9$ Hz, 4H; Ar-CH$_2$-Ar$_{\text{ax}}$), 3.88 (m, 16H; OCH$_2$-), 3.08 (d, $^2J=$

12.3 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.07 (d, ^2J=12.3 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 1.96 (m, 8H; -CH$_2$-), 1.50–1.10 (2×m, 104H; -CH$_2$-), 0.90 ppm (t, ^3J=6.8 Hz, 12H; -CH$_3$); ESI-MS: *m*/*z* (%): calcd for $C_{124}H_{180}N_8O_{12}$: 1973.37; found: 1997.45 (100) $[M+Na]^+$.

Bis[2]catenane 4(M,8): This compound was obtained from bisloop **3(M,8)** and tetraurea **1(M,5)**; yield 66%; m.p. >245°C (decomp); ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ=10.00 (s, 2H; NH), 9.83 (s, 2H; NH), 9.75 (s, 2H; NH), 9.74 (s, 1H; NH), 9.73 (s, 1H; NH), 8.56 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.35 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.31 (d, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 8.24 (d, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 8.04 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.96 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.94 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.74 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.54 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.47 (s, 2H; NH), 7.39 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.36 (s, 2H; NH), 7.35 (d, ^3J=6.5 Hz, 2H; Ar$_{meta}$-H), 7.21 (t, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 7.20–7.15 (d, overlap with the solvent signal, 2H; Ar$_{meta}$-H), 7.13 (t, ^3J=8.5 Hz, 2H; Ar$_{meta}$-H), 7.10 (t, ^3J=7.8 Hz, 2H; Ar$_{meta}$-H), 7.01 (t, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 6.53 (s, 2H; NH), 6.82 (s, 2H; NH), 6.78 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.72 (dd, ^3J=8.5, ^4J=2.0 Hz, 2H; Ar$_{meta}$-H), 6.67 (dd, ^3J=8.2, ^4J=2.0 Hz, 2H; Ar$_{meta}$-H), 6.60 (br dt, ^3J=7.5, $^4J\approx$1 Hz, 2H; Ar$_{meta}$-H), 6.18 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 6.09 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 5.97 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 5.94 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 4.26 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.23 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.20–4.00 (m, 8H; -OCH$_2$-), 4.16 (d, ^2J=13.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.07 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 3.91 (m, 2H; -OCH$_2$-), 3.85–3.70 (m, 6H; -OCH$_2$-), 3.60 (s, 6H; -OCH$_3$), 3.53 (s, 6H; -OCH$_3$), 3.52 (s, 6H; -OCH$_3$), 3.43 (s, 6H; -OCH$_3$), 3.19 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.11 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.03 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 2.85 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 1.90–1.60 (m, 8H; -CH$_2$-), 1.50–1.30 (m, 8H; -CH$_2$-), 1.30–1.05 (m, 24H; -CH$_2$-), 1.05–0.90 ppm (m, 8H; -CH$_2$-); ESI-MS: *m*/*z* (%): calcd for $C_{152}H_{168}N_{16}O_{24}$: 2601.24; found: 2753.40 (100) $[M+CHCl_3+MeOH]^+$.

Bis[2]catenane 4(M,10): This compound was obtained from bisloop **3(M,10)** and tetraurea **1(M,6)**; yield 50%; m.p. >240°C (decomp); ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ=9.84 (s, 2H; NH), 9.82 (s, 2H; NH), 9.76 (s, 2H; NH), 9.74 (s, 2H; NH), 8.42 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.34 (br dd, ^3J=7.8 Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 8.31 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.28 (br dd, ^3J=8.2 Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 8.06 (d, ^4J=2.0 Hz, 2H; Ar$_{calix}$-H), 8.05 (d, ^4J=2.0 Hz, 2H; Ar$_{calix}$-H), 7.92 (d, ^4J=2.0 Hz, 2H; Ar$_{calix}$-H), 7.91 (d, ^4J=2.0 Hz, 2H; Ar$_{calix}$-H), 7.55 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.43 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.40 (s, 2H; NH), 7.35 (br dd, ^3J=6.8 Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 7.25–7.13 (overlap with the solvent signal, 2×s, 4H; NH, d and 2×t, 6H; Ar$_{meta}$-H), 7.10 (t, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 7.03 (t, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 6.93 (s, 2H; NH), 6.74 (dd, ^3J=7.8, ^4J=1.4 Hz, 2H; Ar$_{meta}$-H), 6.68 (dd, ^3J=8.2, ^4J=1.0 Hz, 2H; Ar$_{meta}$-H), 6.58 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.50 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.22 (d, ^4J=2.3 Hz, 2H; Ar$_{calix}$-H), 6.18 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 6.11 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 6.09 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 4.24 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.19 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.17 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.12 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.05–3.70 (m, 16H; -OCH$_2$-), 3.58 (s, 6H; -OCH$_3$), 3.56 (s, 6H; -OCH$_3$), 3.47 (s, 6H; -OCH$_3$), 3.44 (s, 6H; -OCH$_3$), 3.24 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.13 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.06 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 2.97 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 1.70 (m, 4H; -CH$_2$-), 1.64 (m, 4H; -CH$_2$-), 1.55–0.95 ppm (4×m, 56H; -CH$_2$-); ESI-MS: *m*/*z* (%): calcd for $C_{160}H_{184}N_{16}O_{24}$: 2713.36; found: 2810.42 (100) $[M+THF+Na]^+$.

Bis[2]catenane 4(M,14): This compound was obtained from bisloop **3(M,14)** and tetraurea **1(M,8)**; yield 70%; m.p. >235°C (decomp); ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ=9.79 (s, 2H; NH), 9.72 (s, 2H; NH), 9.70 (s, 2H; NH), 9.63 (s, 2H; NH), 8.29 (dd, ^3J=8.2, ^4J=1.4 Hz, 2H; Ar$_{meta}$-H), 8.19 (dd, ^3J=8.2, ^4J=1.4 Hz, 2H; Ar$_{meta}$-H), 8.14 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.07 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 8.04 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 8.01 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.82 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.78 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.55 (br dd, ^3J=8.2 Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 7.50–7.45 (m, 6H; NH and two signals of Ar$_{meta}$-H), 7.36 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.33 (s, 2H; NH), 7.20 (s, 2H; NH), 7.20–7.15 (m, overlap with the solvent signal, 4H; NH and Ar$_{meta}$-H), 7.07 (t, ^3J=7.5 Hz, 2H; Ar$_{meta}$-H), 7.06 (t, ^3J=7.0 Hz, 2H; Ar$_{meta}$-H), 7.05 (t, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 6.57 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.54 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.48 (dd, ^3J=8.5, ^4J=2.0 Hz, 2H; Ar$_{meta}$-H), 6.44 (dd, ^3J=8.2, ^4J=2.0 Hz, 2H; Ar$_{meta}$-H), 6.15 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 6.13 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 6.12 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 6.07 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 4.27 (d, ^2J=11.2 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.23 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.22 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.18 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 3.90–3.70 (m, 16H; -OCH$_2$-), 3.615 (s, 6H; -OCH$_3$), 3.610 (s, 6H; -OCH$_3$), 3.58 (s, 6H; -OCH$_3$), 3.56 (s, 6H; -OCH$_3$), 3.24 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.19 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.16 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.12 (d, ^2J=12.3 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 1.80–1.00 ppm (6×m, 96H; -CH$_2$-); ESI-MS: *m*/*z* (%): calcd for $C_{176}H_{216}N_{16}O_{24}$: 2937.61; found: 1492.93 (100) $[M+2Na]^{2+}$, 2962.83 (95) $[M+Na]^+$.

Bis[2]catenane 4(M,20): This compound was obtained from bisloop **3(M,20)** and the tetraurea **1(M,11)**; yield 82%; m.p. >235°C (decomp); ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ=9.82 (s, 2H; NH), 9.82 (s, 2H; NH), 9.81 (s, 2H; NH), 9.80 (s, 2H; NH), 8.17 (dd, ^3J=7.8, ^4J=1.0 Hz, 2H; Ar$_{meta}$-H), 8.14 (dd, ^3J=7.8, ^4J=1.0 Hz, 2H; Ar$_{meta}$-H), 8.07 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 8.06 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 8.01 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 8.01 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.98 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 7.93 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.78 (dd, ^3J=8.0, ^4J=1.0 Hz, 2H; Ar$_{meta}$-H), 7.71 (dd, ^3J=8.2, ^4J=1.0 Hz, 2H; Ar$_{meta}$-H), 7.63 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.57 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.25 (s, 2H; NH), 7.21 (s, 2H; NH), 7.18–7.00 (2×s and 4×t, overlap with the solvent signal, 12H; NH and Ar$_{meta}$-H), 6.62 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.59 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.55 (dd, ^3J=8.9, ^4J=2.0 Hz, 2H; Ar$_{meta}$-H), 6.53 (dd, ^3J=8.5, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.12 (br d, unresolved coupling, 4H; Ar$_{calix}$-H), 6.08 (d, ^4J=1.4 Hz, 2H; Ar$_{calix}$-H), 4.30 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.28 (d, ^2J=12.3 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.26 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.24 (d, ^2J=12.3 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 3.90–3.72 (m, 16H; -OCH$_2$-), 3.70 (s, 6H; -OCH$_3$), 3.69 (s, 6H; -OCH$_3$), 3.61 (s, 6H; -OCH$_3$), 3.60 (s, 6H; -OCH$_3$), 3.26 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.22 (d, ^2J=11.0 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.19 (d, ^2J=11.0 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.15 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 1.59 (m, 8H; -CH$_2$-), 1.53 (m, 8H; -CH$_2$-), 1.45–1.10 ppm (m, 128H; -CH$_2$-); ESI-MS: *m*/*z* (%): calcd for $C_{200}H_{264}N_{16}O_{24}$: 3273.99; found: 1661.03 (100) $[M+2Na]^{2+}$.

Bis[2]catenane 4(P,8): This compound was obtained from bisloop **3(P,8)** and tetraurea **1(P,5)**; yield 67%; m.p. >256°C (decomp); ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ =10.20 (s, 2H; NH), 9.98 (s, 2H; NH), 9.94 (s, 2H; NH), 9.93 (s, 2H; NH), 8.59 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.36 (br dd, ^3J=8.2 Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 8.31 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.26 (d, ^3J=7.8 Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 8.21 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 8.15 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 8.03 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.78 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 7.65 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.47 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.45 (br dd, overlapped with the next signal, 2H; Ar$_{meta}$-H), 7.44 (s, 2H; NH), 7.39 (s, 2H; NH), 7.24 (t, ^3J=7.8 Hz, 2H; Ar$_{meta}$-H), 7.20–7.12 (d, overlap with the solvent signal, 2H; Ar$_{meta}$-H), 7.12 (t, ^3J=8.3 Hz, 2H; Ar$_{meta}$-H), 7.06 (t, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 7.00 (t, ^3J=8.2 Hz, 2H; Ar$_{meta}$-H), 6.82 (s, 2H; NH), 6.76 (dd, ^3J=8.5, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.71 (dd, ^3J=8.2, ^4J=1.7 Hz, 2H; Ar$_{meta}$-H), 6.68 (dd, ^3J=8.5, ^4J=2.0 Hz, 2H; Ar$_{meta}$-H), 6.63 (s, 2H; NH), 6.61 (dd, ^3J=8.2, ^4J=1.4 Hz, 2H; Ar$_{meta}$-H), 6.39 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 6.29 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 6.11 (d, ^4J=2.7 Hz, 2H; Ar$_{calix}$-H), 6.12 (d, ^4J=2.4 Hz, 2H; Ar$_{calix}$-H), 4.58 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.56 (d, ^2J=12.3 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.53 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.41 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.25–3.95 (m, 8H; -OCH$_2$-), 3.90 (m, 2H; -OCH$_2$-), 3.85–3.65 (m, 20H; -OCH$_2$-), 3.60 (m, 2H; -OCH$_2$-), 3.34 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.24 (d, ^2J=11.9 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.19 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 2.96 (d, ^2J=11.6 Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 2.18 (m, 4H; -CH$_2$-), 2.10–1.95 (m, 8H; -CH$_2$-), 1.95–1.75 (m, 10H; -CH$_2$-), 1.73–1.60

(m, 2H; -CH$_2$-), 1.55–1.30 (m, 36H; -CH$_2$-), 1.30–1.05 (m, 36H; -CH$_2$-), 0.99 (t, $^3J=7.2$ Hz, 6H; -CH$_3$), 0.96 (t, $^3J=7.2$ Hz, 6H; -CH$_3$), 0.95 (t, $^3J=7.5$ Hz, 6H; -CH$_3$), 0.94 ppm (t, $^3J=7.7$ Hz, 6H; -CH$_3$); ESI-MS: *m/z* (%): calcd for $C_{184}H_{232}N_{16}O_{24}$: 3049.74; found: 1590.97 (62) $[M+C_6D_6+2Na]^{2+}$, 3158.88 (100) $[M+C_6D_6+Na]^+$.

Bis[2]catenane 4(P,20): This compound was obtained from bisloop **3(P,20)** and tetraurea **1(P,11)**; yield 88%; m.p. >247°C (decomp); ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25°C): $\delta=10.02$ (s, 2H; NH), 10.00 (s, 2H; NH), 9.99 (s, 4H; NH), 8.21 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 8.20–8.15 (4× m, 8H; Ar$_{meta}$-H, Ar$_{calix}$-H), 8.10 (br d and br t, 4H; Ar$_{calix}$-H, Ar$_{meta}$-H), 8.04 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 7.74 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.67 (br dd, $^3J\approx7.8$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 7.66 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.59 (dd, $^3J=7.8$, $^4J\approx1.0$ Hz, 2H; Ar$_{meta}$-H), 7.30 (s, 2H; NH), 7.20–7.10 (2×s and 4×t, overlap with the solvent signal, 12H; NH and Ar$_{meta}$-H), 7.04 (s, 2H; NH), 6.64 (dd, $^3J=8.2$, $^4J=2.0$ Hz, 2H; Ar$_{meta}$-H), 6.60 (dd, $^3J=8.2$, $^4J=2.0$ Hz, 2H; Ar$_{meta}$-H), 6.55 (dd, $^3J=8.5$, $^4J=1.7$ Hz, 2H; Ar$_{meta}$-H), 6.52 (dd, $^3J=8.5$, $^4J=1.7$ Hz, 2H; Ar$_{meta}$-H), 6.29 (br d, unresolved coupling, 4H; Ar$_{calix}$-H), 6.25 (d, $^4J=2.0$ Hz, 2H; Ar$_{calix}$-H), 4.58 (d, $^2J\approx11.0$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.56 (d, $^2J\approx11.0$ Hz, 4H; Ar-CH$_2$-Ar$_{ax}$), 4.54 (d, $^2J=11.0$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 3.95–3.65 (m, 32H; -OCH$_2$-), 3.36 (d, $^2J=11.6$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.31 (d, $^2J=11.9$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.30 (d, $^2J=11.9$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.25 (d, $^2J=11.6$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 2.15 (m, 8H; -CH$_2$-), 2.04 (m, 8H; -CH$_2$-), 1.61 (m, 8H; -CH$_2$-), 1.55–1.10 (m, 168H; -CH$_2$-), 1.04 (br t, $^3J\approx6.0$ Hz, 6H; -CH$_3$), 1.03 (br t, $^3J\approx6.0$ Hz, 6H; -CH$_3$), 0.96 ppm (t, $^3J=7.2$ Hz, 12H; -CH$_3$); ESI-MS: *m/z* (%): calcd for $C_{232}H_{328}N_{16}O_{24}$: 3722.49; found: 1885.47 (100) $[M+2Na]^{2+}$.

Bis[2]catenane 5(P,8/14): This compound was obtained from bisloop **3(P,8)** and tetraurea **1(P,8)**; yield 81%; m.p. >242°C (decomp); ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25°C): $\delta=10.04$ (s, 2H; NH), 10.00 (s, 1H; NH), 9.96 (s, 1H; NH), 9.95 (s, 2H; NH), 9.89 (s, 1H; NH), 9.83 (s, 1H; NH), 8.47 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 8.42 (br dd, $^3J=7.8$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 8.40 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 8.29 (br dd, $^3J=7.8$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 8.28 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.27–8.22 (m, 2H; Ar$_{meta}$-H, 1H; Ar$_{calix}$-H), 8.15 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 8.13 (br d, $^3J=7.8$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 8.12 (m, 2H; Ar$_{calix}$-H), 8.01 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 7.84 (m, 2H; Ar$_{calix}$-H), 7.81 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 7.61 (br dd, $^3J=8.2$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 7.57(br t, unresolved coupling, 1H; Ar$_{meta}$-H), 7.55 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 7.52, 7.43, 7.427, 7.418, (4×s, each 1H; NH), 7.40 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 7.37 (br dd, $^3J=8.2$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 7.30, 7.28 (2×s, each 1H; NH), 7.25 (t, $^3J=8.2$ Hz, 1H; Ar$_{meta}$-H), 7.20–7.00 (m, overlapping with the solvent signal, 6H; Ar$_{meta}$-H), 6.73 (s, 1H; NH), 6.72, 6.70, 6.68, 6.63, 6.61, 6.55, 6.50 (7×dd, $^3J=8.2$, $^4J=1.7$ Hz, each 1H; Ar$_{meta}$-H), 6.44 (s, 1H; NH), 6.39 (dd, $^3J=8.2$, $^4J=1.7$ Hz, 1H; Ar$_{meta}$-H), 6.37 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.36 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.35 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.29 (m, 2H; Ar$_{meta}$-H), 6.27 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.12 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.06 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 4.62 (d, $^2J=11.6$ Hz, 1H; Ar-CH$_2$-Ar$_{ax}$), 4.55 (d, $^2J=11.6$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.54, 4.52, 4.49, 4.46, 4.41 (5×d, $^2J=11.6$ Hz, each 1H; Ar-CH$_2$-Ar$_{ax}$), 4.17, 4.07 (2×m, each 2H; -OCH$_2$-), 3.95–3.50 (m, 28H; -OCH$_2$-), 3.41, 3.34, 3.28, 3.25, 3.22, 3.20, 3.08, 2.97 (8×d, $^2J=11.9$ Hz, each 1H; Ar-CH$_2$-Ar$_{eq}$), 2.20–1.80 (2×m, 16H; -CH$_2$-), 1.80–0.90 ppm (m, 126H; -CH$_2$-, -CH$_3$); ESI-MS: *m/z* (%): calcd for $C_{196}H_{256}N_{16}O_{24}$: 3217.93; found: 1632.99 (100) $[M+2Na]^{2+}$, 3242.97 (90) $[M+Na]^+$.

Bis[2]catenane 5(P,8/20): This compound was obtained from bisloop **3(P,8)** and tetraurea **1(P,11)**; yield 64%; m.p. >250°C (decomp); ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25°C): $\delta=10.08$, 10.06, 10.05, 10.02, 9.98, 9.95 (6×s, each 1H; NH), 9.93 (s, 2H; NH), 8.45 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 8.39 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 8.28 (br dd, $^3J=8.2$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 8.26–8.20 (m, 4H; Ar$_{meta}$-H, 2H; Ar$_{calix}$-H), 8.16 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 8.14 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 8.12 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 8.07 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 8.05 (br dd, $^3J=8.2$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 7.94, 7.93, 7.92 (3×d, $^4J=2.4$ Hz, each 1H; Ar$_{calix}$-H), 7.78 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 7.72 (br dd, $^3J=8.2$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 7.71, 7.60, 7.53 (3×br t, unresolved coupling, each 1H; Ar$_{meta}$-H), 7.49, 7.40 (2×br dd, $^3J=8.2$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 7.39, 7.33, 7.27, 7.25, 7.24 (5×s, each 1H; NH), 7.20–7.00 (8×t, overlapping with the solvent signal, 8H; Ar$_{meta}$-H), 6.73 (dd, $^3J=8.5$, $^4J=1.7$ Hz, 1H; Ar$_{meta}$-H), 6.72 (s, 1H; NH), 6.70, 6.68, 6.66, 6.63, 6.59 (5×dd, $^3J=8.5$, $^4J=1.7$ Hz, 4×1H; 2H; Ar$_{meta}$-H), 6.51 (s, 1H; NH), 6.50 (dd, $^3J=8.5$, $^4J=1.7$ Hz, 1H; Ar$_{meta}$-H), 6.35 (d, $^4J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.31 (br d, unresolved coupling, 3H; Ar$_{calix}$-H), 6.28, 6.25, 6.11 (3×d, $^4J=2.4$ Hz, 2×1H; 2H; Ar$_{calix}$-H), 4.65–4.52 (m, 6H; Ar-CH$_2$-Ar$_{ax}$), 4.50, 4.46 (2×d, $^2J=11.6$ Hz, each 1H; Ar-CH$_2$-Ar$_{ax}$), 4.19, 4.08 (2×m, each 2H; -OCH$_2$-), 3.95–3.50 (m, 28H; -OCH$_2$-), 3.40, 3.35, 3.31, 3.264, 3.261, 3.20, 3.12, 3.04 (8×d, $^2J=11.6$ Hz, each 1H; Ar-CH$_2$-Ar$_{eq}$), 2.25–1.85 (several m, 16H; -OCH$_2$CH$_2$-), 1.80–0.90 ppm (m, 150H; -CH$_2$-, -CH$_3$); ESI-MS: *m/z* (%): calcd for $C_{208}H_{280}N_{16}O_{24}$: 3386.11; found: 1717.08 (100) $[M+2Na]^{2+}$.

Bis[2]catenane 4(D,10): This compound was obtained from bisloop **3(D,10)** and tetraurea **1(D,6)**; yield 50%; m.p. >246°C (decomp); ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25°C): $\delta=10.03$ (s, 2H; NH), 9.95 (s, 4H; NH), 9.93 (s, 2H; NH), 8.46 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.37 (m, 4H; Ar$_{meta}$-H), 8.29 (br dd, $^3J=7.8$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 8.20 (d, $^4J=2.0$ Hz, 2H; Ar$_{calix}$-H), 8.18 (d, $^4J=2.0$ Hz, 2H; Ar$_{calix}$-H), 8.04 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 7.99 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 7.62 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.51 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.42 (br d, $^3J=7.8$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 7.37 (s, 2H; NH), 7.36 (s, 2H; NH), 7.21 (t, $^3J=8.2$ Hz, 2H; Ar$_{meta}$-H), 7.20–7.12 (d, overlap with the solvent signal, 2H; Ar$_{meta}$-H), 7.11 (t, $^3J=8.2$ Hz, 2H; Ar$_{meta}$-H), 7.10 (t, $^3J=7.8$ Hz, 2H; Ar$_{meta}$-H), 7.02 (t, $^3J=8.2$ Hz, 2H; Ar$_{meta}$-H), 6.96 (s, 2H; NH), 6.85 (s, 2H; NH), 6.75 (dd, $^3J=8.2$, $^4J=2.0$ Hz, 2H; Ar$_{meta}$-H), 6.68 (dd, $^3J=8.2$, $^4J=1.2$ Hz, 2H; Ar$_{meta}$-H), 6.57 (dd, $^3J=8.2$, $^4J=1.6$ Hz, 2H; Ar$_{meta}$-H), 6.50 (dd, $^3J=8.2$, $^4J=1.6$ Hz, 2H; Ar$_{meta}$-H), 6.40 (d, $^4J=2.0$ Hz, 2H; Ar$_{calix}$-H), 6.38 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.26 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.24 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 4.58 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.55 (d, $^2J=11.7$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.53 (d, $^2J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.50 (d, $^2J=12.5$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.10–3.50 (m, 32H; -OCH$_2$-), 3.36 (d, $^2J=12.1$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.25 (d, $^2J=11.4$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.22 (d, $^2J=11.4$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.11 (d, $^2J=11.7$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 2.30–1.90 (m, 16H; -CH$_2$-),1.80–1.50 (m, 8H; -CH$_2$-), 1.50–1.00 (m, 168H; -CH$_2$-), 0.96 ppm (t, $^3J=6.7$ Hz, 24H; -CH$_3$); ESI-MS: *m/z* (%): calcd for $C_{232}H_{328}N_{16}O_{24}$: 3722.49; found: 1885.38 (100) $[M+2Na]^{2+}$, 1921.42 (54) $[M+THF+2Na]^{2+}$.

Bis[2]catenane 4(D,14): This compound was obtained from bisloop **3(D,14)** and tetraurea **1(D,8)**; yield 97%; m.p. >250°C (decomp); ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25°C): $\delta=10.02$ (s, 2H; NH), 9.95 (s, 2H; NH), 9.93 (s, 2H; NH), 9.87 (s, 2H; NH), 8.34 (br dd, $^3J=7.8$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 8.31 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 8.20 (br dd, $^3J=8.2$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 8.18–8.16 (m, 4H; Ar$_{meta}$-H, Ar$_{calix}$-H), 8.15 (d, $^4J=2.0$ Hz, 2H; Ar$_{calix}$-H), 7.96 (d, $^4J=2.0$ Hz, 2H; Ar$_{calix}$-H), 7.94 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 7.55–7.50 (br dd and br t, 4H; Ar$_{meta}$-H), 7.45 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.42 (br d, $^3J\approx8$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 7.41 (s, 2H; NH), 7.35 (s, 2H; NH), 7.25 (s, 2H; NH), 7.20–7.12 (t, overlap with the solvent signal, 2H; Ar$_{meta}$-H), 7.11 (t, $^3J=8.2$ Hz, 2H; Ar$_{meta}$-H), 7.05 (t, $^3J=8.2$ Hz, 2H; Ar$_{meta}$-H), 7.01 (t, $^3J=8.2$ Hz, 2H; Ar$_{meta}$-H), 6.95 (s, 2H; NH), 6.63 (dd, $^3J=8.2$, $^4J=2.0$ Hz, 2H; Ar$_{meta}$-H), 6.47 (dd, $^3J=8.2$, $^4J=1.7$ Hz, 2H; Ar$_{meta}$-H), 6.45 (dd, $^3J=8.2$, $^4J=1.76$ Hz, 2H; Ar$_{meta}$-H), 6.43 (dd, $^3J=8.2$, $^4J=1.7$ Hz, 2H; Ar$_{meta}$-H), 6.36 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.33 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.30 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.26 (d, $^4J=2.4$ Hz, 2H; Ar$_{calix}$-H), 4.61 (d, $^2J=11.6$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.57 (d, $^2J=12.6$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.54 (d, $^2J=12.3$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.51 (d, $^2J=11.6$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.10–3.50 (m, 32H; -OCH$_2$-), 3.36 (d, $^2J=11.6$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 3.29 (d, $^2J=11.2$ Hz, 4H; Ar-CH$_2$-Ar$_{eq}$), 3.23 (d, $^2J=11.9$ Hz, 2H; Ar-CH$_2$-Ar$_{eq}$), 2.30–2.00 (m, 16H; -CH$_2$-), 1.80–1.05 (2×m, 8H; -CH$_2$-), 1.50–1.00 (m, 208H; -CH$_2$-), 0.97 (t, $^3J=6.7$ Hz, 24H; -CH$_3$) ppm; ESI-MS: *m/z* (%): calcd for $C_{248}H_{360}N_{16}O_{24}$: 3946.74; found: 1632.99 (100) $[M+2Na]^{2+}$, 3242.97 (90) $[M+Na]^+$.

Monoloop-diBoc: A solution of bisurethane (0.5 g, 0.73 mmol) in DMF (50 mL) and a solution of 1,2-diBoc-protected tetraaminocalix[4]arene (0.54 g, 0.56 mmol, and 3–5 drops of triethylamine) in DMF (50 mL) were dropped over 12 h into a 250 mL round-bottomed flask. After the mixing of the two solutions, the yellow reaction mixture was stirred for 24 h. The solvent was then evaporated to dryness and the residue was dissolved in dichloromethane (250 mL) and washed with K_2CO_3 solution (3–5 × 200 mL, until the water layer was colorless) and once with water (200 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed at reduced pressure to give a final volume of 4–5 mL. The pure product was obtained after column chromatography (ethyl acetate/hexane 1:4). Yield 50 %; ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 60 °C): $\delta = 8.44$ (s, 2H; NH), 8.19 (s, 2H; NH), 8.00 (s, 2H; NH), 7.23 (t, $^{4}J=2.1$ Hz, 2H; Ar$_{meta}$-H), 7.09 (t, $^{3}J=8.1$ Hz, 2H; Ar$_{meta}$-H), 7.00 (d, $^{4}J=2.2$ Hz, 2H; Ar$_{calix}$-H), 6.79 (br s, 4H; Ar$_{calix}$-H), 6.69, 6.67 (dd, $^{3}J=8.1$, $^{4}J=1.2$ Hz, 2H; Ar$_{meta}$-H), 6.49 (d, $^{4}J=2.2$ Hz, 2H; Ar$_{calix}$-H), 6.49, 6.47 (dd, $^{3}J=8.1$, $^{4}J=2.4$ Hz, 2H; Ar$_{meta}$-H), 4.37 (d, $^{2}J=12.7$ Hz, 1H; Ar-CH$_2$-Ar$_{ax}$), 4.35 (d, $^{2}J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.34 (d, $^{2}J=12.5$ Hz, 1H; Ar-CH$_2$-Ar$_{ax}$), 3.94 (t, $^{3}J=6.2$ Hz, 4H; OCH$_2$-), 3.86–3.81 (m, 8H; OCH$_2$-), 3.08–3.02 (m, 4H; Ar-CH$_2$-Ar$_{eq}$), 1.90–1.85 (m, 8H; -CH$_2$-), 1.69 (m, 4H; -CH$_2$-), 1.44–1.38 (m, 40H; *t*Bu+-CH$_2$-), 0.93 ppm (m, 12H; -CH$_3$); ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 60 °C): $\delta=159.09$, 152.82, 152.24, 151.35, 151.17, 140.95, 134.32, 134.14, 134.03, 133.97, 133.10, 133.00, 129.06, 118.99, 118.83, 118.74, 118.33, 110.36, 107.59, 104.83, 78.27, 74.49, 67.20, 30.88, 30.79, 30.60, 29.08, 28.32, 28.25, 27.78, 25.15, 22.00, 13.62 ppm; ESI-MS: *m*/*z* (%): calcd for $C_{80}H_{108}N_6O_{12}$: 1344.80; found: 1368.00 (100) $[M+Na]^+$.

Monoloop bisalkenyl 6(P,8): The compound was synthesized from the monoloop-diBoc derivative by the described procedure.[15] Yield 86 %; m.p. > 190 °C (decomposition without melting); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 60 °C): $\delta=8.25$ (s, 2H; NH), 8.19 (s, 2H; NH), 8.01 (s, 2H; NH), 8.00 (s, 2H; NH), 7.21 (t, $^{3}J=2.1$ Hz, 2H; Ar$_{meta}$-H), 7.08–7.04 (m, 6H; Ar$_{meta}$-H), 7.02 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.86 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.81, 6.79 (dd, $^{3}J=8.0$, $^{4}J=1.5$ Hz, 2H; Ar$_{meta}$-H), 6.74 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.67, 6.65 (dd, $^{3}J=7.0$, $^{4}J\approx1.0$ Hz, 2H; Ar$_{meta}$-H), 6.59 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.49, 6.47 (dd, $^{3}J=8.0$, $^{4}J=1.9$ Hz, 4H; Ar$_{meta}$-H), 5.85–5.75 (m, 2H; =C-H), 5.01–4.91 (m, 4H, =CH$_2$), 4.386 (d, $^{2}J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.382 (d, $^{2}J=12.9$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.0–3.88 (m, 16H; OCH$_2$-), 3.15 (overlapping with the signal of the solvent, 4H; Ar-CH$_2$-Ar$_{eq}$), 2.01 (m, 4H; -CH$_2$-), 1.90 (m, 8H; -CH$_2$-), 1.57–1.51 (m, 8H; -CH$_2$-), 1.51–1.30 (m, 36H; -CH$_2$-), 0.95 ppm (t, $^{3}J=6.9$ Hz, 12H; -CH$_3$); ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 60 °C): $\delta=158.79$, 152.03, 150.92, 140.70, 140.65, 138.30, 134.07, 134.02, 133.99, 133.96, 132.98, 132.93, 128.82, 118.21, 118.12, 117.80, 114.04, 110.13, 110.02, 107.34, 107.28, 104.48, 104.32, 74.28, 67.04, 66.93, 32.55, 30.60, 30.46, 30.26, 28.86, 28.26, 28.02, 27.97, 27.78, 27.76, 27.54, 24.89, 24.85, 21.76, 13.37 ppm; ESI-MS: *m*/*z* (%): calcd for $C_{100}H_{130}N_8O_{12}$: 1634.98; found: 1637.10 (100) $[M+H]^+$, 1659.08 (84) $[M+Na]^+$.

Monoloop bisalkenyl 6(P,11): The compound was synthesized from the monoloop-diBoc derivative by the described procedure.[15] Yield 77 %; m.p. > 190 °C (decomposition without melting); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 60 °C): $\delta=8.25$ (s, 2H; NH), 8.19 (s, 2H; NH), 8.02 (s, 2H; NH), 8.00 (s, 2H; NH), 7.21 (br t, unresolved coupling, 2H; Ar$_{meta}$-H), 7.07–7.04 (m, 6H; Ar$_{meta}$-H), 7.02 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.86 (d, $^{4}J=2.2$ Hz, 2H; Ar$_{calix}$-H), 6.78 (br dd, $^{3}J=8.0$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 6.73 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.65 (br dd, $^{3}J=7.0$ Hz, unresolved coupling, 2H; Ar$_{meta}$-H), 6.59 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.48, 6.46 (dd, $^{3}J=8.0$, $^{4}J=1.9$ Hz, 4H; Ar$_{meta}$-H), 5.84–5.73 (m, 2H, =C-H), 5.00–4.90 (m, 4H, =CH$_2$), 4.37 (d, $^{2}J=12.9$ Hz, 4H; Ar-CH$_2$-Ar$_{ax}$), 3.95–3.85 (m, 16H; OCH$_2$-), 3.08 (overlapping with the signal of the solvent, 4H; Ar-CH$_2$-Ar$_{eq}$), 2.01 (m, 4H; -CH$_2$-), 1.90 (m, 8H; -CH$_2$-), 1.57–1.51 (m, 8H; -CH$_2$-), 1.51–1.43 (m, 48H; -CH$_2$-), 0.96 ppm (t, $^{3}J=7.0$ Hz, 12H; -CH$_3$); ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 °C): $\delta=158.79$, 152.02, 150.91, 150.89, 140.69, 140.64, 138.36, 134.07, 134.02, 133.99, 132.98, 132.93, 128.81, 118.20, 118.11, 118.08, 118.06, 117.79, 113.98, 110.12, 110.01, 107.35, 107.29, 104.49, 104.30, 74.28, 67.05, 66.92, 32.61, 30.25, 28.86, 28.42, 28.31, 28.28, 28.25, 27.99, 27.82, 27.54, 25.04, 24.85, 21.76, 13.38 ppm; ESI-MS: *m*/*z* (%): calcd for $C_{106}H_{142}N_8O_{12}$: 1719.07; found: 1743.17 (100) $[M+Na]^+$.

Bis[2]catenane 7(P,8+14): This compound was obtained from monoloop **5(P,8)**. Yield 41 %; m.p. > 200 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): $\delta=10.07$ (s, 1H; NH), 10.04 (s, 1H; NH), 10.01 (s, 1H; NH), 9.97 (s, 1H; NH), 9.916 (s, 1H; NH), 9.912 (s, 1H; NH), 9.86 (s, 1H; NH), 9.79 (s, 1H; NH), 8.47 (t, $^{4}J=2.0$ Hz, 1H; Ar$_{meta}$-H), 8.42 (t, $^{4}J=1.9$ Hz, 1H; Ar$_{meta}$-H), 8.36, 8.34 (br dd, $^{3}J=8.0$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 8.35, 8.33 (dd, $^{3}J=7.8$, $^{4}J=1.4$ Hz, 1H; Ar$_{meta}$-H), 8.31–8.28 (m, 2H; Ar$_{meta}$-H, 1H; Ar$_{calix}$-H), 8.23 (d, $^{4}J=2.4$ Hz, 1H; Ar$_{calix}$-H), 8.20 (t, $^{4}J=2.0$ Hz, 2H; Ar$_{meta}$-H), 8.11 (br dd, $^{3}J=7.8$ Hz, unresolved coupling, 1H; Ar$_{meta}$-H), 8.06 (d, $^{4}J=2.4$ Hz, 1H; Ar$_{calix}$-H), 8.04 (d, $^{4}J=2.7$ Hz, 1H; Ar$_{calix}$-H), 7.98 (d, $^{4}J=2.4$ Hz, 1H; Ar$_{calix}$-H), 7.90 (d, $^{4}J=2.7$ Hz, 1H; Ar$_{calix}$-H), 7.89 (d, $^{4}J=2.7$ Hz, 1H; Ar$_{calix}$-H), 7.74 (d, $^{4}J=2.7$ Hz, 1H; Ar$_{calix}$-H), 7.63 (t, $^{4}J=2.0$ Hz, 1H; Ar$_{meta}$-H), 7.57–7.54 (m, 2H; Ar$_{meta}$-H, 1H; NH), 7.48 (s, 1H; NH), 7.47 (s, 1H; NH), 7.43, 7.41 (br dd, $^{3}J\approx8$, $^{4}J\approx1$ Hz, 1H; Ar$_{meta}$-H), 7.41, 7.39 (br dd, $^{3}J\approx8$, $^{4}J\approx1$ Hz, 1H; Ar$_{meta}$-H), 7.36 (t, $^{4}J=2.0$ Hz, 1H; Ar$_{meta}$-H), 7.33 (br t, unresolved coupling, 1H; Ar$_{meta}$-H), 7.32 (s, 1H; NH), 7.22 (t, $^{3}J=8.0$ Hz, 1H; Ar$_{meta}$-H), 7.20 (t, $^{3}J=8.0$ Hz, 1H; Ar$_{meta}$-H), 7.18–7.08 (m, overlapping with the solvent signal, 2H; Ar$_{meta}$-H, 4H; NH), 7.08 (t, $^{3}J=7.7$ Hz, 1H; Ar$_{meta}$-H), 7.05 (t, $^{3}J=8.2$ Hz, 1H; Ar$_{meta}$-H), 7.00 (t, $^{3}J=8.3$ Hz, 1H; Ar$_{meta}$-H), 6.99 (t, $^{3}J=8.2$ Hz, 1H; Ar$_{meta}$-H), 6.78 (s, 1H; NH), 6.77, 6.75 (dd, $^{3}J=8.2$, $^{4}J=1.7$ Hz, 1H; Ar$_{meta}$-H), 6.72, 6.70 (dd, $^{3}J=8.2$, $^{4}J=1.7$ Hz, 1H; Ar$_{meta}$-H), 6.697 and 6.67 (dd, $^{3}J=8.2$, $^{4}J=1.7$ Hz, 1H; Ar$_{meta}$-H), 6.63, 6.61 (dd, $^{3}J=8.2$, $^{4}J=1.4$ Hz, 1H; Ar$_{meta}$-H), 6.62, 6.60 (dd, $^{3}J=8.2$, $^{4}J=2.0$ Hz, 1H; Ar$_{meta}$-H), 6.57, 6.55 (dd, $^{3}J=8.2$, $^{4}J=2.0$ Hz, 1H; Ar$_{meta}$-H), 6.46, 6.44 (dd, $^{3}J=8.2$, $^{4}J=2.0$ Hz, 1H; Ar$_{meta}$-H), 6.41 (s, 1H; NH), 6.39, 6.37 (dd, $^{3}J=8.2$, $^{4}J=1.9$ Hz, 1H; Ar$_{meta}$-H), 6.37 (d, $^{4}J=2.7$ Hz, 1H; Ar$_{calix}$-H), 6.34 (d, $^{4}J=2.4$ Hz, 2H; Ar$_{calix}$-H), 6.31 (d, $^{4}J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.29 (d, $^{4}J=2.7$ Hz, 1H; Ar$_{meta}$-H), 6.28 (d, $^{4}J=2.7$ Hz, 1H; Ar$_{calix}$-H), 6.08 (d, $^{4}J=2.4$ Hz, 1H; Ar$_{calix}$-H), 6.07 (d, $^{4}J=2.4$ Hz, 1H; Ar$_{calix}$-H), 4.61 (d, $^{2}J=11.6$ Hz, 2H; Ar-CH$_2$-Ar$_{ax}$), 4.56, 4.55, 4.48, 4.47, 4.46, 4.38 (6 × d, $^{2}J=11.6$ Hz, each 1H; Ar-CH$_2$-Ar$_{ax}$), 4.28–4.07 (2 × m, each 2H; -OCH$_2$-), 3.90–3.55 (m, 28H; -OCH$_2$-), 3.38, 3.35, 3.27, 3.26, 3.24, 3.17, 3.14, 2.91 (8 × d, $^{2}J=11.9$ Hz, each 1H; Ar-CH$_2$-Ar$_{eq}$), 2.5–1 ppm unresolved multiplets; ESI-MS: *m*/*z* (%): calcd for $C_{196}H_{256}N_{16}O_{24}$: 3217.93; found: 1633.07 (100) $[M+2Na]^{2+}$.

X-ray structure analysis: Single crystals of **4(P,10)** suitable for X-ray analysis were obtained from chloroform/methanol. The structure could be completely resolved; it clearly shows the open capsule and all four $C_{10}H_{20}$ chains.

$2(C_{96}H_{124}N_8O_{12})\cdot 2CHCl_3\cdot 5CH_3OH$, formula weight 3563.01, trigonal, space group $R\bar{3}$, $a=76.875(2)$, $c=18.5091(7)$ Å, $V=94730(5)$ Å^3, $Z=18$, colorless, block-shaped crystal, STOE-IPDS-II two-circle diffractometer, $T=173$ K, MoK$_\alpha$ radiation, 2θ range = 2.74–50.08°, 261400 reflections collected, 36746 independent reflections ($R_{int}=0.1021$), empirical absorption correction (MULABS, Blessing, 1995), structure solution with SHELXS-90 (Sheldrick, 1990), refinement on F^2 with SHELXL-97 (Sheldrick, 1997), $R1[I>2\sigma(I)]=0.219$, GOF = 1.67. The methylene chains were refined with restraints of 1.50(1) Å for 1–2 and 2.4(1) Å for 1–3 distances. The methanol C−O distances were restrained to 1.40(1) Å and the C−Cl distances to 1.70(1) Å.

CCDC-637006 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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