Rational Synthesis of Multicyclic Bis[2]catenanes

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Abstract: Bis-loop tetraurea calix[4]arene **6** has been prepared by acylation of the wide-rim calix[4]arene tetraamine **1** with the activated bis(urethane) **8** under dilution conditions. Similarly the bis(Boc-protected) tetraamine **2** is converted into the mono-loop derivative **3** which after deprotection and acylation gives the bisalkenyl derivative **5**. In apolar solvents this tetraurea calix[4]arene **5** forms regioselectively a single hydrogen-bonded homodimer, from which the bis[2]catenane **10a** is formed in 49% by a metathesis reaction followed by hydrogenation. Bis-loop derivative **6** forms no homodimers for steric reasons, but a stoichiometric mixture with the open-chain tetraalkenyl derivative **7a** contains exclusively the heterodimer. Metathesis and subsequent hydrogenation now yields 65% of the pure bis[2]catenane **10a** which could not be isolated from the complex reaction mixture obtained from the homodimer **7a·7a**. The chirality of **10a** (D_2 symmetry) has been verified by optical resolution using HPLC on a chiral stationary phase.

Keywords: calixarenes · catenanes · hydrogen bonds · metathesis · self-assembly

Introduction

The synthesis of molecules with novel interesting topologies remains an attractive field and a permanent challenge in supramolecular chemistry.[1] Doubly interlocked [2]catenanes,[2] molecular necklaces[3] or daisy chains,[4] and dendrimers with rotaxane-like mechanical branching points[5] may be mentioned. "Knotaxanes", rotaxanes with chiral knots (knotanes) as stoppers,[6] represent one of the most recent examples. The increasingly rapid progress is directly linked to an improved understanding of the preorganization of suitable precursor molecules by "self-assembly" through reversible bonds. Coordination to metal cations, a classical example in the controlled synthesis of catenanes,[7] has been successfully used in combination with other noncovalent attractive forces to achieve more ambitious goals[2,3] such as the first synthetic steps towards Borromean rings.[8] Preorganization of reactants through hydrogen bonds was also frequently the key factor for the effective synthesis of rotaxanes or catenanes.[9] The binding of dialkylammonium cations to large crown ethers[10] or of phenolates to macrocyclic lactams[11] may be taken as examples. Recently the simultaneous interaction of inorganic anions with both the axle and a linear amide as precursor for a macrocycle was used to prepare [*n*]rotaxanes.[12] The metathesis reaction between alkenyl groups has been frequently used to synthesize macrocycles[13] or to stabilize various (self-assembled) species by covalent links.[14] "Reactive macrocycles" containing double bonds can be even "opened" to thread into another macrocycle or to bind to an axle with voluminous stoppers, and closed again, thus leading to the thermodynamically most stable catenanes[15] or rotaxanes,[16] respectively.

We recently showed that the preorganization of the two tetraurea calix[4]arenes in a hydrogen-bonded dimer **I**[17,18] can be used to prepare hitherto unknown multicyclic bis[2]-catenanes **II** by a metathesis reaction between alkenyl groups attached to the urea residues (followed by hydrogenation of the double bonds).[19,20,21] However, in this statistical approach a doubly bridged mono[2]catenane **III** and a tetrabridged capsule **IV** (Figure 1) were isolated as further products of a complete conversion of all alkenyl groups *within* a dimer, since the metathesis reaction occurs not only between alkenyl groups attached to the same calix[4]arene (α-connection), but also between the two calix[4]arenes of a dimer (β-connection). Most probably, products with "isolated" alkenyl residues are formed in addition.

It seems possible to shift the outcome of the metathesis reaction towards α- or β-connection by appropriate structural changes. The alkenyl groups could be attached, for in-

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  DOI: 10.1002/chem.200400195

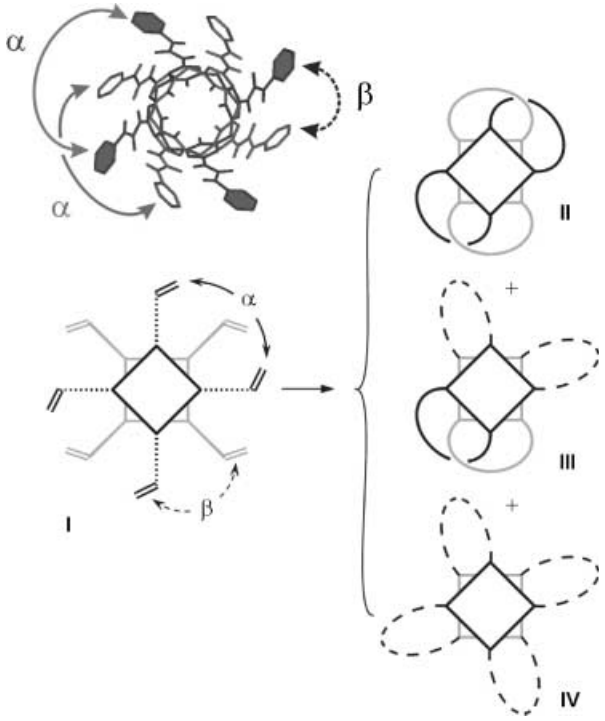


Figure 1. Schematic representation of the products formed by metathesis reaction of the hydrogen bonded dimer **I** of a tetraalkenylurea calix[4]arene, for example, **7a·7a**.

stance, in the *para* position instead of the *meta* position, or longer rigid spacers could be introduced between the urea and alkenyl functions. Molecular models suggest, however, that a complete suppression of, for example, the β-connection, will be impossible in such a way. However, a more rational synthesis of the desired bis[2]catenane **II**[22] should be possible, using the controlled dimerization of suitably designed tetraureas as precursors.

Development of a new synthetic strategy: Tetraurea derivatives of the AABB type[23] usually form two regioisomeric homodimers. *Only one* homodimer is formed, however, if two urea residues R in A (or B) are connected by an aliphatic chain.[24] In this dimer the two loops do not overlap and one of the open-chain urea residues must (be able to) slip through the loop of the other calix[4]arene. The formation of a single homodimer **V** for such mono-loop derivatives was recently shown for one example.[24]

Double-loop compounds, in which pairs of *adjacent* urea residues are covalently connected should not homodimerize at all, since the formation of homodimers is necessarily accompanied by an overlap of loops. However, in the presence of an equimolar amount of an open-chain tetraurea, heterodimers **VI** should be formed exclusively,[25] since this is the only way, to "saturate" all urea functions in a cyclic hydrogen bonded array.[26]

As illustrated schematically in Figure 2, only one "β-connection" is possible in homodimers **V**, leading to a product with two "isolated double bonds", for which no further metathesis reaction is possible within the dimer. Assuming the same probability for each alkenyl group to react with the metathesis catalyst, and also the same probability to close a ring with each of the available double bonds, the bis[2]catenane **II** should be formed with a statistical probability of 75%.[27] In the case of the heterodimer **VI**, where only α-connections are possible, this probability is 100%, as long as the metathesis reaction occurs quantitatively within one dimer, since two double bonds remain in *adjacent* positions whatever the first connection is.

As indicated in Figure 2, the rings formed by metathesis reactions can be different in size (or even in structure), from the rings/loops of the starting calixarene. This paves the way to the preparation of isomeric catenanes containing the same interlocking ring pairs (the ring size being indicated by *n* and *m*), attached, however, to different calixarene skeletons.

Synthesis of mono- and bis-loop tetraurea calix[4]arenes: In general, macrocyclic diureas can be prepared by reaction of a diamine with a diisocyanate under (high) dilution conditions. Instead of a diisocyanate we used the activated diurethane **8** (Scheme 1) which is more stable and easier to purify, a factor important especially for cyclization reactions. It can be obtained from *m*-nitrophenol by *O*-alkylation with 1,10-dibromodecane, followed by hydrogenation of the nitro groups and *N*-acylation with *p*-nitrophenyl chloroformate.

The bis-loop derivative **6** was directly obtained from the tetraaminocalix[4]arene **1** with 2.5 mol of **8** in DMF in the presence of triethylamine. The analogous reaction with the bis-Boc-protected derivative **2** gave the mono-loop **3** in 74% yield after purification. Deprotection (96% of **4**) and

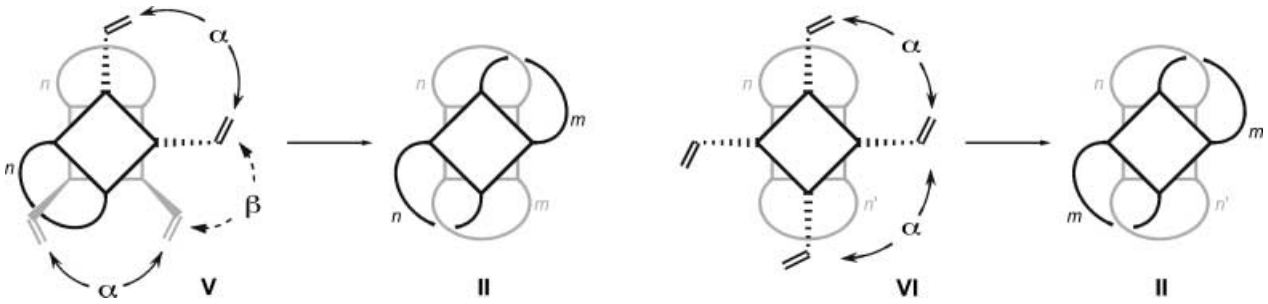
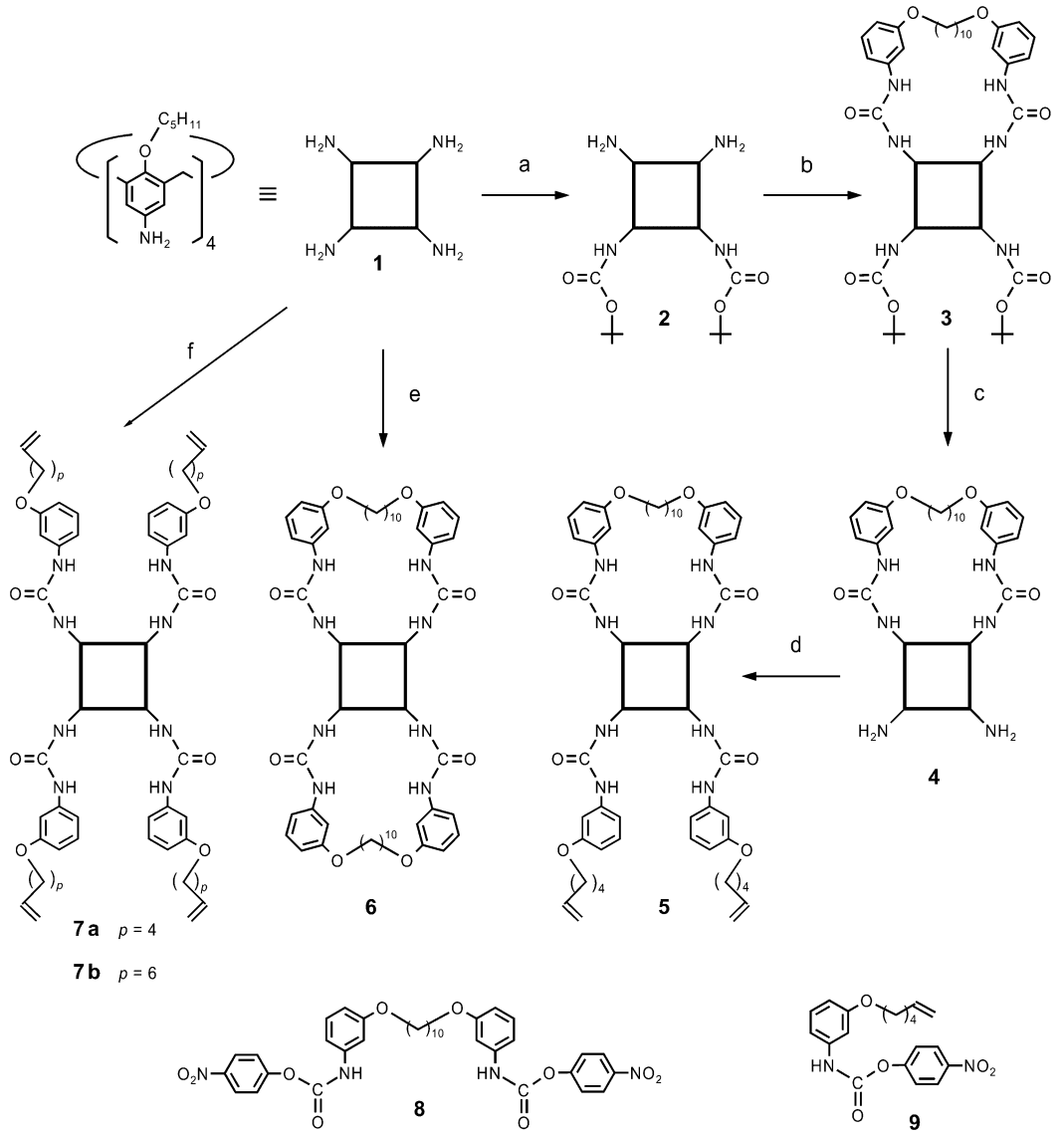


Figure 2. Selective preparation of bis[2]catenanes **II** from homodimers **V** and heterodimers **VI** by the metathesis between pendant alkenyl groups. Potential differences in ring size are indicated by *n*, *n*′, and *m*.



Scheme 1. Synthesis of mono-loop (**5**) and double-loop (**6**) tetraurea derivatives. The starting tetraaminocalix[4]arene tetraether in the cone conformation[30] is represented as a square (**1**). Conditions: a) see ref. [29]; b) DMF, Et_3N, slow addition of **8** (1.25 mol), 74%; c) TFA, $CHCl_3$; 4 h, 96%; d) urethane **9**, $CHCl_3$, 12 h, 96%; e) similar to b (2.5 mol **8**); f) urethane **9**, $CHCl_3$, 12 h, 88%.

acylation with **9** finally led to the mono-loop tetraurea **5** in 96%. The lower yield of **6** (38%) in comparison to **3** (74%) may be partly due to *trans*-cavity bridging of opposite amino functions. This suggests that **6** could be prepared by a second cyclization of **4**, a pathway, which allows also the synthesis of double-loop compounds with different loops.

The ^{1}H NMR spectra of mono- and bis-loop compounds **5** and **6** in solvents such as [D_6]DMSO and [D_8]THF reveal their C_S- and C_{2V}-symmetrical structure, respectively. Four singlets for NH protons and four *m*-coupled doublets for the aryl protons of the calixarene skeleton (integrating for two protons each) are found for **5** (Figure 3a), while **6** shows two singlets for NH and two *m*-coupled doublets for calixarene Ar-H protons (integrating for two protons each; Figure 4a).

Synthesis of bis[2]catenanes: In apolar solvents, such as [D]chloroform or [D_6]benzene the NH signals for **5** are

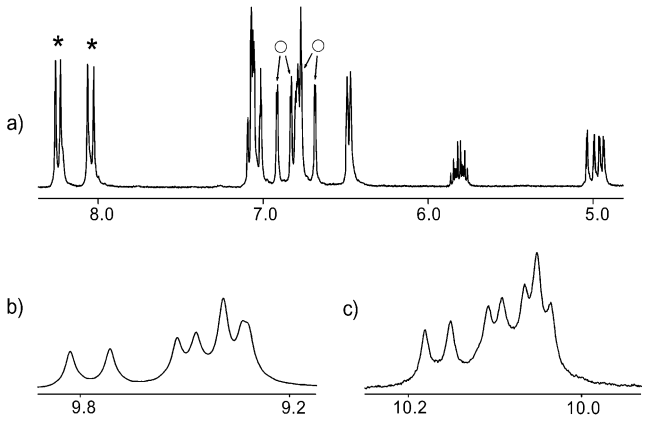


Figure 3. Sections of the ^{1}H NMR spectra (400 MHz) of **5**; a) "monomer" in [D_6]DMSO, NH (asterisk) and Ar_{calix}-H (circle) are labeled as examples; b) dimer in [D]chloroform; c) dimer in [D_6]benzene only the most lowfield-shifted NH protons are shown.

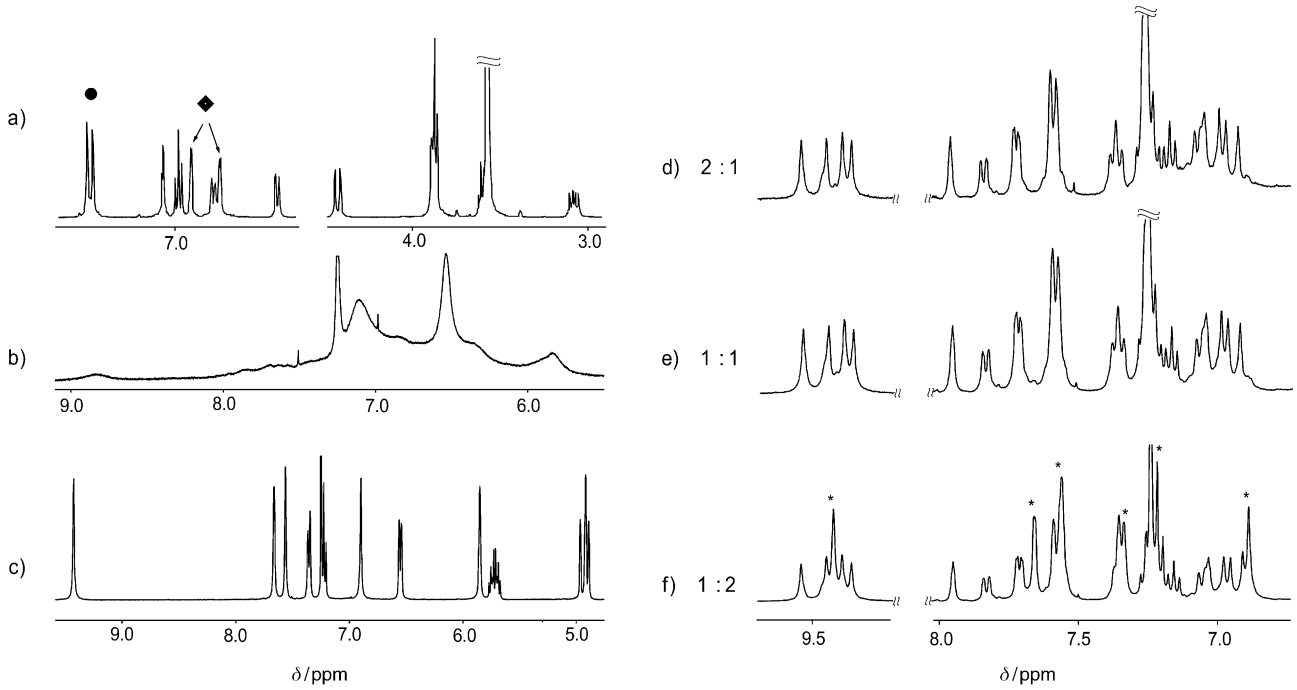


Figure 4. Section of the ^{1}H NMR spectra (400 MHz) of a) **6** "monomer" in [D_8]THF, NH (●) and Ar_{calix}-H (◆) are labeled as examples; b) **6** in [D]chloroform; c) **7a** in [D]chloroform; and d)–f) mixtures of **6** and **7a** in the ratio 2:1, 1:1, and 1:2; signals of **7a·7a** are labeled with an asterisk.

partly shifted to higher field (Figure 3b,c), typical for the formation of a hydrogen-bonded, capsular dimer. A careful analysis proves the formation of a single homodimer **5·5** (type **V**) with C_1 symmetry. Metathesis reaction with such a solution under conditions employed previously (CH_2Cl_2 as solvent containing 1–5% of benzene as a good guest, Grubbs′ catalyst, $c = 1.2 \cdot 10^{-5}$ M to suppress reactions between dimers)[19] in fact, furnished the bis[2]catenane **10a** (type **II**) in 49% (after purification by column chromatography), whereas the reaction mixture obtained by metathesis of the homodimer **7a·7a** did not allow the isolation of **10a**. The analogous compound **10b** (n = m = 14) with larger loops was obtained in only 5–12% from reactions with **7b·7b**.[19] This clearly demonstrates the advantage of the new synthetic strategy.

The double-loop compound **6** shows a broad, featureless spectrum in [D]chloroform (Figure 4b) that indicates unspecific aggregation, but not the formation of a well-defined species. However, sharp signals of a single dimer appear upon addition of **7a** (Figure 4d and e). This must be the heterodimer **6·7a** (type **VI**), since the signals of the homodimer **7a·7a** (type **I**, Figure 4c) can be observed only, if **7a** is added in excess (Figure 4f). Metathesis reaction with a 1:1 mixture of **6** and **7a**, containing only the heterodimer furnished the bis[2]catenane **10a** in 65% yield, which is convincing evidence that the developed strategy is valid.

Bis[2]catenanes of type **II** are "permanently" chiral and cannot racemize when the hydrogen bonds between the urea functions are broken. Their NMR spectra in solvents such as [D]chloroform show C_2 symmetry due to the directionality of the hydrogen bonds.[19] However the compounds remain chiral (D_2 symmetry) in hydrogen-bond breaking solvents. Consequently their enantiomers can be separated by chromatography on chiral stationary phases. For **10a** this is illustrated in Figure 5.

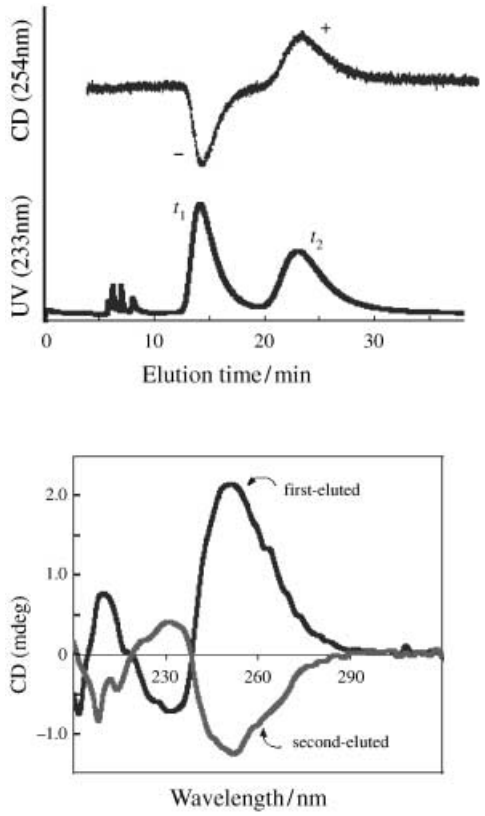


Figure 5. a) Chromatographic separation of **10a**. Column: Chiralcel OD, eluent: hexane/ethanol (90/10, v/v), flow rate: 0.5 mL min^{-1}; b) CD spectra of both fractions, proving that they consist of enantiomers, solvent: hexane/ethanol (90/10, v/v), cell length: 25 mm.

Conclusion

A new strategy for the synthesis of calix[4]arene-derived bis[2]catenanes **II** by a metathesis reaction between pendant alkenyl residues has been developed. It is based on the *regioselective homodimerization* of mono-loop dialkenyl derivatives **5** and on the *selective heterodimerization* of bis-loop derivatives **6** with tetraalkenyl derivatives **7**. The molecular design of these tetraurea calix[4]arenes minimizes or eliminates the number of incorrect covalent connections within a dimer. Thus, the yield of pure product could be increased up to 65%. The synthesis is flexible and allows various structural modifications. Both pathways are complementary with respect to the preparation of regioisomeric bis[2]catenanes. Thus, the way is open for the synthesis of a large variety of topologically chiral capsules in which the release or exchange of the included guest is fine-tuned by the catenane structure.

Experimental Section

General: DMF (peptide synthesis grade) was purchased from ACROS. Dichloromethane (p.a. grade) was kept over sodium hydroxide for one day before it was used in the metathesis reactions. The Grubbs' catalyst[28] (bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride) was purchased from Strem. Deuterated solvents were bought from Deutero GmbH. All reactions were carried out under nitrogen. Column chromatography was performed with silica gel (Merck, 0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded at 25°C on a Bruker DRX400 Avance Instrument at 400 and 100 MHz, respectively. Chemical shifts were calibrated to the residual signal of the deuterated solvent. Mass spectra were obtained on a Finnigan MAT 8230 spectrometer. Melting points are not corrected.

Compound **2** was prepared as described in reference [29].

Derivative 3: A solution of diurethane **8** (0.5 g, 0.73 mmol) in DMF (50 mL) and a solution of diamine **2** (0.54 g, 0.56 mmol, and 3–5 drops of triethylamine) in DMF (50 mL) were added under stirring during 12 h to a 1-L round-bottom flask filled with DMF (550 mL). The yellow reaction mixture was stirred for a further 24 h at room temperature. Then, the solvent was evaporated, and the residue was dissolved in dichloromethane (250 mL), and washed with K_2CO_3 solution (3–5 × 200 mL) until the aqueous layer was colorless) and with water (1 × 200 mL). The organic layer was dried over $MgSO_4$ and the solution was concentrated at reduced pressure to 4–5 mL. The pure product was obtained after column chromatography (eluent ethyl acetate/hexane 1:4) as a white powder (0.56 g; 74%); m.p. 270°C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ = 8.51 (s, 2H; NH), 8.21 (s, 2H; NH), 8.02 (s, 2H; NH), 7.10 (t, ^3J = 8.1 Hz, 2H; Ar$_{meta}$-H), 7.08 (t, ^4J = 2.2 Hz, 2H; Ar$_{meta}$-H), 6.87 (d, ^4J = 2.4 Hz, 2H; Ar$_{calix}$-H), 6.82 and 6.80 (dd, ^3J = 8.2 Hz, ^4J = 1.72 Hz, 2H; Ar$_{meta}$-H), 6.80 (brs, 4H; Ar$_{calix}$-H), 6.62 (brd, 2H; Ar$_{calix}$-H), 6.49 and 6.47 (dd, ^3J = 8.1 Hz, ^4J = 2.2 Hz, 2H; Ar$_{meta}$-H), 4.36 (d, ^2J = 12.72 Hz, 4H; Ar-CH$_2$-Ar ax), 4.34 (d, ^2J = 12.96 Hz, 4H; Ar-CH$_2$-Ar ax), 4.33 (d, ^2J = 12.72 Hz, 4H; Ar-CH$_2$-Ar ax), 3.93 (t, ^3J = 6.2 Hz, 4H; OCH$_2$-), 3.86–3.80 (m, 8H; OCH$_2$-), 3.10 (d, ^2J = 13.72 Hz, 4H; Ar-CH$_2$-Ar eq), 3.06 (d, ^2J = 13.44 Hz, 4H; Ar-CH$_2$-Ar eq), 3.03 (d, ^2J = 14.2 Hz, 4H; Ar-CH$_2$-Ar eq), 1.91–1.85 (m, 8H; -CH$_2$-), 1.68 (q, ^3J = 6.5 Hz, 4H; -CH$_2$-), 1.41–1.35 (m, 34H; *t*Bu + -CH$_2$-), 1.29 (m, 12H; -CH$_2$-), 0.94 ppm (brt, 12H; -CH$_3$); ^{13}C NMR ([D$_6$]DMSO, 60°C): δ = 158.80, 152.56, 151.97, 151.05, 150.92, 140.71, 134.03, 133.91, 133.77, 133.72, 132.84, 132.77, 128.89, 118.67, 118.56, 118.48, 118.23, 110.08, 107.28, 104.54, 78.01, 74.26, 66.93, 30.52, 30.40, 28.86, 28.84, 28.09, 27.97, 27.86, 27.79, 27.54, 27.53, 24.89, 21.77, 13.39 ppm; FD MS: *m*/*z*: 1373.9 [M^+].

Calix[4]arene diamine 4: Trifluoracetic acid (15 mL) was added to a solution of **3** (0.31 g, 0.23 mmol) in chloroform (15 mL). The reaction mixture was stirred under nitrogen for four hours, diluted with toluene (20 mL), and evaporated. The residue was dissolved in dichloromethane, washed with water until neutrality, and dried over $MgSO_4$. The pure product was obtained after precipitation with hexane as a white powder (0.26 g; 96%). m.p. >200°C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ = 8.35 (s, 2H; NH), 8.18 (s, 2H; NH), 7.10 (m, 4H; Ar$_{meta}$-H), 6.83 (s, 2H; Ar$_{calix}$-H), 6.78 (d, ^3J = 8.1 Hz, 2H; Ar$_{meta}$-H), 6.62 (s, 2H; Ar$_{calix}$-H), 6.47 (d, ^3J = 8.8 Hz, 2H; Ar$_{meta}$-H), 5.97 (s, 4H; Ar$_{calix}$-H), 4.35 (brs, 4H; NH$_2$), 4.33 (d, ^2J = 12.8 Hz, 1H; Ar-CH$_2$-Ar ax), 4.24 (d, ^2J = 12.8 Hz, 2H; Ar-CH$_2$-Ar ax), 4.17 (d, ^2J = 12.5 Hz, 1H; Ar-CH$_2$-Ar ax), 3.90 (t, ^3J = 5.8 Hz, 4H; OCH$_2$-), 3.80 (t, ^3J = 6.98 Hz, 4H; OCH$_2$-), 3.78 (m, 4H; OCH$_2$-), 3.08 (d, ^2J = 12.8 Hz, 1H; Ar-CH$_2$-Ar eq), 2.95 (d, ^2J = 12.8 Hz, 2H; Ar-CH$_2$-Ar eq), 2.81 (d, ^2J = 12.5 Hz, 1H; Ar-CH$_2$-Ar eq), 1.90–1.85 (m, 8H; -CH$_2$-), 1.66 (brq, 4H; -CH$_2$-), 1.36 (m, 16H; -CH$_2$-), 1.28 (m, 12H; -CH$_2$-), 0.95 ppm (brt, 12H; -CH$_3$).

Mono-loop derivative 5: A solution of **4** (0.24 g, 0.2 mmol), **9** (0.144 g, 0.4 mmol) and a few drops of triethylamine in DMF (10 mL) was stirred for two days at room temperature. Similar workup as described for **3** gave **5** as a white powder (0.31 g; 96%); m.p. >190°C (decomp); ^{1}H NMR ([D$_6$]DMSO, 60°C): δ = 8.25 (s, 2H; NH), 8.22 (s, 2H; NH), 8.06 (s, 2H; NH), 8.02 (s, 2H; NH), 7.09–7.05 (m, 6H; Ar$_{meta}$-H), 7.01 (t, ^4J = 2.04 Hz, 2H; Ar$_{meta}$-H), 6.91 (d, ^4J = 2.36 Hz, 2H; Ar$_{calix}$-H), 6.83 (d, ^4J = 2.72 Hz, 2H; Ar$_{calix}$-H), 6.80–6.77 (m, 6H; Ar$_{meta}$-H), 6.76 (d, ^4J = 2.4 Hz, 2H; Ar$_{calix}$-H), 6.68 (d, ^4J = 2.4 Hz, 2H; Ar$_{calix}$-H), 6.48 (brs, 2H; Ar$_{meta}$-H), 6.46 (brs, 2H; Ar$_{meta}$-H), 5.84–5.77 (m, 2H; -C*H*=CH$_2$), 5.03–4.94 (m, 4H; -CH=C*H*$_2$), 4.37 (d, ^2J = 12.56 Hz, 4H; Ar-CH$_2$-Ar ax), 3.88 (m, 16H; OCH$_2$-), 3.20 (m, Ar-CH$_2$-Ar eq + H$_2$O), 2.07 (m, 4H; -CH$_2$-),1.90 (q, ^3J = 7.14 Hz, 8H; -CH$_2$-), 1.71–1.64 (m, 8H; -CH$_2$-), 1.52–1.47 (m, 4H; -CH$_2$-), 1.41–1.39 (m, 16H; -CH$_2$-), 1.28–1.25 (m, 12H; -CH$_2$-),0.94 ppm (t, ^3J = 6.98 Hz, 12H; -CH$_3$); ^{13}C NMR ([D$_6$]DMSO): δ = 158.97, 152.29, 152.27, 151.12, 140,96, 140.93, 138.45, 134.40, 134.36, 133.28, 133.26, 129,30, 118.27, 118.20, 118.16, 114.83, 110.16, 110.09, 107.28, 104.35, 104.15, 74.74, 74.72, 66.94, 48.52, 32.77, 30.49, 29.31, 28.39, 28.17, 28.14, 28.10, 27.90, 25.16, 24.67, 22.27, 13.92 ppm; FD MS: *m*/*z*: 1629.87 [M + Na$^+$].

Double loop derivative 6: A solution of diurethane **8** (0.85 g, 1.25 mmol) in DMF (50 mL) and a solution of tetraamine **1** (0.38 g, 0.50 mmol) and triethylamine (3–5 drops) in DMF (50 mL) were added under stirring over 12 h to a 1-L round-bottom flask filled with DMF (400 mL), and the yellow reaction mixture was stirred for three days. Then, the solvent was evaporated and the residue was dissolved in chloroform (250 mL), washed with K_2CO_3 solution (3–5 × 200 mL, until the aqueous layer was colorless), and with water (1 × 200 mL). The organic layer was dried over $MgSO_4$ and concentrated at reduced pressure to 4–5 mL. The product was isolated by column chromatography (eluent tetrahydrofuran/hexane 1:2) and recrystallized from tetrahydrofuran/methanol, to yield **6** as a white powder (0.3 g; 38%); m.p. > 250°C (decomp); ^{1}H NMR ([D$_8$]THF): δ = 7.49 (s, 4H; NH), 7.47 (s, 4H; NH), 7.07 (d, ^4J = 2.0 Hz, 4H; Ar$_{meta}$-H), 6.98 (t, ^3J = 8.2 Hz, 4H; Ar$_{meta}$-H), 6.90 (d, ^4J = 2.6 Hz, 4H; Ar$_{calix}$-H), 6.79 and 6.76 (dd, ^3J = 8.1 Hz; ^4J = 1.4 Hz, 4H; Ar$_{meta}$-H), 6.74 (d, ^4J = 2.4 Hz, 4H; Ar$_{calix}$-H), 6.42 and 6.40 (dd, ^3J = 8.1 Hz; ^4J = 1.6 Hz, 4H; Ar$_{meta}$-H), 4.44 (d, ^2J = 12.9 Hz, 4H; Ar-CH$_2$-Ar ax), 3.89–3.85 (m, 16H; OCH$_2$-), 3.08 (d, ^2J = 13.2 Hz, 2H; Ar-CH$_2$-Ar eq), 3.06 (d, ^2J = 13.2 Hz, 2H; Ar-CH$_2$-Ar eq), 1.96 (m, 8H; -CH$_2$-), 1.77 (m, 8H; -CH$_2$-), 1.49–1.43 (m, 24H; -CH$_2$-),1.30 (m, 16H; -CH$_2$-), 0.96 ppm (t, ^3J = 7.0 Hz, 12H; -CH$_3$); ^{13}C NMR ([D$_8$]THF): δ = 160.67, 153.03, 152.63, 142.46, 135.87, 135.81, 134.97, 129.81, 119.27, 119.00, 111.08, 108.16, 105.54, 75.92, 75.92, 67.97, 32.21, 32.09, 30.90, 30.02, 29.71, 29.64, 29.51, 26.69, 23.77, 14.60 ppm; FD MS: *m*/*z*: 1582.8 [M^+].

Tetraurea 7a: A solution of **1** (0.5 g, 0.65 mmol), **9** (1 g, 2.8 mmol), and triethylamine (few drops) in DMF (30 mL) was stirred for two days at room temperature. Similar workup described for **3**, gave **7a** as a white powder (0.93 g; 88%); m.p. 210–213°C; ^{1}H NMR ([D$_6$]DMSO): δ = 8.31 (s, 4H; NH), 8.16 (s, 4H; NH), 7.10–7.05 (m, 8H; Ar$_{meta}$-H), 6.79 (s, 8H; Ar$_{calix}$-H), 6.76 (d, ^3J = 8.2 Hz, 4H; Ar$_{meta}$-H), 6.47 (d, ^3J = 7.0 Hz, 4H; Ar$_{meta}$-H), 5.77 (m, 4H; -C*H*=CH$_2$), 5.02 (d, ^2J = 17.2 Hz, 4H; -CH=C*H*$_2$), 4.94 (d, ^3J = 9.9 Hz, 4H; -CH=C*H*$_2$), 4.33 (d, ^2J = 12.7 Hz, 4H; Ar-CH$_2$-Ar ax), 3.87 (t, ^3J = 6.4 Hz, 8H; OCH$_2$-), 3.81 (t, ^3J = 6.4 Hz, 8H; OCH$_2$-), 3.11 (d, ^2J = 12.7 Hz, 4H; Ar-CH$_2$-Ar eq), 2.06 (q, ^3J = 6.8 Hz, 8H; -C*H*$_2$CH=CH$_2$), 1.90 (m, 8H; -CH$_2$-), 1.67 (q, ^3J = 7.6 Hz, 8H; -CH$_2$-), 1.47 (q, ^3J = 7.7 Hz, 8H; -CH$_2$-), 1.40 (br m, 16H; C*H*$_2$CH$_3$), 0.94 ppm (brt, 12H; CH$_3$); ^{1}H NMR ([D$_1$]chloroform): δ = 9.43 (s, 8H; NH), 7.66

and 5.85 (two AB d, ^4J=1.8 Hz, 16H; Ar_{calix}-H), 7.56 (brt, 8H; Ar_{meta}-H), 7.35 (d, ^3J=7.9 Hz, 8H; Ar_{meta}-H), 7.23 (t, ^3J=8.1 Hz, 8H; Ar_{meta}-H), 6.90 (s, 8H; NH), 6.54 (dd, ^3J=8.1 Hz, ^4J=1.6 Hz, 8H; Ar_{meta}-H), 5.73 (m, 8H; -C*H*=CH_2), 4.94 (dd, ^3J=18.3 Hz, ^4J=1.4 Hz, 8H; -CH=CH_2), 4.88 (d, ^3J=10.8 Hz, 8H; -CH=CH_2), 4.21 and 2.83 (two d, ^2J=11.8 Hz, 16H; Ar-CH_2-Ar ax and eq), 3.90–3.75 (m, 16H; OCH_2-), 3.70–3.60 (m, 16H; OCH_2-), 1.99 (q, ^3J=7.1 Hz, 16H; -CH_2CH=CH_2), 1.92 (q, ^3J=6.7 Hz, 16H; -CH_2-), 1.68 (q, ^3J=8.0 Hz, 16H; -CH_2-), 1.35 (m, 32H; -CH_2-), 1.27 (q, ^3J=7.2 Hz, 16H; -CH_2-), 0.94 ppm (t, ^3J=7.3 Hz, 24H; -CH_3); ^{13}C NMR ([D_6]DMSO): δ=158.94, 152.26, 151.07, 140.95, 138.42, 134.34, 133.25, 129.25, 118.14, 114.81, 110.11, 107.25, 104.15, 74.71, 66.90, 32.75, 30.54, 29.30, 28.08, 27.89, 24.66, 22.25, 13.91 ppm; FD MS: *m*/*z*: 1634.1 [M^+ + 1].

Diurethane 8: Compound **8** was prepared in three steps: a) Dinitro derivative: A slurry of 3-nitrophenol (1.53 g, 11 mmol), 1,10-dibromodecane (1.5 g, 5 mmol), and potassium carbonate (1.52 g, 11 mmol) in acetonitrile (50 mL) was refluxed for two days (TLC control , eluent ethyl acetate/hexane 1:2). The solvent was evaporated under reduced pressure and the crude product was taken up in dichloromethane (250 mL). The organic layer was washed with water until the aqueous phase remained colorless (2–4×100 mL), dried over $MgSO_4$, and concentrated. Precipitation with methanol gave the dinitro derivative as a white compound (1.75 g; 84%); m.p. 80–81°C; ^{1}H NMR ([D]chloroform): δ=7.79 and 7.77 (ddd, ^3J=8.1 Hz, ^4J=2.2 Hz, ^4J=0.9 Hz, 2H; Ar-H), 7.70 (t, ^4J=2.3 Hz, 2H; Ar-H), 7.39 (t, ^3J=8.2 Hz, 2H; Ar-H), 7.20 and 7.18 (ddd, ^3J=8.4 Hz, ^4J=2.5 Hz, ^4J=0.9 Hz, 2H; Ar-H), 4.01 (t, ^3J=6.6 Hz, 4H; OCH_2-), 1.80 (q, ^3J=6.5 Hz, 4H; -CH_2 -), 1.48–1.43 (m, 4H; -CH_2 -), 1.37–1.32 ppm (m, 8H; -CH_2 -); ^{13}C NMR ([D]chloroform): δ=159.66, 149.21, 129.82, 121.66, 115.50, 108.65, 68.70, 29.41, 29.26, 28.97, 25.91 ppm; FD MS: *m*/*z*: 416.3 [M^+].

b, c) The dinitro derivative (2.0 g, 4.8 mmol) was dissolved in acetone (125 mL) and hydrogenated (1 atm) in the presence of Raney-nickel until the hydrogen uptake was completed (~3 h). The catalyst was filtered off, washed with acetone (2×25 mL), and the solvent was evaporated. The white solid residue was dissolved in dioxane (150 mL). 4-Nitrophenyl chloroformate (2.25 g, 11.15 mmol) was added and the mixture was refluxed for 24 h (a clear solution was obtained in ~3 h). The solvent was evaporated to dryness and the residue was triturated with chloroform. The desired product **8**, a white powder, was filtered off, washed with chloroform (2×15 mL) and dried (2.88 g; 94%); m.p. 177–178°C (decomp); ^{1}H NMR ([D_6]DMSO): δ=10.41 (s, 2H; NH), 8.30 and 7.53 (2d, ^3J=8.9 Hz, 8H; Ar-H), 7.21 (t, ^3J=8.1 Hz, 2H; Ar_{meta}-H), 7.15 (s, 2H; Ar_{meta}-H), 7.06 and 7.04 (dd, ^3J=8.1 Hz, 2H; Ar_{meta}-H), 6.65 and 6.63 (2brd, ^3J=7.7 Hz, 2H; Ar_{meta}-H), 3.91 (t, ^3J=6.24 Hz, 4H; OCH_2-), 1.68 (q, ^3J=6.6 Hz, 4H; -CH_2 -), 1.38 (m, 4H; -CH_2 -), 1.28 ppm (m, 8H; -CH_2 -); ^{13}C NMR ([D_6]DMSO): δ=159.01, 155.49, 150.36, 144.49, 139.19, 129.66, 125.12, 122.81, 110.74, 109.14, 104.97, 67.26, 66.25, 28.82, 28.63, 28.51, 25.38 ppm.

Urethane 9: Compound **9** was prepared in three steps: a) 3-Hexenyloxyacetanilide: A mixture of 3-hydroxyacetanilide (1.634 g, 10.8 mmol), ω-bromohexene-1 (2.041 g, 11.9 mmol), and K_2CO_3 (1.641 g, 11.9 mmol) in DMF (20 mL) was stirred at 70°C for 6 h. After cooling, the reaction mixture was poured into water (150 mL) and extracted with chloroform (4×20 mL). The organic layer was washed with water (2×20 mL), dried over $MgSO_4$, and evaporated at reduced pressure. After recrystallization from hexane (15 mL), a white crystalline powder was obtained (2.04 g; 65%). m.p. 69°C; elemental analysis (%) calcd for $C_{12}H_{17}NO$: 72.07, H 8.21, N 6.00; found: C 72.10, H 8.03, N 5.90; ^{1}H NMR ([D]chloroform): δ=7.30 (brs, 1H; NH), 7.25 (s, 1H; Ar-H), 7.17 (t, ^3J=7.6 Hz, 1H; Ar-H), 6.92 (d, ^3J=7.6 Hz, 1.H; Ar-H), 6.63 (d, ^{3}J=8.2 Hz, 1.H; Ar-H), 5.82 (m, 1H; -C*H*=CH_2), 5.02 (dd, ^2J=17.0 Hz, ^3J=1.2 Hz, 1H; -CH=CH_2), 4.96 (dd, ^2J=10.0 Hz, ^3J=1.0 Hz, 1H; -CH=CH_2), 3.94 (t, ^3J=6.5 Hz, 2H; OCH_2-), 2.15 (s, 3H; $COCH_3$), 2.10 (q, ^3J=7.0 Hz, 2H; CH_2CH=CH_2), 1.77 (q, ^3J=7.3 Hz, 2H; -CH_2-), 1.54 ppm (q, ^3J=7.3 Hz, 2H; -CH_2-); ^{13}C NMR ([D]chloroform): δ=159.66, 139.04, 138.51, 129.58, 129.45, 114.70, 111.72, 110.62, 106.17, 67.77, 33.39, 28.64, 25.28, 24.68 ppm; FD MS: *m*/*z*: 233.4 [M^+].

b) 3-Hexenyloxyaniline: A solution of 3-hexenyloxyacetanilide (0.27 g, 1.16 mmol) and NaOH (1.62 g, 40.5 mmol) in a mixture of ethanol (20 mL) and water (2 mL) was refluxed for 6 h. After cooling, the mixture was evaporated under reduced pressure, water (200 mL) was added, and the mixture was extracted with dichloromethane (4×20 mL). The organic layer was washed with water (2×30 mL), dried over $MgSO_4$, and evaporated, to give a yellow oil (0.21 g; 95%). Elemental analysis (%) calcd for $C_{12}H_{17}NO$: 75.35, H 8.91, N 7.32; found: C 75.10, H 9.02, N 7.12; ^{1}H NMR ([D]chloroform): δ=7.07 (t, ^3J=8.2 Hz, 1H; Ar-H), 6.35 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 1H; Ar-H), 6.29 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 1H; Ar-H), 6.25 (t, ^3J=1.8 Hz, 1H; Ar-H), 5.86 (m, 1H; -C*H*=CH_2), 5.07 (dd, ^2J=17.0 Hz, ^3J=1.8 Hz, 1H; -CH=CH_2), 4.96 (d, ^3J=10.6 Hz, 1H; CH=CH_2), 3.94 (t, ^3J=6.5 Hz, 2H; OCH_2-), 3.63 (brs, 2H; NH_2), 2.15 (q, ^3J=7 Hz, 2H; CH_2CH=CH_2), 1.81 (q, ^3J=8.2 Hz, 2H; -CH_2-), 1.59 ppm (q, ^3J=7.6 Hz, 2H; -CH_2-); ^{13}C NMR ([D]chloroform): δ=160.09, 147.68, 138.44, 129.87, 114.55, 107.60, 104.36, 101.46, 67.35, 33.29, 28.60, 25.19 ppm; FD MS: *m*/*z*: 191.6 [M^+].

c) A solution of 3-hexenyloxyaniline (1.9 g, 10 mmol) and 4-nitrophenyl chloroformate (2.0 g, 10 mmol) in a mixture of chloroform (45 mL) and tetrahydrofuran (30 mL) was refluxed for 12 h. The solvents were evaporated and the residue was dissolved in chloroform and precipitated with diethyl ether, to yield **9** as a white compound (2.7 g; 77%); m.p. 102–103°C; ^{1}H NMR ([D]chloroform): δ=8.27 and 7.38 (2d, ^3J=9.1 Hz, 4H; Ar-H), 7.22 (t, ^3J=8.2 Hz, 1H; Ar_{meta}-H), 7.13 (s, 1H; Ar_{meta}-H), 6.92 (brs, 1H; NH), 6.91 and 6.89 (dd, ^3J=8.1 Hz, ^4J=1.9 Hz, 1H; Ar_{meta}-H), 6.69 and 6.67 (dd, ^3J=8.2 Hz, ^4J=2.3 Hz, 2H; Ar_{meta}-H), 5.86–5.76 (m, 1H; -C*H*=CH_2), 5.04–4.95 (m, 2H; -CH=CH_2), 3.96 (t, ^3J=6.4 Hz, 2H; OCH_2-),2.14–2.09 (m, 2H; -CH_2-), 1.82–1.76 (m, 2H; -CH_2 -), 1.60–1.52 ppm (m, 2H; -CH_2-); ^{13}C NMR ([D]chloroform): δ=159.92, 155.31, 150.02, 145.08, 138.45, 137.76, 129.95, 125.20, 122.13, 114.75, 110.91, 110.79, 105.28, 67.86, 33.37, 28.61, 25.26 ppm; FD MS: [M^+] was not detected due to decomposition.

Bis[2]catenane 10a: a) From the homodimer: A solution of **5** (0.2 g, 0.12 mmol) in benzene (50 mL) was stirred at room temperature for three hours. The formation of the homodimer was monitored by ^{1}H NMR spectroscopy. The solution was diluted with dichloromethane (1 L) and a solution of Grubbs′ catalyst (10 mg, 12.4 μmol) in dichloromethane (25 mL) was added. The reaction mixture was stirred for two days, two drops of DMSO were added, and the stirring was continued for 12 h. The solution was concentrated to about 400 mL and washed with water (2×400 mL), dried over $MgSO_4$, and evaporated. The residue was disolved in THF (20 mL) and hydrogen (1 atm) added in the presence of PtO_2 (50 mg). A white compound was obtained after chromatographic separation (eluent chloroform/ethyl acetate 95 : 5) and crystallization from chloroform/methanol mixture gave **10a** (0.4 g, 49%).

b) From the heterodimer: A solution of **6** (0.2 g, 0.12 mmol) and **7a** (0.2 g, 0.12 mmol) in benzene (10 mL) was prepared by stirring at 40°C for two days. The complete formation of the heterodimer was monitored and confirmed and by ^{1}H NMR spectrosocpy. The metathesis reaction, hydrogenation, and the chromatographic purification was carried out as described above. Compound **10a** was obtained as a white precipitate (0.26 g; 65%); m.p. >200°C (decomp); ^{1}H NMR ([D_6]benzene): δ=10.07 (s, 2H; NH), 10.00 (s, 2H; NH), 9.98 (s, 2H; NH), 9.96 (s, 2H; NH), 8.47 (brt, 2H; Ar_{meta}-H), 8.40 and 8.38 (dd, ^3J=8.8 Hz; ^4J=0.9 Hz, 2H; Ar_{meta}-H), 8.37 (brt, 2H; Ar_{meta}-H), 8.31 and 8.29 (dd, ^3J=8.2 Hz; ^4J=0.9 Hz, 2H; Ar_{meta}-H), 8.21 and 6.39 (two AB d, ^4J=2.5 Hz, 4H; Ar_{calix}-H), 8.19 and 6.40 (two AB d, ^4J=2.5 Hz, 4H; Ar_{calix}-H), 8.01 and 6.23 (two AB d, ^4J=2.5 Hz, 4H; Ar_{calix}-H), 7.96 and 6.24 (two AB d, ^4J=2.5 Hz, 4H; Ar_{calix}-H), 7.63 (brt, 2H; Ar_{meta}-H), 7.50 (brt, 2H; Ar_{meta}-H), 7.43 and 7.42 (dd, ^3J=8.8 Hz; ^4J=0.9 Hz, 2H; Ar_{meta}-H), 7.41 (s, 2H; NH), 7.37 (s, 2H; NH), 7.21–7.19 (m, 4H; Ar_{calix}-H), 7.11 (t, ^4J=8.2 Hz, 2H; Ar_{meta}-H), 7.09 (t, ^4J=8.2 Hz, 2H; Ar_{meta}-H), 7.00 (t, ^4J=8.2 Hz, 2H; Ar_{meta}-H), 6.98 (s, 2H; NH), 6.81 (s, 2H; NH), 6.77 and 7.75 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 2H; Ar_{meta}-H), 6.69 and 6.67 (dd, ^3J=8.2 Hz, ^4J=1.4 Hz, 2H; Ar_{meta}-H), 6.56 and 6.54 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 2H; Ar_{meta}-H), 6.48 and 6.46 (dd, ^3J=8.2 Hz; ^4J=1.8 Hz, 2H; Ar_{meta}-H), 4.54 (d, ^2J=12.0 Hz, 2H; Ar-CH_2-Ar ax), 4.51 (d, ^2J=11.7 Hz, 2H; Ar-CH_2-Ar ax), 4.47 (d, ^2J=10.8 Hz, 2H; Ar-CH_2-Ar ax), 4.44 (d, ^2J=11.4 Hz, 4H; Ar-CH_2-Ar ax), 4.15–3.50 (m, 32H; OCH_2-), 3.35 (d, ^2J=12.0 Hz, 2H; Ar-CH_2-Ar eq), 3.22 (d, ^2J=11.7 Hz, 2H; Ar-CH_2-Ar eq), 3.21 (d, ^2J=11.4 Hz, 2H; Ar-CH_2-Ar eq), 3.08 (d, ^2J=11.8 Hz, 2H; Ar-CH_2-Ar eq), 2.15–1.90 (m, 16H; -CH_2-), 1.72–1.58 (m, 8H; -CH_2-), 1.50–1.10 (m, 88H; -CH_2-), 1.00–0.93 ppm (m, 24H; -CH_3); ^{13}C NMR ([D]chloroform): δ=160.08, 159.96, 159.89, 154.52, 154.24, 154.18, 153.93, 151.45, 151.41, 151.23, 151.18, 140.69, 140.61, 135.52, 135.33, 135.27, 134.99, 134.78,

134.52, 134.24, 133.24, 133.11, 133.01, 132.86, 131.09, 131.00, 130.21, 117.88, 117.82, 117.43, 116.69, 116.63, 116.33, 116.26, 110.81, 110.76, 110.70, 110.52, 110.18, 109.34, 109.27, 104.18, 104.15, 103.60, 103.41, 75.93, 75.74, 75.48, 75.31, 68.73, 68.66, 67.89, 67.74, 30.68, 30.61, 30.44, 30.31, 29.91, 29.72, 29.69, 29.23, 29.03, 28.92, 28.72, 28.65, 28.63, 28.53, 28.36, 28.29, 28.16, 28.09, 25.99, 25.87, 25.54, 25.41, 22.87, 22.84, 22.76, 22.74, 14.23, 14.20, 14.13, 14.10 ppm; MALDI-TOF MS: m/z: 3187.7 [$M + Na^+$].

Acknowledgement

Financial support for these studies by the Deutsche Forschungsgemeinschaft (Bo523/14–2) and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Prof. M. Schmidt (Institut für Physikalische Chemie) for the possibility to measure MALDI-TOF mass spectra, and Dr. B. Mathiasch for his assistance in the NMR experiments.

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Received: November 10, 2003
Revised: March 10, 2004

Published online: April 29, 2004

