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Fine-Tuning the Dimerization of Tetraureacalix[4]arenes

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Abstract: Calix[4]arenes substituted by four urea residues at their wide rim form hydrogen-bonded homo- and heterodimeric capsules in apolar solvents. If urea groups are covalently connected to loops or substituted by bulky residues, the dimerization may be restricted to those pairs in which the loops do not overlap and for which the residues are small enough to pass the loops. In the present study, we describe the dimerization properties of tetraureas with one, two (adjacent or opposite), three, or four loops and those bearing (additionally) up to four residues of different size: **a** = tolyl, **b** = 3,5-di-*tert*-butylphenyl, **c** = 4-propyloxy-3,5-di-(*tert*-butylphenyl)phenyl, and **d** = 4-[tris-(4-*tert*-butylphenyl)methyl]phenyl. For compounds with four loops of different size ($-O-(CH_2)_n-O-$chains with $n = 10$, 14, and 20 connecting the *m*-positions of the urea phenyl residues) a clear "stepwise" sorting scheme could be established, in which the bulkiest residue **d** is excluded by all tetraloop compounds and the smallest residue **a** can pass only the smallest loops ($n = 10$). The medium-sized residues **b** or **c** are tolerated by $n = 14$ and 20 or only by $n = 20$. Selectivities can be built up also on geometrical factors. A trisloop compound, for instance, combines only with a tetraurea bearing a single bulky residue and tetraureas with two bulky substituents in adjacent or opposite position are distinguished by the bisloop derivatives with adjacent or opposite loops. The impossibility to form a homodimer of a monoloop compound containing two bulky residues leads to its selective heterodimerization with a derivative bearing three bulky groups. Subtle effects for "borderline" cases, in which the dimerization or reorganization takes a longer time, are also discussed.

Keywords: calixarenes · dimerization · hydrogen bonds · self-assembly · supramolecular chemistry

Introduction

The fascinating area of "self-assembly" presently attracts the attention of many scientists. Starting with a small number of selected "building blocks" it offers almost unlimited possibilities for the construction of various intriguing architectures[1] and allows the realization of rather ambitious ideas. From a synthetic point of view, the additional advantages of self-assembly cannot be overestimated. Usually it does not require complicated syntheses, whereas it often affords "quantitative" yields, since wrong connections between the building blocks are automatically repaired.

Hydrogen bonding is one of the tools for self-organization, which is frequently chosen also by nature. In contrast to other reversible interactions, there is still a "certain directionality", which can be used to build artificial assemblies or to construct complex supramolecular structures.

Tetraureacalix[4]arenes **1**, which form hydrogen-bonded, dimeric capsules[2] in apolar solvents (Scheme 1), represent a system that is particularly interesting. Various multimacrocyclic compounds,[3] numerous catenanes[3b,4] and rotaxanes,[5] hydrogen-bonded polymers,[6] informational (or "smart") polymers,[7] and self-assembled dendritic architectures[8] were developed based on this dimerization.

To realize some of the mentioned structures an exclusive heterodimerization of two different tetraureas has been required for which until now only a few examples are known. The stoichiometric mixture of a tetraaryl urea **1** and a tetratosyl urea **2**, for instance, contains only the heterodimer **1·2**, whereas a mixture of two (similar) tetraaryl (or tetraalkyl)

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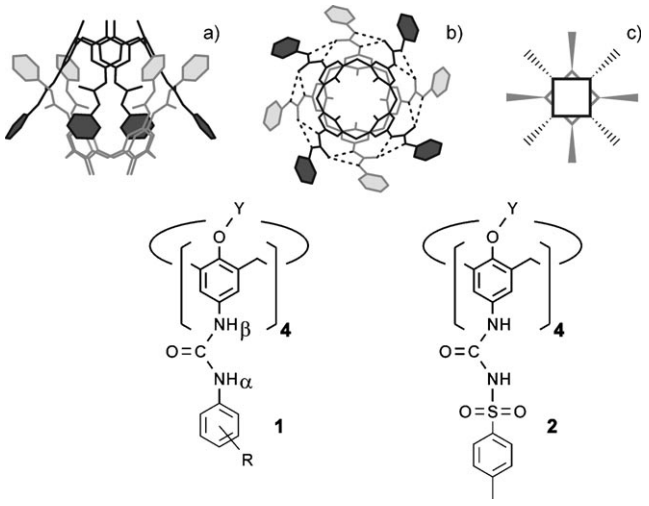
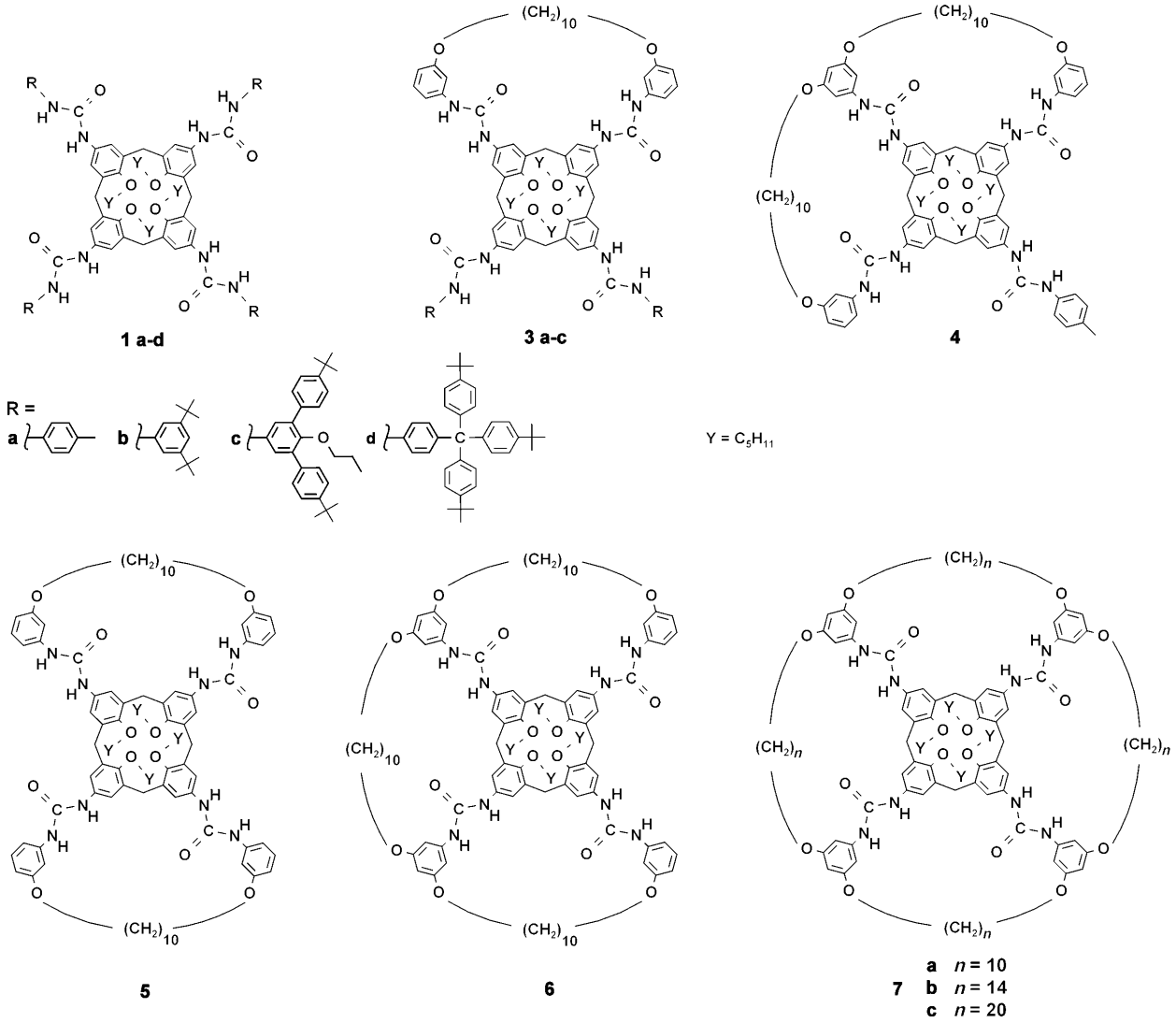


Scheme 1. Top: Dimeric capsule of a tetraaryl tetraureacalix[4]arene **1**: a) side view; b) top view, hydrogen bonds are indicated by dashed lines; c) graphical representation of the dimer. Bottom: Structural formulae of tetraaryl and tetratosyl tetraureacalix[4]arenes **1** and **2**.

ureas usually contains the two homodimers and the respective heterodimer.[9] The serendipitous observation of this heterodimerization was the first example of an exclusive "social self-sorting behavior" reported for the dimerization of tetraureacalix[4]arenes.[10,11] It occurs due to a subtle difference in the hydrogen-bonding pattern of arylurea and tosylurea groups, which requires a sterically less-favorable conformation for half of the tosylurea residues in the homodimer **2·2**.[12]

During our attempts to obtain inherently chiral dimers from achiral tetraureacalix[4]arenes[13] we have studied compounds of the AABB-type **3a**,[4] in which two adjacent urea residues are covalently connected by an aliphatic chain to form a "loop". The observation of only one of two potential regioisomeric homodimers strongly suggested that dimers with overlapping loops cannot be formed, whereas those between open-chained and loop-containing tetraureas can and should be formed exclusively. Indeed, solutions containing the calixarenes **4**–**7** show only broad NMR spectra, since for the dimerization no arrangement can be found in which



loops are not overlapping. Thus, their mixtures with tetraureas of type **1** or **2** contain a second type of exclusively formed heterodimers **1·(4–7)** or **2·(4–7)**.

Recently, we could extend this selectivity, showing that bulky urea residues can be found that make the formation of certain tetraurea dimers impossible, since they cannot pass a respective loop.[14] Tentatively two basic rules for the dimerization of tetraureacalix[4]arenes were formulated:

1) Dimers with overlapping loops cannot be formed.
2) Dimers cannot be formed if a bulky residue has to pass a loop.

The first rule has been confirmed for various examples with $O-(CH_2)_n-O$ chains up to $n=20$ connecting the *m*-positions[15] of phenylureas. Never was the formation of capsules with overlapping loops observed.

Based on loops with $n=10$ and bulky residues 4-propyloxy-3,5-di-(*tert*-butylphenyl)phenyl that cannot pass these loops, a sorting scheme could be realized for 11 tetraureas, for which instead of $0.5\times11\times(11+1)=66$ dimers only 6 dimers are formed.[16]

In this paper we describe the fine-tuning of the second rule, establishing a correlation between the size of "bulky" substituents and the length of the loops by which the penetration can be safely excluded.

Results and Discussion

Control by size: To check the compatibility between loops and bulky residues of different sizes the tetraureas **1a–d** were mixed with tetraloop compounds **7a–c** under conditions suitable for the dimerization. Table 1 summarizes results obtained for all combinations within three days after mixing (a complete scheme, containing also all homodimers is shown in Figure S1, Supporting Information). The smallest tetratolyl urea **1a** easily forms dimers with all tetraloop derivatives **7a–c**, whereas the 3,5-di-*tert*-butylphenyl residues of **1b** are already too large to pass through the loops of **7a** ($n=10$). The replacement of the *tert*-butyl groups in **1b** by the 4-*tert*-butylphenyl residues (**1c**) makes the formation of the dimers **1c·7a** and **1c·7b** impossible; however, the capsule **1c·7c** was observed immediately after mixing. Finally, no heterodimers were found in the mixtures of the tetraurea **1d** that bears the most voluminous substituents with any of the proposed tetraloop compounds **7**.[17]

Table 1. Dimerization of tetraureas **1a–d** with **7a–c**.

Compound	1a	1b	1c	1d
7a ($n=10$)	+	–	–	–
7b ($n=14$)	+	+	–	–
7c ($n=20$)	+	+	+	–

By using these observations, a selective dimerization based on incompatible sizes of loops and urea residues can be developed. Thus, when the six tetraureas **1a–c** and **7a–c** are mixed in stoichiometric amounts,[18] only three heterodimers **1a·7a**, **1b·7b**, and **1c·7c** (from nine possible heterodimeric combinations) are observed in solution (Figure 1d).

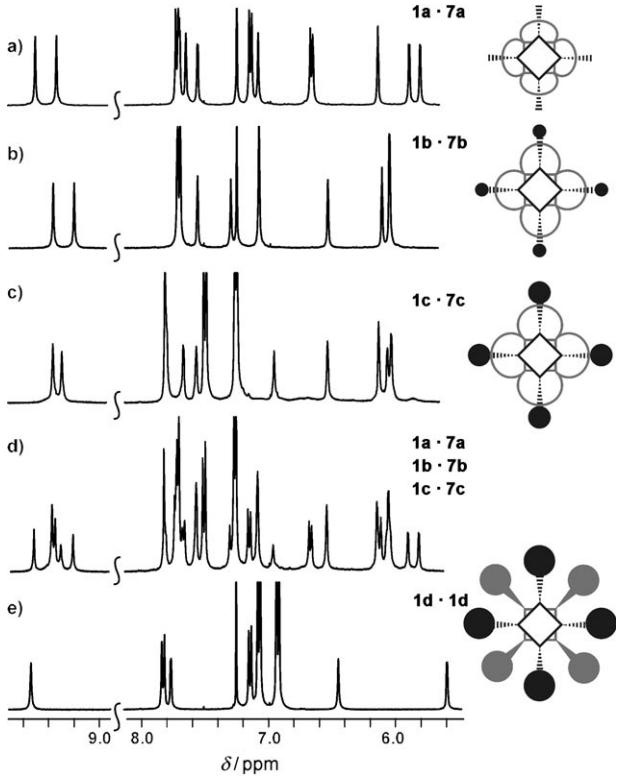
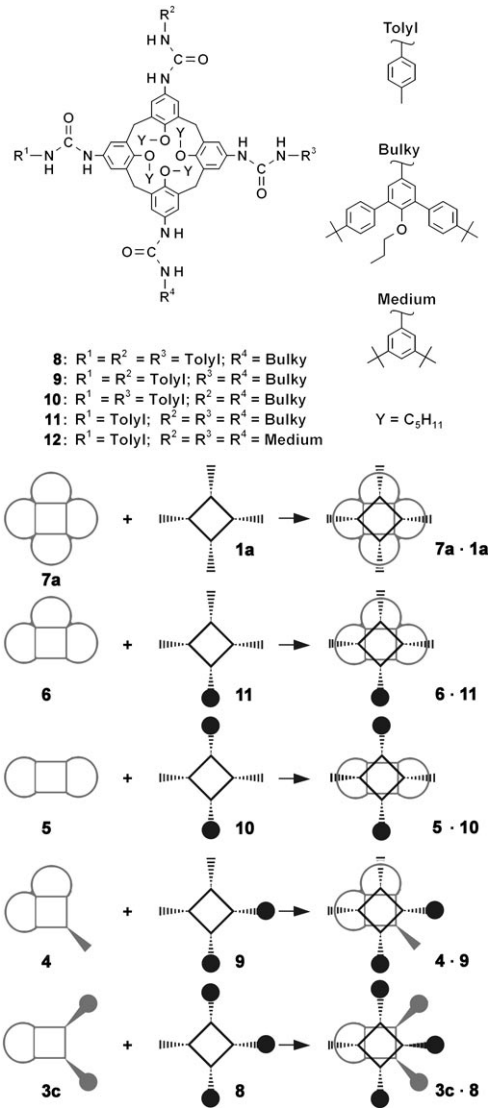


Figure 1. Sections of the ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of a) the heterodimer **1a·7a**, b) the heterodimer **1b·7b**, c) the heterodimer **1c·7c**, d) the mixture of heterodimers **1a·7a**, **1b·7b**, and **1c·7c**, and e) the homodimer **1d·7d**.

This can be easily explained by the rules mentioned above. Due to the first rule, the tetraloop derivatives **7a–c** cannot form dimers with each other, although the tendency to dimerize is peculiar to all tetraureas. From the three proposed partners **1a–c**, **7a** can form a capsule only with **1a** (Figure 1a), since the urea residues of **1b**,**c** are too large to pass through its loops (second rule). Therefore, **1a** and **7a** are completely consumed, forming a heterodimer. According to the same principle **1b** is paired with **7b**. Finally, the only partner remaining for **1c** is the tetraurea **7c** (Figure 1c). A mixture containing additionally the bulkiest tetraurea **1d** would contain additionally also its homodimer **7d·7d** (four dimers from 16 sterically possible combinations).[19]

Control by geometry: Selective dimerization can be also controlled by the number (or the position) of the loops of one calixarene and the number and position of the bulky residues of the partner (Scheme 2). In accordance to the rules described above the tetraloop derivative **7a**[20] can



Scheme 2. Schematic representation of the selective recognition controlled by geometry.

form heterodimers only with tetraurea **1a** containing four small residues. Consequently, a partner for the trisloop derivative **6**[3a] can possess only one bulky substituent, whereas the monoloop derivative **3c**[21] can dimerize with a tetraurea bearing three bulky residues. For the bisloop derivatives **4**[3a] and **5**,[3b] two bulky residues are potentially possible, provided they have the appropriate position.

Equimolar mixtures of the bisloop compound **5** with **9** or of bisloop compound **4** with **10** do not contain heterodimers. Their spectra correspond to the homodimers **9·9** and **10·10**, respectively, accompanied by broad signals for unpaired **4** or **5**. However, if these two solutions **5**/**9** and **4**/**10** are combined, the NMR spectrum is in total agreement with a mixture of the two heterodimers **4·9** and **5·10** (compare Figure S2, Supporting Information).

The tetraureacalix[4]arenes **1c** or **1d** bearing four (more or less) bulky substituents should not be able to form heterodimers with any of the loop-containing derivatives **3**–**7** with $n=10$, which can be demonstrated in a similar way. If only loop compounds are present as "potential partners", **1c** or **1d** always form only their homodimers, whereas the loop compounds remain unpaired.

Subtle effects and borderline cases: The simple picture described above is not entirely correct, when tetraurea molecules with loops of larger size ($n>10$) are studied. Although **1b** (with four medium-sized residues) does not form heterodimers with **7a** (containing four small loops),[22] the solution of the monoloop compound **3b** in $CDCl_3$ contains only the homodimer **3b·3b** after three days, as shown by the clear NMR spectrum in Figure 2. In the characteristic NH region

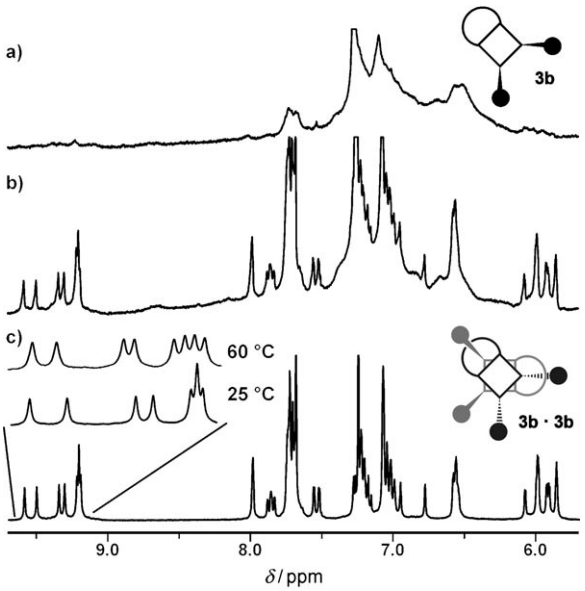


Figure 2. Sections of the ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of the monoloop derivative **3b** a) immediately after mixing, b) 1 day after mixing, and c) 3 days after mixing.

of the spectrum,[23] eight signals corresponding to the NH_α protons of the dimer can be clearly observed. This shows that the mutual penetration of a single loop with $n=10$ by a 3,5-di-*tert*-butylphenyl residue is obviously possible.

Much slower formation of heterodimers is observed when the bisloop compound **5** ($n=10$) is added to the homodimer **1b·1b**. Like the tetraloop compound **7a**, the bisloop analogue **5** cannot form homodimers due to overlapping loops. However, its tendency to dimerize is obviously strong enough to form heterodimers with **1b**, and after three weeks the signals of the homodimer **1b·1b** are practically completely replaced by those of the heterodimer **5·1b**.

This seeming "contradiction", the fact that **1b** can penetrate the two loops of **5** and not the four equally sized loops of **7a** can be understood by a higher flexibility of **5** in comparison to **7a**, and by a "pinched" cone conformation of **1b**, which allows its combination with the bisloop **5**, but is detrimental to the dimerization with **7a**, since in the said confor-

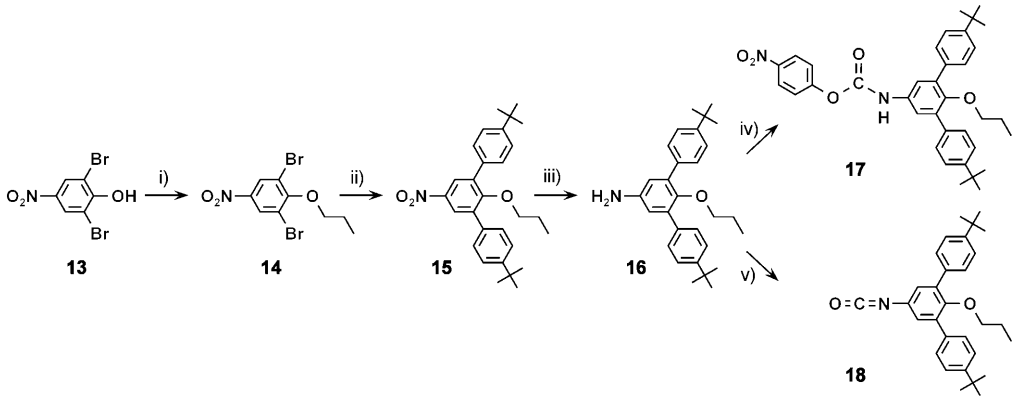
mation two of the di-*tert*-butylphenyl urea residues are bent outwards. The pinched cone conformation necessary for the passage of two opposite urea residues through two opposite loops hinders the passage of the two urea groups bent outwards through the remaining loops! The observation that heterodimers are not formed in the mixtures of **1b**/**4** and **1b**/**6** confirms this suggestion.

This explanation is additionally substantiated by the following observation. A 1:1 mixture of tetraureas **12** and **3b** contains only one heterodimer (exclusively!) immediately after mixing, since the homodimerization of **3b** is kinetically slower than the formation of **3b·12**, with the tolyl residue penetrating the loop. However, in the same measure, as **3b·3b** is slowly formed, also the homodimers **12·12** (two regioisomers), the two other regioisomeric heterodimers **3b·12** (with a bulky residue passing the loop) appear. This leads finally to a much more complicated NMR spectrum (see Figure S3, Supporting Information).

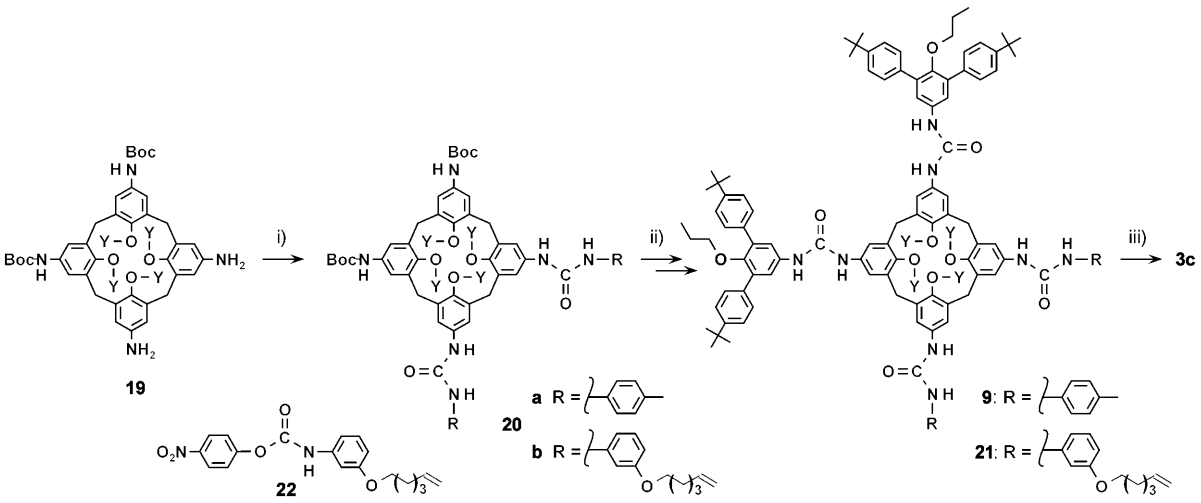
Syntheses: The synthesis of a bulky acylating agent necessary to prepare tetraureas **1c**, **3c**, and **8**–**11** is shown in Scheme 3. Alkylation of 2,6-dibromo-4-nitrophenol **13** with propyl iodide in the presence of K_2CO_3 afforded compound **14** in 95% yield. It was converted in the next step to **15** (76%) by Suzuki coupling with 4-*tert*-butylphenylboronic acid. The catalytic hydrogenation to **16** (100%), followed by its reaction with 4-nitrophenyl chloroformate finally gave the active urethane **17** in 85% yield. Isocyanate **18** was prepared in situ from the aniline **16** and triphosgene in toluene and was used without additional purification.

Tetraureas **8** and **10** were made from the known tritolyl urea monoamine[24] and 1,3-ditolylurea-2,4-diamine,[25] respectively, by acylation with isocyanate **18**.

The synthesis of the 1,2-di-bulky tetraurea **9** and the monoloop derivative **3c** is illustrated in Scheme 4. The amine **19**, *tert*-butoxycarbonyl (Boc)-protected in the 1,2-positions,[26] was reacted with tolyl isocyanate or with the active urethane **22** to give the di-ureas **20a** and **20b** both in 68% yield. Deprotection and subsequent acylation with iso-



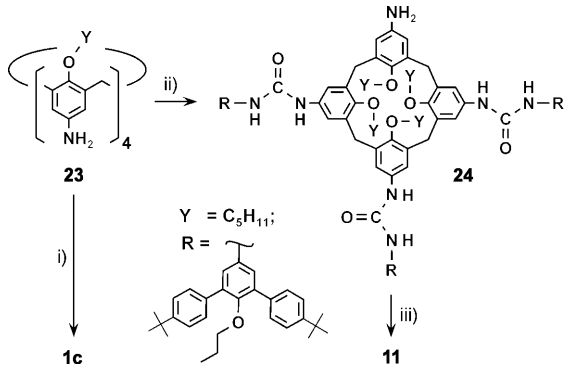
Scheme 3. Synthesis of a bulky acylating agent. i) PrI, K_2CO_3, CH_3CN; ii) 4-*tert*-butylphenylboronic acid; Na_2CO_3, $Pd(PPh_3)_4$, dioxane/water; iii) Raney-Ni, toluene/EtOH; iv) *p*-nitrophenyl chloroformate, THF/$CHCl_3$; v) triphosgene, toluene.



Scheme 4. Synthesis of the tetraureas **3b** and **9**. i) Tol-NCO, CH_2Cl_2 for **20a**; active urethane **22**, Et_3N, $CHCl_3$, reflux for **20b**; ii) trifluoroacetic acid (TFA), CH_2Cl_2; **18**, toluene; iii) for **21** Grubbs catalyst, CH_2Cl_2/C_6H_6; reduction (PtO_2).

cyanate **18** led to the tetraureas **9** (90%) and **21** (89%) with two bulky urea residues. Tetraurea **21** was finally converted to the monoloop derivative **3c** (54%) by olefin metathesis and subsequent hydrogenation.

The synthesis of the tetraureas **1c** and **11** started with the tetraamino calix[4]arene **23** (Scheme 5). Compound **1c** (89%) was obtained directly through the reaction of **23** with isocyanate **18**. The acylation with the active urethane **17**, which was used as a mild acylating agent since it allows trisubstituted products to be formed with higher yields without column purification, afforded the respective tri-urea monoamine derivative **24** (73%). In the last step, it was easily converted to **11** (76%) with tolyl isocyanate.



Scheme 5. Synthesis of the tetraureas **1c** and **11**. i) **18**, toluene; ii) **17**, Et_3N, $CHCl_3$, reflux; iii) Tol-NCO, CH_2Cl_2.

Conclusion

A simple rule for the dimerization of tetraurea calix[4]arenes emerges: a dimer cannot be formed if a bulky residue attached to the urea function has to pass (through) a loop connecting two adjacent urea functions. This rule has been extended and further differentiated. Four tetraurea calix[4]arenes bearing residues with increasing size were synthesized, which can distinguish three different tetraloop tetraurea calix[4]arenes. For tetraureacalix[4]arenes bearing one to three loops or bulky substituents examples were found for which the dimerization is controlled by this number and by their position. These results offer further possibilities to control the formation of dimers in mixtures of tetraureacalix[4]arenes. Their use for the construction of suitable building blocks by the covalent connection of appropriate tetraureacalix[4]arenes via their narrow rim finally will lead to the construction of well-defined assemblies under conditions suitable for the dimerization of tetraureacalix[4]arenes.

Experimental Section

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

As previously verified,[27] data for elemental analyses of organic calixarenes are often misleading, due to inclusion of solvent molecules, and cannot be considered appropriate criteria of purity. However, the identities of the reported compounds were unambiguously established by their spectroscopic data.

Compounds **1a**,[9] **1d**,[28] **3a**,[4] **4**,[3a] **5**,[3b,c] **6**,[3a] **7a**,[20] **7b**,[3c] and **7c**[29] were prepared according to previously reported procedures.

2,6-Dibromo-1-propoxy-4-nitrobenzene (14): A mixture of 2,6-dibromo-4-nitrophenol **13** (7.00 g, 23.6 mmol), K_2CO_3 (16.3 g, 118 mmol), and propyl bromide (14.5 g, 10.7 mL, 118 mmol) was refluxed for 4 days in CH_3CN (250 mL). When the alkylation was complete, the color of the mixture changed from bright orange to pale yellow (the conversion was controlled by TLC, $CHCl_3$/hexane 1:3). Water (20 mL) was added to dissolve K_2CO_3 and CH_3CN was evaporated under reduced pressure. Then water (150 mL) was added to the residue, the precipitate was filtered, washed with water, and dried in air. Compound **14** (7.59 g, 95%) was obtained as a yellow solid. M.p. 66–68°C; ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 1.11$ (t, $^3J(H,H) = 7.3$ Hz, 3H; CH_3), 1.88–1.97 (m, 2H; CH_2), 4.06 (t, $^3J(H,H) = 6.6$ Hz, 2H; OCH_2), 8.40 ppm (s, 2H; Ar*H*); MS (FD): *m*/*z* (%): calcd for $C_9H_9Br_2NO_3$: 338.98; found: 339.0 (100) $[M]^+$.

2,6-Bis(4-*tert*-butylphenyl)-1-propoxy-4-nitrobenzene (15): Nitrogen was bubbled for 1 h through a solution of **14** (3.17 g, 9.35 mmol), 4-*tert*-butylphenylboronic acid (4.99 g, 28.1 mmol), and Na_2CO_3 (8.92 g, 84.2 mmol) in 1,4-dioxane/water (300:80 mL); then $Pd(PPh_3)_4$ (1.62 g, 1.40 mmol) was added and the reaction mixture was stirred at 75°C for 24 h, cooled down and evaporated. The residue was dissolved in dichloromethane (200 mL), washed with water (3×100 mL), and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by column chromatography ($CHCl_3$/hexane 1:3). Compound **15** (3.17 g, 76%) was obtained as a light-yellow powder. M.p. 130–132°C; ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 0.51$ (t, $^3J(H,H) = 7.6$ Hz, 3H; CH_3), 1.17–1.24 (m, 2H; CH_2), 1.37 (s, 18H; $C(CH_3)_3$), 3.25 (t, $^3J(H,H) = 6.4$ Hz, 2H; OCH_2), 7.47 (d, $^3J(H,H) = 8.3$ Hz, 4H; Ar*H*), 7.54 (d, $^3J(H,H) = 8.3$ Hz, 4H; Ar*H*), 8.21 ppm (s, 2H; Ar*H*); MS (FD): *m*/*z* (%): calcd for $C_{29}H_{35}NO_3$: 445.61; found: 445.1 (100) $[M]^+$.

2,6-Bis(4-*tert*-butylphenyl)-1-propoxy-4-aminobenzene (16): The terphenyl **15** (0.50 g, 1.12 mmol) was dissolved in toluene/ethanol (20:5 mL) and hydrogenated for 8 h at room temperature in the presence of Raney-Ni. The catalyst was filtered off and washed with toluene (2×10 mL). The combined organic solutions were evaporated under reduced pressure. Amine **16** (0.47 g, 100%) was obtained as a light-brown powder. M.p. 117–119°C; ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 0.47$ (t, $^3J(H,H) = 7.3$ Hz, 3H; CH_3), 1.09–1.17 (m, 2H; CH_2), 1.35 (s, 18H; $C(CH_3)_3$), 3.08 (t, $^3J(H,H) = 6.4$ Hz, 2H; OCH_2), 3.59 (br s, 2H; NH_2), 6.67 (s, 2H; Ar*H*), 7.40 (d, $^3J(H,H) = 8.3$ Hz, 4H; Ar*H*), 7.52 ppm (d, $^3J(H,H) = 8.3$ Hz, 4H; Ar*H*); MS (FD): *m*/*z* (%): calcd for $C_{29}H_{37}NO$: 415.62; found: 415.1 (100) $[M]^+$.

4-Nitrophenyl-*N*-[3,5-bis(4-*tert*-butylphenyl)-4-propoxyphenyl]carbamate (17): A solution of amine **16** (0.47 g, 1.13 mmol) and 4-nitrophenyl chloroformate (0.30 g, 1.47 mmol) in $CHCl_3$/THF 1:1 (50 mL) was refluxed for 12 h. The solvents were evaporated and the product was precipitated from Et_2O/hexane. Active urethane **17** (0.56 g, 85%) was obtained as light-yellow flakes. M.p. 171–173°C; ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 0.50$ (t, $^3J(H,H) = 7.3$ Hz, 3H; CH_3), 1.14–1.22 (m, 2H; CH_2), 1.35 (s, 18H; $C(CH_3)_3$), 3.15 (t, $^3J(H,H) = 6.4$ Hz, 2H; OCH_2), 6.95 (br s, 1H; N*H*), 7.38–7.43 (m, 8H; Ar*H*), 7.54 (d, $^3J(H,H) = 8.3$ Hz, 4H; Ar*H*), 8.27 ppm (d, $^3J(H,H) = 9.3$ Hz, 2H; Ar*H*); MS (ESI): *m*/*z* (%): calcd for $C_{36}H_{40}N_2O_5$: 580.73; found: 603.3 (12) $[M+Na]^+$, 1183.7 (17) $[2M+Na]^+$, 1765.0 (26) $[3M+Na]^+$.

2,6-Bis(4-*tert*-butylphenyl)-1-propoxy-4-isocyanatobenzene (18): Triphosgene (0.24 g, 0.79 mmol) was added to the solution of aniline **16** (0.33 g, 0.79 mmol) in toluene (20 mL) under nitrogen. The solution was stirred for 0.5 h at room temperature, 1 h at 50°C, and 1 h at 80°C. The toluene

was removed under reduced pressure (bath temperature: ~70 °C), toluene (20 mL) was added and evaporated once again. The isocyanate **18** obtained in this way was used without further purification.

5,11,17,23-Tetrakis[3,5-bis(4-*tert*-butylphenyl)-4-propoxyphenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (1c): Tetraamino calix[4]arene **23**[30] (0.10 g, 0.13 mmol) was added to a solution of freshly prepared isocyanate **18** (0.79 mmol) in toluene (20 mL) under nitrogen and the mixture was stirred overnight at room temperature. Then methanol (70 mL) was added, the precipitate was filtered, and dried in air. Tetraurea **1c** (0.30, 89%) was obtained as a white crystalline powder. M.p. 290–292 °C (dec); ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.48 (t, ^3J(H,H) = 7.3 Hz, 12H; CH_3), 0.95 (m, 12H; TolCH_3), 1.06–1.14 (m, 8H; CH_2), 1.30 (s, 72H; C(CH_3)$_3$), 1.41 (m, 16H; CH_2), 1.92 (m, 8H; CH_2), 3.01–3.07 (m, 12H; ArCH_2Ar, OCH_2), 3.85 (m, 8H; OCH_2), 4.43 (d, ^2J(H,H) = 13.2 Hz, 4H; ArCH_2Ar), 6.80 (s, 8H; ArH), 7.35–7.37 (m, 24H; ArH), 7.45 (d, ^2J(H,H) = 8.3 Hz, 16H; ArH), 7.56 (s, 4H; NH), 7.62 ppm (s, 4H; NH); MS (ESI): *m*/*z* (%): calcd for $C_{168}H_{208}N_8O_{12}$: 2531.58; found: 2553.7 (38) [*M*+Na]$^+$, 1288.4 (100) [*M*+Na+H]$^{2+}$.

5,11,17-Tris[4-methylphenylureido]-23-[3,5-bis(4-*tert*-butylphenyl)-4-propoxy-phenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (8): By following the typical procedure for **1c**, product **8** was formed (84%) as a white powder by starting from the respective tritolyl urea.[24] M.p. 230–233 °C (dec); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.42 (t, ^3J(H,H) = 7.2 Hz, 3H; OCH$_2$CH$_2$CH_3), 0.93 (m, 12H; CH_3), 1.03–1.15 (m, 2H; OCH$_2$CH_2CH$_3$), 1.30 (s, 18H; C(CH_3)$_3$), 1.39 (m, 16H; CH_2), 1.90 (m, 8H; CH_2), 2.15 (s, 3H; TolCH_3), 2.20 (s, 6H; TolCH_3), 3.03 (t, ^3J(H,H) = 6.0 Hz, 2H; OCH_2CH$_2$CH$_3$), 3.09 (d, ^2J(H,H) = 12.8 Hz, 4H; ArCH_2Ar), 3.78 (t, ^3J(H,H) = 7.0 Hz, 4H; OCH_2), 3.84 (t, ^3J(H,H) = 7.0 Hz, 4H; OCH_2), 4.33 (d, ^2J(H,H) = 12.8 Hz, 4H; ArCH_2Ar), 6.72 (s, 2H; ArH), 6.75 (s, 2H; ArH), 6.87 (m, 4H; ArH), 6.90 (d, ^3J(H,H) = 8.3 Hz, 2H; Tol$H$), 7.00 (d, ^3J(H,H) = 8.3 Hz, 4H; Tol$H$), 7.17 (d, ^3J(H,H) = 8.3 Hz, 2H; Tol$H$), 7.22 (d, ^3J(H,H) = 8.3 Hz, 4H; Tol$H$), 7.28 (s, 2H; ArH), 7.44 (m, 8H; ArH), 8.05 (s, 1H; NH), 8.17–8.19 (m, 4H; NH), 8.23 (s, 2H; NH), 8.32 ppm (s, 1H; NH); MS (ESI): *m*/*z* (%): calcd for $C_{102}H_{124}N_8O_9$: 1606.17; found: 1628.9 (100) [*M*+Na]$^+$.

5,17-Bis[4-methylphenylureido]-11,23-bis[3,5-bis(4-*tert*-butylphenyl)-4-propoxy-phenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (10): By following the typical procedure described for **1c**, product **10** was formed (84%) by starting from the respective 1,3-ditolyl urea[25] as a white crystalline powder. M.p. 252–255 °C (dec); ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.49 (t, ^3J(H,H) = 7.3 Hz, 6H; CH_3), 0.96 (t, ^3J(H,H) = 7.1 Hz, 12H; CH_3), 1.07–1.16 (m, 4H; CH_2), 1.32 (s, 36H; C(CH_3)$_3$), 1.44 (m, 16H; CH_2), 1.88–1.96 (m, 8H; CH_2), 2.19 (s, 6H; TolCH_3), 3.02–3.07 (m, 8H; ArCH_2Ar, OCH_2), 3.79 (t, ^3J(H,H) = 7.6 Hz, 4H; OCH_2), 3.92 (t, ^3J(H,H) = 7.6 Hz, 4H; OCH_2), 4.43 (d, ^2J(H,H) = 12.7 Hz, 4H; ArCH_2Ar), 6.68 (s, 4H; ArH), 6.91 (d, ^2J(H,H) = 8.3 Hz, 4H; Tol$H$), 6.94 (s, 4H; ArH), 7.17 (d, ^2J(H,H) = 8.3 Hz, 4H; Tol$H$), 7.31 (s, 2H; NH), 7.38–7.40 (m, 12H; ArH), 7.46 (s, 2H; NH), 7.48 (d, ^2J(H,H) = 8.3 Hz, 8H; ArH), 7.64 (s, 2H; NH), 7.68 ppm (s, 2H; NH); MS (ESI): *m*/*z* (%): calcd for $C_{124}H_{152}N_8O_{10}$: 1914.64; found: 1937.4 (100) [*M*+Na]$^+$.

5,11-Bis(*tert*-butylcarbamoyl)-17,23-bis(4-methylphenylureido)-25,26,27,28-tetrapentoxycalix[4]arene (20a): Tolyl isocyanate (0.17 g, 1.29 mmol) was added to a solution of diamino calix[4]arene **19**[26] (0.42 g, 0.43 mmol) in dichloromethane (20 mL) and the mixture was stirred at room temperature overnight. Then methanol (10 mL) was added and the solvents were evaporated. The residue was treated with acetonitrile (15 mL) and the resulting precipitate was filtered off and purified by column chromatography (THF/hexane 1:3) to give **20a** (0.36 g, 68%) as a white powder. M.p. 187–190 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.93 (m, 12H; CH_3), 1.37 (m, 34H; CH_2, C-(CH_3)$_3$), 1.89 (m, 8H; CH_2), 2.21 (s, 6H; TolCH_3), 3.05 (m, 4H; ArCH_2Ar), 3.80 (m, 8H; OCH_2), 4.31 (m, 4H; ArCH_2Ar), 6.78 (m, 8H; ArH), 7.03 (d, ^3J(H,H) = 8.3 Hz, 4H; Tol$H$), 7.25 (d, ^3J(H,H) = 8.3 Hz, 4H; Tol$H$), 8.14 (s, 2H; NH), 8.18 (s, 2H; NH), 8.76 ppm (brs, 2H; NH); MS (ESI): *m*/*z* (%): calcd for $C_{74}H_{98}N_6O_{10}$: 1231.64; found: 1253.8 (100) [*M*+Na]$^+$, 2485.5 (23) [2*M*+Na]$^+$.

5,11-Bis(*tert*-butylcarbamoyl)-17,23-bis[3-(hex-5-enyloxy)phenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (20b): A solution of diamino calix[4]arene **19**[26] (0.41 g, 0.42 mmol), active urethane **22**[4] (0.45 g, 1.27 mmol), and Et$_3$N (0.2 mL) in CHCl$_3$ (25 mL) was refluxed for 3 days. The reaction mixture was diluted with chloroform (50 mL), washed with a 15% aqueous solution of K$_2$CO$_3$ (4×20 mL) and then with water (3×20 mL), dried (MgSO$_4$), and evaporated. The residue was purified by column chromatography (ethyl acetate/hexane 1:4). Calix[4]-arene **20b** (0.40 g, 68%) was obtained as a white powder. M.p. 165–167 °C (dec); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.93 (m, 12H; CH_3), 1.37 (m, 34H; CH_2, C(CH_3)$_3$), 1.45–1.52 (m, 4H; CH_2), 1.66–1.73 (m, 4H; CH_2), 1.88–1.91 (m, 8H; CH_2), 2.04–2.10 (m, 4H; CH_2), 3.01 (d, ^2J(H,H) = 13.2 Hz, 1H; ArCH_2Ar), 3.06 (d, ^2J(H,H) = 13.2 Hz, 2H; ArCH_2Ar), 3.11 (d, ^2J(H,H) = 13.2 Hz, 1H; ArCH_2Ar), 3.77–3.83 (m, 8H; OCH_2), 3.91 (t, ^3J(H,H) = 6.4 Hz, 4H; OCH$_2$), 4.28–4.34 (m, 4H; ArCH_2Ar), 4.94–5.04 (m, 4H; CH=CH_2), 5.76–5.86 (m, 2H; CH=CH$_2$), 6.49 (d×d, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.0 Hz, 2H; ArH), 6.74–6.81 (m, 10H; ArH), 7.08–7.12 (m, 4H; ArH), 8.17 (s, 2H; NH), 8.29 (s, 2H; NH), 8.75 ppm (brs, 2H; NH); MS (ESI): *m*/*z* (%): calcd for $C_{84}H_{114}N_6O_{12}$: 1399.88; found: 1421.0 (100) [*M*+Na]$^+$.

5,11-Bis[3,5-bis(4-*tert*-butylphenyl)-4-propoxyphenylureido]-17,23-bis[3-(hex-5-enyloxy)phenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (21)

Boc deprotection: A solution of **20b** (0.39 g, 0.28 mmol) and TFA (1 mL) in CH$_2$Cl$_2$ (25 mL) was stirred for 2 h at room temperature. Then water (10 mL) was added and the resulting organic layer was separated, washed with a 10% aqueous solution of K$_2$CO$_3$ (2×10 mL) and with water (3×10 mL), dried (MgSO$_4$), and evaporated to give 5,11-diamino-17,23-bis-[3-(hex-5-enyloxy)phenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (0.31 g, 94%) as light-brown solid. M.p. 150–155 °C (dec); ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.95 (m, 12H; CH_3), 1.40 (m, 16H; CH_2), 1.49–1.57 (m, 4H; CH_2), 1.69–1.76 (m, 4H; CH_2), 1.85–1.90 (m, 8H; CH_2), 2.06–2.11 (m, 4H; CH_2), 2.50 (brs, 4H; NH_2),2.81 (d, ^2J(H,H) = 13.2 Hz, 1H; ArCH_2Ar), 2.94 (d, ^2J(H,H) = 13.2 Hz, 2H; ArCH_2Ar), 3.03 (d, ^2J(H,H) = 13.2 Hz, 1H; ArCH_2Ar), 3.73–3.84 (m, 8H; OCH_2), 3.88 (t, ^3J(H,H) = 6.4 Hz, 4H; OCH$_2$), 4.28 (d, ^2J(H,H) = 13.2 Hz, 1H; ArCH_2Ar), 4.34 (d, ^2J(H,H) = 13.2 Hz, 2H; ArCH_2Ar), 4.41 (d, ^2J(H,H) = 13.2 Hz, 1H; ArCH_2Ar), 4.90–5.01 (m, 4H; CH=CH_2), 5.75–5.85 (m, 2H; CH=CH$_2$), 5.93–5.95 (m, 4H; ArH), 6.42 (d×d, ^3J(H,H) = 8.3, ^4J(H,H) = 2.0 Hz, 2H; ArH), 6.50 (s, 2H; ArH), 6.77–6.79 (m, 4H; ArH), 7.01 (t, ^3J(H,H) = 8.1 Hz, 2H; ArH), 7.25 (s, 2H; ArH), 7.42 (s, 2H; NH), 7.69 ppm (s, 2H; NH); MS (ESI): *m*/*z* (%): calcd for $C_{74}H_{98}N_6O_8$: 1199.64; found: 1221.7 (100) [*M*+Na]$^+$.

Acylation: The diamino calix[4]arene (0.29 g, 0.24 mmol) was added to a solution of freshly prepared isocyanate **18** (0.85 mmol) in toluene (20 mL) under nitrogen. The reaction mixture was stirred overnight at room temperature. Then methanol (50 mL) was added to the solution, the formed precipitate was filtered off, washed with methanol, and dried in air. Tetraurea **21** (0.48 g, 95%) was obtained as a white crystalline powder. M.p. 282–284 °C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.49 (t, ^3J(H,H) = 7.3 Hz, 6H; CH$_3$), 0.96 (m, 12H; CH_3), 1.07–1.14 (m, 4H; CH_2), 1.33 (s, 36H; C(CH_3)$_3$), 1.42–1.44 (m, 16H; CH_2), 1.48–1.55 (m, 4H; CH_2), 1.67–1.74 (m, 4H; CH_2), 1.94 (m, 8H; CH_2), 2.04–2.09 (m, 4H; CH_2), 3.04–3.07 (m, 8H; ArCH_2Ar, OCH_2), 3.82–3.88 (m, 12H; OCH$_2$), 4.43 (d, ^2J(H,H) = 13.2 Hz, 4H; ArCH_2Ar), 4.88–5.00 (m, 4H; CH=CH_2), 5.73–5.83 (m, 2H; CH=CH$_2$), 6.30 (d×d, ^3J(H,H) = 8.3, ^4J(H,H) = 2.0 Hz, 2H; ArH), 6.54 (d, ^3J(H,H) = 7.8 Hz, 2H; ArH), 6.77–6.83 (m, 10H; ArH), 7.31 (s, 2H; ArH), 7.34 (s, 4H; ArH), 7.40 (d, ^3J(H,H) = 8.3 Hz, 8H; ArH), 7.48–7.51 (m, 14H; NH, ArH), 7.56 (s, 2H; NH), 7.59 ppm (s, 2H; NH); MS (ESI): *m*/*z* (%): calcd for $C_{134}H_{168}N_8O_{12}$: 2082.88; found: 2105.4 (23) [*M*+Na]$^+$.

5,11-Bis(4-methylphenylureido)-17,23-bis[3,5-bis(4-*tert*-butylphenyl)-4-propoxy-phenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (9): This product was prepared from **20a** by following the typical procedure described for **21**.

Boc deprotection: 5,11-Diamino-17,23-bis-(4-metyl-phenylureido)-25,26,27,28-tetrapentoxy-calix[4]arene (90%) was obtained as a brownish powder. M.p. 190–195 °C (dec); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.92 (t, ^3J(H,H) = 7.0 Hz, 12H; CH_3), 1.37 (m, 16H; CH_2), 1.87 (m, 8H; CH_2), 2.22 (s, 6H; TolCH_3), 2.80 (d, ^2J(H,H) = 12.4 Hz, 1H;

ArCH_2Ar), 2.94 (d, ^2J(H,H) = 12.8 Hz, 2H; ArCH_2Ar), 3.08 (d, ^2J(H,H) = 12.8 Hz, 1H; ArCH_2Ar), 3.69 (m, 4H; OCH_2), 3.79 (m, 4H; OCH_2), 4.16 (d, ^2J(H,H) = 12.4 Hz, 1H; ArCH_2Ar), 4.25 (d, ^2J(H,H) = 12.8 Hz, 2H; ArCH_2Ar), 4.31 (br s, 4H; NH_2), 4.33 (d, ^2J(H,H) = 12.8 Hz, 1H; ArCH_2Ar), 5.96 (s, 4H; Ar*H*), 6.72 (d, ^4J(H,H) = 2.4 Hz, 2H; Ar*H*), 6.78 (d, ^4J(H,H) = 2.4 Hz, 2H; Ar*H*), 7.04 (d, ^3J(H,H) = 8.2 Hz, 4H; Tol*H*), 7.26 (d, ^3J(H,H) = 8.2 Hz, 4H; Tol*H*), 8.16 (s, 2H; N*H*), 8.23 ppm (s, 2H; N*H*); MS (ESI): *m/z* (%): calcd for $C_{64}H_{82}N_6O_6$: 1031.40; found: 1053.8 (100) $[M+Na]^+$, 2085.2 (12) $[2M+Na]^+$.

Acylation: Tetraurea **9** (84%) was obtained as a beige solid. M.p. 290–292°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 75°C): δ = 0.45 (t, ^3J(H,H) = 7.2 Hz, 6H; CH_3), 0.95 (t, ^3J(H,H) = 7.0 Hz, 12H; CH_3), 1.10 (m, 4H; CH_2), 1.33 (s, 36H; C(CH_3)$_3$), 1.41 (m, 16H; CH_2), 1.90 (m, 8H; CH_2), 2.18 (s, 6H; TolCH_3), 3.09 (t, ^3J(H,H) = 6.2 Hz, 4H; OCH_2), 3.10 (d, ^2J(H,H) = 12.8 Hz, 4H; ArCH_2Ar), 3.87 (t, ^3J(H,H) = 7.2 Hz, 8H; OCH_2), 4.39 (d, ^2J(H,H) = 12.8 Hz, 4H; ArCH_2Ar), 6.78 (m, 6H; Ar*H*), 6.84 (br d, 2H; Ar*H*), 6.92 (d, ^3J(H,H) = 8.1 Hz, 4H; Tol*H*), 7.19 (d, ^3J(H,H) = 8.1 Hz, 4H; Tol*H*), 7.29 (s, 4H; Ar*H*), 7.44 (m, 16H; Ar*H*), 7.92 (s, 2H; N*H*), 8.01 (s, 2H; N*H*), 8.04 (s, 2H; N*H*), 8.18 ppm (s, 2H; N*H*); MS (ESI): *m/z* (%): calcd for $C_{102}H_{124}N_8O_9$: 1914.64; found: 980.1 (21) $[M+Na+H]^{2+}$, 1937.2 (100) $[M+Na]^+$.

Monoloop calix[4]arene 3c: A solution of tetraurea **21** (0.47 g, 0.23 mmol) and tetratosyl urea **2** (0.36 g, 0.25 mmol) in CH_2Cl_2/benzene 2:1 (450 mL) was stirred for 12 h at room temperature. Then nitrogen was bubbled through the solution for 1 h, Grubbs's catalyst (1st generation; 0.037 g, 0.045 mmol) was added and the stirring was continued for 2 days. After the addition of Et_3N (1.5 mL), the reaction mixture was stirred for 1 h and then the solvents were evaporated. The residue was purified by column chromatography (ethyl acetate/hexane 1:3 followed by 1:1). The white solid obtained after evaporation was dissolved in THF (25 mL) and hydrogenated over 6 h at room temperature in the presence of the Pt_2O (0.05 g). The catalyst was filtered and the solvent was evaporated. The residue was reprecipitated with methanol from $CHCl_3$/acetone solution to give **3c** (0.28 g, 54%) as a white powder. M.p. 258–260°C (dec); ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ = 0.49 (t, ^3J(H,H) = 7.3 Hz, 6H; CH_3), 0.96 (m, 12H; CH_3), 1.07–1.16 (m, 4H; CH_2), 1.32 (s, 44H; C-(CH_3)$_3$, CH_2), 1.42–1.46 (m, 16H; CH_2), 1.68–1.74 (m, 8H; CH_2), 1.94 (m, 8H; CH_2), 3.03–3.08 (m, 8H; ArCH_2Ar, OCH_2), 3.83–3.88 (m, 12H; OCH_2), 4.43 (d, ^2J(H,H) = 13.2 Hz, 4H; ArCH_2Ar), 6.30 (d × d, ^3J(H,H) = 8.3, ^4J(H,H) = 2.0 Hz, 2H; Ar*H*), 6.65–6.70 (m, 4H; Ar*H*), 6.80–6.84 (m, 6H; Ar*H*), 6.92 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar*H*), 7.15 (s, 2H; Ar*H*), 7.33 (s, 4H; Ar*H*), 7.39 (d, ^3J(H,H) = 8.3 Hz, 8H; Ar*H*), 7.48 (d, ^3J(H,H) = 8.3 Hz, 8H; Ar*H*), 7.50 (s, 2H; N*H*), 7.52 (s, 4H; N*H*), 7.61 ppm (s, 2H; N*H*); MS (ESI): *m/z* (%): calcd for $C_{132}H_{166}N_8O_{12}$: 2056.84; found: 2079.2 (100) $[M+Na]^+$.

5-Amino-11,17,23-tris[3,5-bis(4-*tert*-butylphenyl)-4-propoxyphenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (24): A solution of tetraamino calix[4]arene **23**[30] (0.10 g, 0.13 mmol), active urethane **17** (0.34 g, 0.59 mmol), and Et_3N (0.2 mL) in $CHCl_3$ (15 mL) was refluxed for 2 days. The solvent was evaporated and the residue was triturated with MeOH (50 mL). The formed precipitate was filtered off and dried in air. Calix[4]arene **24** (0.20 g, 73%) was obtained as a pale-brown powder. M.p. 237–239°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 100°C): δ = 0.42–0.47 (m, 9H; CH_3), 0.94 (m, 12H; CH_3), 1.06–1.13 (m, 6H; CH_2), 1.32 (s, 54H; C(CH_3)$_3$), 1.41 (m, 16H; CH_2), 1.87 (m, 8H; CH_2), 2.97 (d, ^2J(H,H) = 13.2 Hz, 2H; ArCH_2Ar), 3.07–3.13 (m, 8H; OCH_2, ArCH_2Ar), 3.78–3.91 (m, 8H; OCH_2), 3.98 (br s, 2H; NH_2), 4.32 (d, ^2J(H,H) = 13.2 Hz, 2H; ArCH_2Ar), 4.39 (d, ^2J(H,H) = 13.2 Hz, 2H; ArCH_2Ar), 6.01 (s, 2H; Ar*H*), 6.72 (d, ^4J(H,H) = 2.4 Hz, 2H; Ar*H*), 6.77 (s, 2H; Ar*H*), 6.81 (d, ^4J(H,H) = 2.4 Hz, 2H; Ar*H*), 7.29 (s, 4H; Ar*H*), 7.32 (s, 2H; Ar*H*), 7.39–7.50 (m, 24H; Ar*H*), 7.89 (s, 2H; N*H*), 8.00 (s, 1H; N*H*), 8.08 (s, 1H; N*H*), 8.11 ppm (s, 2H; N*H*); MS (ESI): *m/z* (%): calcd for $C_{138}H_{173}N_7O_{10}$: 2089.96; found: 2112.4 (100) $[M+Na]^+$.

5-[4-Methylphenylureido]-11,17,23-tris[3,5-bis(4-*tert*-butylphenyl)-4-propoxy-phenylureido]-25,26,27,28-tetrapentoxycalix[4]arene (11): By starting from the tri-urea **24** and tolyl isocyanate, the typical procedure described for **1c** produced **8** (76%) as a white powder. M.p. 269–270°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 75°C): δ = 0.41–0.46 (m, 9H; CH_3), 0.94 (m, 12H; CH_3), 1.06–1.11 (m, 6H; CH_2), 1.30 (s, 54H; C(CH_3)$_3$), 1.41 (m, 16H; CH_2), 1.89 (br s, 8H; CH_2), 2.16 (s, 3H; TolCH_3), 3.05–3.12 (m, 10H; OCH_2, ArCH_2Ar), 3.82–3.90 (m, 8H; OCH_2), 4.38 (d, ^2J(H,H) = 12.7 Hz, 4H; ArCH_2Ar), 6.75 (s, 2H; Ar*H*), 6.77 (s, 2H; Ar*H*), 6.80 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar*H*), 6.85 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar*H*), 6.90 (d, ^3J(H,H) = 8.3 Hz, 2H; Tol*H*), 7.17 (d, ^3J(H,H) = 8.3 Hz, 2H; Tol*H*), 7.28 (s, 2H; Ar*H*), 7.29 (s, 4H; Ar*H*), 7.39–7.46 (m, 24H; Ar*H*), 7.92 (s, 1H; N*H*), 8.00 (s, 1H; N*H*), 8.03 (s, 3H; N*H*), 8.18 ppm (s, 3H; N*H*); MS (ESI): *m/z* (%): calcd for $C_{146}H_{180}N_8O_{11}$: 2223.11; found: 2245.4 (100) $[M+Na]^+$.

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