Calixarenes as Stoppers in Rotaxanes

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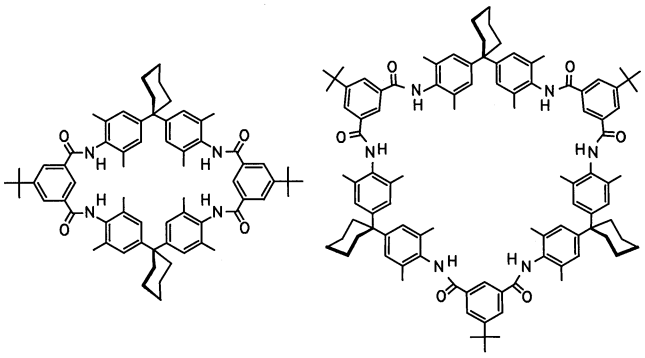
The synthesis of the amide-based rotaxane **7a** bearing calix[4]arene blocking groups is described for the first time. While rotaxane formation fails if a calix[4]arene is functionalized at the upper rim with only an amino or methylamino group lakking any spacer, the prolonged amine **5a** works successfully as stopper unit preventing dethreading of the dimeric wheel **1a** by its size. Rotaxane formation of **8b** was observed only by MALDI-TOF mass spectrometry of the reaction mixture of the amine **5b**, the axle **6** and **1a**. With the larger trimeric wheel **1b** no stable rotaxane could be obtained. It either does not act as a concave template or its opening is too wide, even for the bulky calixarene stoppers.

Introduction

While Harrison's statistical[1] and Schill's multistep[2] rotaxane synthesis were considered laboratory curiosities, in 1983 Sauvage et al.[3] and in 1989 Stoddart et al.[4] introduced template supported strategies[5] for the synthesis of catenanes, and consequently the related rotaxanes became accessible in preparative yields, too. We applied a non-ionic template synthesis[6] to get amide-based rotaxanes with up to 48% yield[7]. Beside our interest in preparing covalently linked rotaxanes[7][8b][9] we aim at testing the flexibility of the template synthesis through structural modification. Recently, we showed the tolerance of the non-ionic concave template towards structural changes of the center part of the axle[8][9][10]. Now we concentrate on enlargements of the wheel. Moreover we are interested in the introduction of additional supramolecular functionality in rotaxane synthesis. Within this scope we synthesized a rotaxane bearing two porphyrin units as stoppers; its di-Zn^{2+} complex could be isolated[11].

Herein we want to employ calix[4]arenes as stopper units, as these are, according to force-field calculations and space-filling models, sterically sufficiently demanding and their solubility in organic solvents can be manipulated by affixing appropriate substituents. Moreover, they show, if functionalized with suitable groups, complexation properties towards metal cations, anions and neutral molecules[12]. It is therefore surprising that so far calixarenes have not been used as stoppers in any of the rotaxane types known.

To approach this aim, we first functionalized calix[4]arenes on the lower rim with four alkane chains in order to fix the cone conformation and to guarantee good solubility, not only for the calixarene building block but also for the axle and rotaxane products. The minimum length of the thread between the stopper units, that was necessary to prevent steric hindrance during the rotaxane formation, was intended to be determined by variation of the spacer between the calixarene ring and the amino group needed for the reaction with the diacid dichlorides **2** and **6**.



1a **1b**

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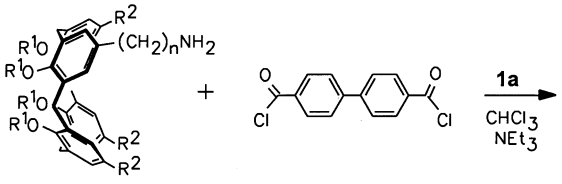
First the "dimeric" macrocycle **1a** was employed in the rotaxane synthesis[8]. It was also intended to test if the hitherto unknown "trimeric" macrocycle **1b** would be able to act as a large wheel for amide-based rotaxanes. Models and force field calculations show that the opening of the ring is small enough to prevent dethreading off the calix stoppers. The more interesting question was if the "trimeric" wheel would allow molecular recognition and threading by the molecular piercing mechanism proposed for the "dimeric" case[10].

Synthesis

"Dimeric" and "trimeric" macrocycles **1a** and **1b** were obtained in a one-pot-synthesis[13] from 5-*tert*-butylisophthaloyl dichloride and 1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane. In contrast to the isophthaloyl dichloride employed in the cyclization[14], the *tert*-butyl analogue has the advantage to prevent here any formation of catenane products due to the presence of the bulky *tert*-butyl groups and the yields of **1a** and **1b** could therefore be raised to 20% and 25%, respectively.

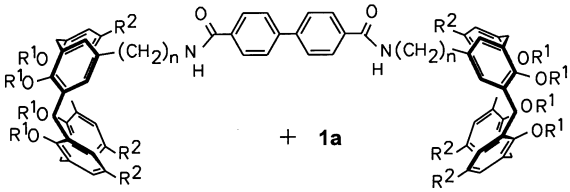
Both **1a** and **1b** were tried as the host part, while the acid dichlorides **2** and **6** were added as guests to form the supramolecular intermediates[10]. The axle **2** was supposed to be long enough to keep the two stopper groups away from each other, but also the 3-chlorosulfonylbenzoyl chloride **6**, that was an excellent guest in other rotaxane synthesis[8c], was tested.

The tetra-*n*-pentyl ether of *p*-*tert*-calix[4]arene in the *cone* conformation was *ipso*-nitrated on the upper rim to yield the mononitro compound **11** in 76% which was subsequently reduced by H_2 or N_2H_4 and Raney-Ni to the amine **3a** (85−90%). This was added together with NEt_3 to a 1:1 mixture of **1a** and **2** in dry $CHCl_3$. Unfortunately, the formation of a rotaxane could not be observed, even not by MALDI spectroscopy of the crude reaction mixture.



3a n=0, R^1=n−C_5H_{11}, R^2=*t*Bu
3b n=1, R^1=n−C_8H_{17}, R^2=H

2

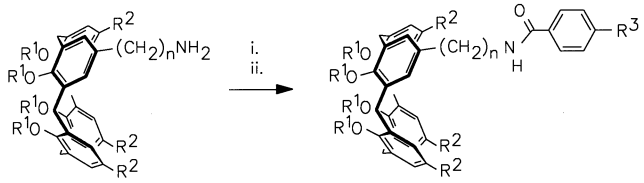


4a n=0, R^1=n−C_5H_{11}, R^2=*t*Bu
4b n=1, R^1=n−C_8H_{17}, R^2=H

It can be assumed that due to the *tert*-butyl groups on the upper rim, pointing all to the same direction as the amine group, threading of the wheel **1a** onto the axle is sterically hindered and therefore the supramolecular complex we postulated[10] between wheel and monoacid chloride-monoamide can not be formed.

The sterically less demanding monoamine **3b** was prepared in good yield according to a literature procedure[15]. It does not bear *p*-*tert*-butyl groups and additionally a CH_2 group separates the amino from the phenyl group. But even in this case no rotaxane could be detected. We attributed this result to the higher reactivity of the amine that reacts to the dumbbell **4b** having "no time" for the formation of the threaded intermediate. At the same time the axle might still be too short with only the two CH_2 spacers. Under the same conditions the synthesis of a rotaxane using **3b** and the "trimer" **1b** failed.

In a second step we prolonged the amine stoppers **3a** and **3b** by a *p*-phenylenecarbonyl unit. Reaction with *p*-nitrobenzoyl chloride and reduction of **16a** and **16b** with H_2/PtO_2 gave **5a** and **5b** in about 55% overall yield.



3a n=0, R^1=n−C_5H_{11}, R^2=*t*Bu
3b n=1, R^1=n−C_8H_{17}, R^2=H

R^3=NH_2 **5a** n=0, R^1=n−C_5H_{11}, R^2=*t*Bu
5b n=1, R^1=n−C_8H_{17}, R^2=H

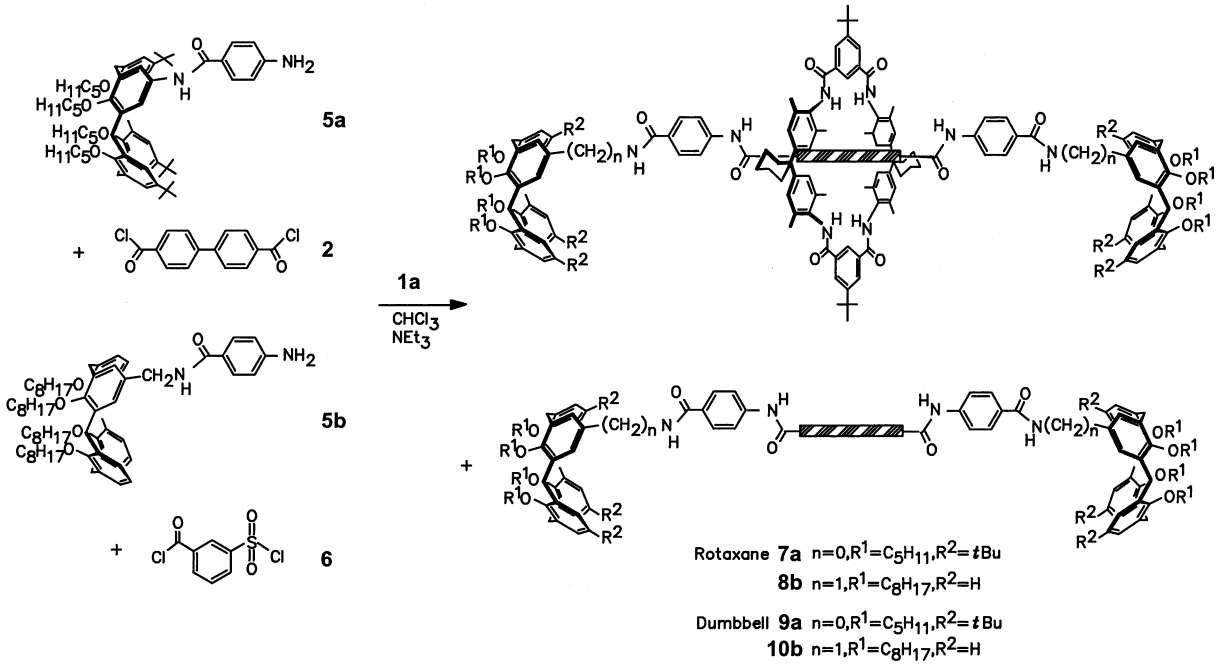
R^3=NO_2 **16a** n=0, R^1=n−C_5H_{11}, R^2=*t*Bu
16b n=1, R^1=n−C_8H_{17}, R^2=H

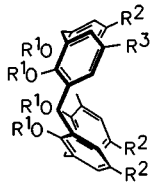
Now the rotaxane synthesis according to the above described method was successful employing 4,4′-biphenyl-1,1′-dicarbonyl dichloride (**2**) and stopper **5a**.

Rotaxane **7a** was isolated in 15% yield and confirmed by elemental analysis, MALDI mass spectrometry, NMR studies and chromatographic methods. Apart from calix[4]-arene protons, all other aromatic protons gave broad signals indicating conformational mobility of the molecule at room temperature in $CHCl_3$. Insoluble in DMSO at room temperature, the rotaxane **7a** dissolves at about 370 K. Its ^{1}H-NMR spectrum at 433 K in [D_6]DMSO shows signals much different from those of a mixture of the dumbbell **9a** and the wheel **1a**. Consequently, rotaxane **7a** was stable to at least 433 K.

A trace of rotaxane **8b**, formed analogously from **5b**, **6** and **1a** was determined in the MALDI mass spectrum but could not be isolated while the dumbbell **10b** was obtained in 68% yield. Further experiments have to show whether the lower yield of **8b** is due to the shorter axle or the more flexible stopper.

Finally we also tested the "trimer" **1b** as a host part, employing the stopper unit **5a** and the diacid dichloride **2**. Re-





11 R^3=NO_2,R^2=*t*Bu,R^1=n-C_5H_{11}
12 R^3=R^2=*t*Bu,R^1=n-C_5H_{11}
13 R^3=CN,R^2=H,R^1=n-C_8H_{17}
14 R^3=Br,R^2=H.R^1=n-C_8H_{17}
15 R^3=Br,R^2=H.R^1=H

markably, no rotaxane was observed in contrast to the reaction with the dimeric wheel **1a**. We suppose a strong competetion of intramolecular H bonding versus intermolecular interactions.

While the "trimeric" macrocycle did not crystallize, single crystals of the dimer **1a** could be obtained from a mixture of dichloromethane and ethyl acetate. Crystal investigations (Figure 2) show a C_i symmetry and the inclusion of two molecules of ethyl acetate. The distance C=O···H−N is about 2.22 Å and 2.65 Å, respectively[16].

Conclusions

These results show that the synthesis of rotaxanes with calix[4]arenes as stoppers can be achieved if attention is payed to a minimum length of the axle between the bulky stopper groups. Furthermore calix[4]arenes and calix[*n*]arenes (n = 5, 6, 8) will be important potential stopper units if a wheel larger than **1a** (e.g. its homologues like **1b**) are employed. Rotaxanes bearing calixarene blocking groups might also better provide crystals for structure investigations that up to now have not been done on rotaxanes of this type.

Figure 1. Roxatane **7a** (A) and a 1:1 mixture of dumbbell **9a** and wheel **1a** (B) in [D_6]DMSO at 433 K

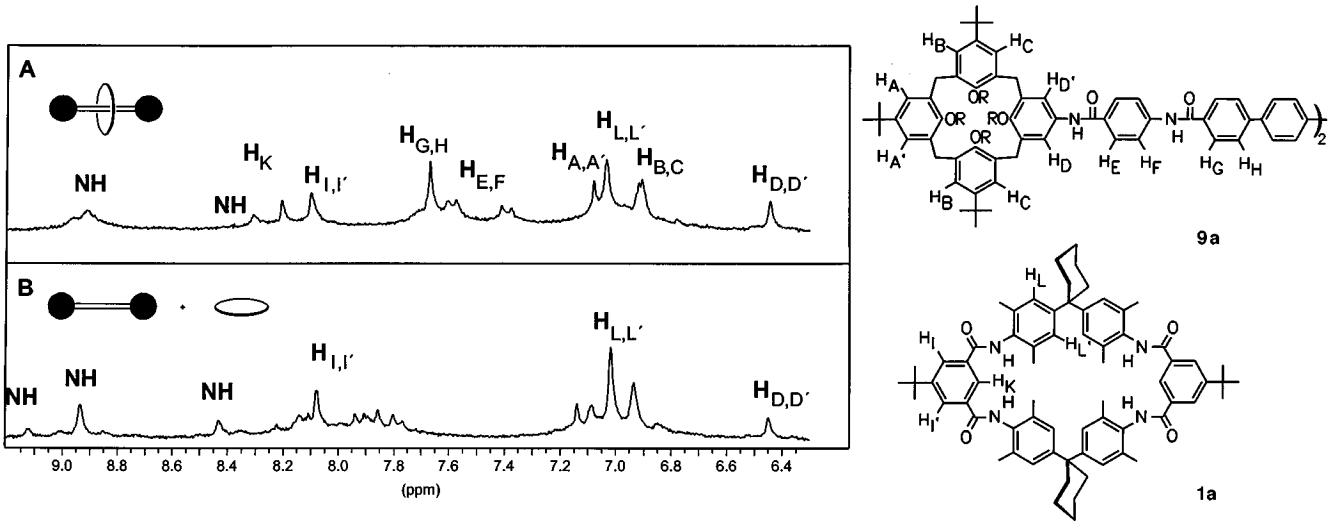
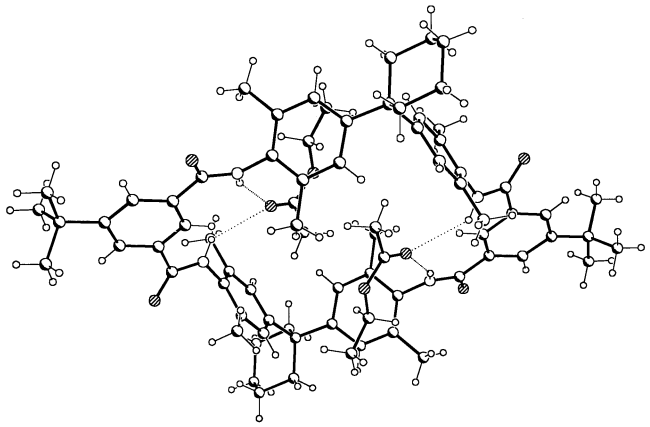


Figure 2. Crystal investigation of **1a**



In the future it will be promising to introduce ligating groups on the lower rim of the calix[4]arene for the complexation of metal cations. It might be possible to exploit new interesting photophysical properties and a variety of new supramolecular structures. The notion of "switching" and "tuning" of rotaxane systems is still a current challenge.

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Experimental Section

Solvents were purified by standard methods and dried if necessary. Reagents were used in commercial quality. TLC was carried out on silica gel 60 F_{254} and CC on silica gel 60, mesh size 63 mm (Merck, Darmstadt, Germany). − Melting points were determined with a capillary melting point apparatus Büchi SMP-20 and are not corrected. − The NMR spectra were measured with AM-250 (^{1}H: 250 MHz, ^{13}C: 62.9 MHz), AM-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) of Bruker Physik AG, Karlsruhe. The NMR signals were assigned by the aid of HH-COSY, CH-COSY and DEPT 135 experiments (Abbrevations: ar = calixarene-aryl, bph = biphenyl, nph = *p*-nitrophenyl, aph = *p*-aminophenyl, ch = cyclohexyl, iso = isophthaloyl). − Microanalysis: Micronalytical department of the "Kekulé-Institut für Organische Chemie und Biochemie", University of Bonn. − MALDI-TOF spectra were recorded with a Micromass TOF spec E (Micromass, Manchester, UK); the matrices used were 9-nitroanthracene (9-NA) and 2,5-dihydroxybenzoic acid (2,5-DHB).

Macrocycle **1a**: A solution of 777 mg (3 mmol) of isophthaloyl dichloride in 250 ml of dry $CHCl_3$ and a solution of 967 g (3mmol) of 1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane and 0.84 ml NEt_3 in 250 ml of dry $CHCl_3$ were added synchronously to 1.2 l of dry $CHCl_3$ at room temperature over a period of 8 h. The solvent was evaporated and the residue purified by column chromatography on silica gel using CH_2Cl_2/ethyl acetate (10:1) to yield 304 mg of **1a** (20%), m.p. > 300°C. − R_f = 0.82 (CH_2Cl_2/ethyl acetate, 8:1). − MALDI-TOF (9-NA); *m/z*: 1040.4 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD, 25°C): δ = 1.24 [s, 18 H, $C(CH_3)_3$], 1.35 (m, 4 H, ch-CH_2), 1.46 (m, 8 H, ch-CH_2), 2.01 (s, 24 H, ar-CH_3), 2.15 (m, 8 H, ch-CH_2), 6.81 (s, 8 H, ar-H), 8.00 (d, 4 H, iso-H, *J* = 1.5 Hz), 8.03 (t, 2 H, iso-H, *J* = 1.4 Hz). − ^{13}C NMR (100.6 MHz, $CDCl_3$/CD_3OD, 25°C): δ = 18.7 (ar-CH_3), 23.1 (ch-CH_2), 26.5 (ch-CH_2), 31.2 [$C(CH_3)_3$], 35.4, 35.5 [$C(CH_3)_3$, ch-CH_2], 45.3 (ch-C_q), 124.2, 126.5, 128.7 (ar-CH), 131.5, 134.4, 135.2, 148.3, 153.7 (C_q), 167.4 (C=O).

Macrocycle **1b**: Elution with CH_2Cl_2/ethyl acetate (7:1) yielded **1b** in 373 mg (25%), m.p. > 300°C. − R_f = 0.18 (CH_2Cl_2/ethyl acetate, 8:1). − MALDI-TOF (9-NA); *m/z*: 1549.1 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD, 25°C): δ = 1.24 [s, 27 H, $C(CH_3)_3$], 1.35 (m, 6 H, ch-CH_2), 1.46 (m, 12 H, ch-CH_2), 2.13 (s, 36 H, ar-CH_3), 2.15 (m, 12 H, ch-CH_2), 6.95 (s, 12 H, ar-H), 8.08 (s, 6 H, iso-H), 8.16 (s, 3 H, iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/CD_3OD, 25°C): δ = 18.5 (ar-CH_3), 22.8 (ch-CH_2), 26.2 (ch-CH_2), 31.0 [$C(CH_3)_3$], 35.1 [$C(CH_3)_3$], 36.9 (ch-CH_2), 45.1 (ch-C_q), 122.9, 126.8, 128.0 (ar-CH), 131.1, 134.5, 135.0, 147.4, 152.7 (C_q), 166.7 (C=O).

5-Amino-11,17,23-tris(1,1-dimethylethyl)-25,26,27,28-tetrakis(1-pentyloxy)calix[4]arene (**3a**): 1.0 g (1 mmol) of compound **11** in 70 ml of toluene was cautiously added to 175 mg N_2H_4 and 50 mg Raney-Ni in 50 ml of boiling toluene. After the reaction had finished portions of N_2H_4 were added until no nitro compound was determined (DC control). The reaction mixture was cooled to room temperature, filtered, the Raney-Ni washed with toluene and the solvent evaporated under reduced pressure. Recrystallization from MeOH gave 822 mg of the amine **3a** (85%), m.p. 72−74°C. − R_f = 0.47 [petroleum ether (40/60)/CH_2Cl_2, 1:2]. − MALDI-TOF (2,5-DHB); *m/z*: 911.4 (M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.83 [s, 9 H, $C(CH_3)_3$], 0.92−0.99 (m, 12 H, CH_3), 1.25−1.56 [m, 34 H, $CH_2CH_2CH_3$, $C(CH_3)_3$], 1.83−2.08 (m, 8 H, OCH_2CH_2), 3.03 (d, 2 H, H_{eq}, *J* = 12.6 Hz), 3.12 (d, 2 H, H_{eq}, *J* = 12.8 Hz), 3.62−3.79 (m, 4 H, OCH_2), 3.75−4.04 (m, 4 H, OCH_2), 4.37 (d, 2 H, H_{ax}, *J* = 12.5 Hz), 4.44 (d, 2 H, H_{ax}, *J* = 12.8 Hz), 5.77 (s, 2 H, ar-H), 6.33 (s, 2 H, ar-H), 6.97 (d, 2 H, ar-H, *J* = 2.4 Hz), 7.06 (d, 2 H, ar-H, *J* = 2.3 Hz). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.1, 14.2, 14.4 (CH_2CH_3), 22.8, 23.0 (CH_2CH_3), 28.3, 28.6, 28.7, 29.9, 30.1, 30.3, 30.9, 31.1, 31.2, 31.7 [arCH$_2$ar, $C(CH_3)_3$, $OCH_2CH_2CH_2$], 33.6, 34.1 [$C(CH_3)_3$], 75.1, 75.4, 75.7 (OCH_2), 124.6, 125.1, 125.7 (*m*-ar), 132.4, 134.4, 134.8, 136.0 (*o*-ar), 143.8, 144.4 (*p*-ar), 153.2, 154.8 (*ipso*-ar).

5-Aminomethyl-25,26,27,28-tetrakis(1-octyloxy)calix[4]arene (**3b**): To 1.0 g (1 mmol) of compound **13** in 100 ml of dry THF was added dropwise 10 ml of 1 M BH_3·THF in THF at 0°C under nitrogen. The mixture was allowed to warm to room temperature and was refluxed for 10 h. Excess BH_3 was destroyed by adding cautiously 20 ml of 2 N HCl. After refluxing for 1 h, the solvents were evaporated under reduced pressure and the product extracted twice with 50 ml of CH_2Cl_2. The organic phase was washed once with 1 N NaOH, water, dried with Na_2SO_4 and concentrated under reduced pressure. Product **3b** was obtained as a colourless oil and was not further purified. Yield 0.874 g (87%). − R_f = 0.31 (CH_2Cl_2/MeOH, 20:1). − MALDI-TOF (2,5-DHB); *m/z*: 925.4 [M + Na^+]. − ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ = 0.85−1.00 (m, 12 H, CH_3), 1.22−1.50 (m, 20 H, CH_2), 1.82−1.99 (m, 8 H, OCH_2CH_2), 3.14 (d, 2 H, H_{eq}, *J* = 13.3 Hz), 3.15 (d, 2 H, H_{eq}, *J* = 13.2 Hz), 3.42 (s, 2 H, CH_2), 3.82 (t, 4 H, OCH_2, *J* = 7.2 Hz), 3.94 (t, 4 H, OCH_2, *J* = 7.4 Hz), 4.45 (d, 4 H, H_{ax}, *J* = 13.2 Hz), 6.37 (s, 2 H, *m*-ar-H), 6.42−6.49 (m, 3 H, *m*-ar-H), 6.67 (t, 2 H, *p*-ar-H, *J* = 6.8 Hz), 6.76 (d, 4 H, *m*-ar-H, *J* = 7.0 Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 26.3, 26.4 ($CH_2CH_2CH_3$), 29.6, 29.7, 29.9, 30.3, 30.4, 31.0 (arCH$_2$ar, CH_2), 46.1 (arCH_2), 75.1, 75.2 (OCH_2), 121.5, 121.9 (*p*-ar), 126.5, 127.8, 128.3, 128.4 (*m*-ar), 134.7, 135.6 (*o*-ar, *p*-ar), 155.2, 156.4, 156.9 (*ipso*-ar).

General Procedure for the Preparation of Rotaxanes **7a** *and* **8b** *and Dumbbells* **4a**, **4b**, **9a** *and* **10b**: To a solution of 0.1 mmol of

wheel **1a** and 0.1 mmol of diacyloyl dichloride in 50 ml of dry $CHCl_3$ were added dropwise at room temp. 0.2 mmol of the amine and several drops of NEt_3 in 40 ml of dry $CHCl_3$ over a period of 4 h. The reaction mixture was stirred for about 12 h, the solvent evaporated under reduced pressure and the residue purified by column chromatography on silica gel.

Dumbbell **4a**: The reaction was carried out using 178 mg (0.2 mmol) of **3a**, 102 mg (0.1 mmol) of **1a** and 28 mg (0.1 mmol) of **2**. − Eluent: $CHCl_3$/hexane (5:1) (R_f = 0.25). − Yield 165 mg (83%), m.p. 186−188°C. − MALDI-TOF (2,5-DHB); *m/z*: 2005.9 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.74 [s, 18 H, $C(CH_3)_3$], 0.97 (t, 24 H, CH_3, *J* = 7.1 Hz), 1.20−1.60 (m, 32 H, $CH_2CH_2CH_3$), 1.42 [s, 36 H, $C(CH_3)_3$], 1.85−2.15 (m, 16 H, OCH_2CH_2), 3.13 (d, 4 H, H_{eq}, *J* = 12.8 Hz), 3.16 (d, 4 H, H_{eq}, *J* = 13.3 Hz), 3.70 (t, 4 H, OCH_2, *J* = 6.9 Hz), 3.74 (t, 4 H, OCH_2, *J* = 6.9 Hz), 4.05 (t, 8 H, OCH_2, *J* = 6.9 Hz), 4.45 (d, 8 H, H_{ax}, *J* = 12.8 Hz), 6.24 (s, 4 H, arH), 6.65 (s, 4 H, ar-H), 7.10 (s, 4 H, ar-H), 7.11 (s, 4 H, ar-H), 7.64 (d, 4 H, bph-H, *J* = 8.4 Hz), 7.71 (d, 4 H, bph-H, *J* = 8.4 Hz). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.1, 14.4 (CH_3CH_2), 22.8, 23.0 (CH_3CH_2), 28.2, 28.6, 28.8, 29.8, 30.2, 30.4, 31.0, 31.3, 31.7, 31.8 [arCH_2ar, $C(CH_3)_3$, $OCH_2CH_2CH_2$], 33.4, 34.1 [$C(CH_3)_3$], 75.1, 75.5, 75.8 (OCH_2), 119.9, 124.4, 125.4, 126.0, 127.3 (*m*-ar, bph-*C*H), 131.4, 132.4, 134.2, 134.9, 135.1, 136.1, 142.7, 143.6, 144.7, 152.6, 153.1, 155.0 (C_q), 164.3 (C=O). − $C_{134}H_{184}N_2O_{10}$ calcd. C 81.17, H 9.35, N 1.41; found C 81.87, H 9.64, N 1.29.

Dumbbell **4b**: The raction was carried out using 180 mg (0.2 mmol) of **3b**, 102 mg (0.1 mmol) of **1a** and 28 mg (0.1 mmol) of **2**. − Eluent: CH_2Cl_2/ethyl acetate (20:1) (R_f = 0.19). − Yield 103 mg (51%), m.p. 86−88°C. − MALDI-TOF (2,5-DHB); *m/z*: 2034.0 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.88−0.97 (m, 24 H, CH_3), 1.25−1.57 (m, 40 H, CH_2), 1.84−2.00 (m, 16 H, OCH_2CH_2), 3.15 (d, 4 H, H_{eq}, *J* = 13.3 Hz), 3.17 (d, 4 H, H_{eq}, *J* = 13.3 Hz), 3.74 (t, 8 H, $=CH_2$, *J* = 6.9 Hz), 3.79 (t, 8 H, OCH_2, *J* = 6.9 Hz), 3.98−4.07 (m, 8 H, OCH_2), 4.15 (d, 4 H, $arCH_2$, *J* = 4.7 Hz), 4.45 (d, 4 H, H_{ax}, *J* = 13.3 Hz), 4.47 (d, 4 H, H_{ax}, *J* = 13.0 Hz), 5.66 (t, 2 H, $arCH_2NH$, *J* = 4.7 Hz), 6.19 (t, 2 H, *p*-ar-H, *J* = 7.4 Hz), 6.28 (s, 4 H, *m*-ar-H), 6.32 (d, 4 H, *m*-ar-H, *J* = 7.6 Hz), 6.83 (t, 4 H, *p*-ar-H, *J* = 7.4 Hz), 6.96 (d, 4 H, *m*-ar-H, *J* = 7.2 Hz), 6.97 (d, 4 H, *m*-ar-H, *J* = 7.2), 7.71 (s, 8 H, bph-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 26.5, 26.2 ($CH_2CH_2CH_3$), 29.5, 29.7, 29.8, 30.0, 30.2, 30.5, 31.0, 32.0 ($arCH_2ar$, CH_2), 43.9 ($arCH_2$), 75.1, 75.3 (OCH_2), 121.2, 122.0 (*p*-ar), 127.0, 127.2, 127.5, 127.6, 128.5, 128.7 (*m*-ar, bph-*C*H), 130.6, 134.1, 134.2, 134.5, 136.2, 136.3, 143.1 (C_q), 155.5, 156.0, 157.3 (*ipso*-ar), 166.9 (C=O). − $C_{136}H_{188}N_2O_{10}$: calcd. C 81.23, H 9.42, N 1.39; found C 82.01, H 9.78, N 1.49.

11,17,23-Tris(1,1-dimethylethyl)-5-(4-nitrophenylcarbonyl)-amino-25,26,27,28-tetrakis(1-pentyloxy)calix[4]arene (**16a**): To a solution of 0.9 g (1 mmol) of compound **3a**, some drops NEt_3 and a catalytic amount of dimethylaminopyridine in 60 ml of dry CH_2Cl_2 was added dropwise 188 mg (1 mmol) of *p*-nitrobenzoyl chloride in 25 ml of dry CH_2Cl_2 at room temp. After stirring for 3 h, the solvent was evaporated and the residue purified by column chromatography using CH_2Cl_2/petroleum ether (40/60), 1:1 as eluent (R_f = 0.17). Compound **16a** was isolated with 70% yield (736 mg), m.p. 116−118°C. − MALDI-TOF (2,5-DHB); *m/z*: 1060.5 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.70 [s, 9 H, $C(CH_3)_3$], 0.92−1.00 (m, 12 H, CH_3), 1.20−1.60 [m, 34 H, $CH_2CH_2CH_3$, $C(CH_3)_3$], 1.82−2.23 (m, 8 H, OCH_2CH_2), 3.13 (d, 2 H, H_{eq}, *J* = 12.9 Hz), 3.14 (d, 2 H, H_{eq}, *J* = 12.6 Hz), 3.65−3.78 (m, 4 H, OCH_2), 4.00−4.12 (m, 4 H, OCH_2), 4.44 (d, 2 H, H_{ax}, *J* = 12.8 Hz), 4.46 (d, 2 H, H_{ax}, *J* = 12.7 Hz), 6.22 (s, 2 H, ar-H), 6.65 (s, 2 H, ar-H), 7.09 (s, 2 H, ar-H), 7.12 (s, 2 H, ar-H), 7.78 (d, 2 H, nph-H, *J* = 8.5 Hz), 8.27 (d, 2 H, nph-H, *J* = 8.0 Hz). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.0, 14.1, 14.4 (CH_3), 22.7, 23.0 (CH_2CH_3), 28.1, 28.6, 28.7, 29.8, 30.1, 30.3, 30.9, 31.2, 31.7 [$arCH_2ar$, $C(CH_3)_3$, CH_2], 33.4, 34.1 [$C(CH_3)_3$], 75.0, 75.4, 75.8 (OCH_2), 119.6, 123.9, 124.3, 125.2, 126.1, 127.7 (*m*-ar, nph-*C*H), 130.8, 132.3, 134.4, 135.0, 136.1, 141.1, 143.4, 144.7, 149.3, 152.9, 153.1, 154.9 (C_q), 162.5 (C=O).

5-N-(4-Nitrophenylcarbonyl)aminomethyl-25,26,27,28-tetrakis-(1-octyloxy)calix[4]arene (**16b**): The preparation was analogous to **16a** using 1.0 g (1.1 mmol) of **3b** and 206 mg (1.1 mmol) of *p*-nitrobenzoyl chloride. − Eluent: CH_2Cl_2 (R_f = 0.25). − Yield 792 mg (68%), m.p. 49−51°C. − MALDI-TOF(2,5-DHB); *m/z*: 1074.5 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.87−0.92 (m, 12 H, CH_3), 1.22−1.58 (m, 20 H, CH_2), 1.83−2.00 (m, 8 H, OCH_2CH_2), 3.156 (d, 2 H, H_{eq}, *J* = 13.0 Hz), 3.160 (d, 2 H, H_{eq}, *J* = 13.8 Hz), 3.73 (t, 4 H, OCH_2, *J* = 6.9 Hz), 3.77 (t, 4 H, OCH_2, *J* = 6.6 Hz), 3.98−4.07 (m, 4 H, OCH_2), 4.10 (d, 2 H, $arCH_2NH$, *J* = 4.4 Hz), 4.45 (d, 2 H, H_{ax}, *J* = 13.0 Hz), 4.47 (d, 2 H, H_{ax}, *J* = 13.3 Hz), 5.62 (br. s, 1 H, NH), 6.07 (t, 1 H, *p*-ar-H, *J* = 7.6 Hz), 6.22 (s, 2 H, *m*-ar-H), 6.23 (d, 2 H, *m*-ar-H, *J* = 7.3 Hz), 6.85 (t, 2 H, *p*-ar-H, *J* = 7.4 Hz), 6.99 (d, 2 H, *m*-ar-H, *J* = 7.4 Hz), 7.02 (d, 2 H, *m*-ar-H, *J* = 7.4 Hz), 7.73 (d, 2 H, nph-H, *J* = 8.6 Hz), 8.32 (d, 2 H, nph-H, *J* = 8.6 Hz). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.1 (CH_3), 22.7, 22.8 (CH_2CH_3), 26.2, 26.6 ($CH_2CH_2CH_3$), 29.5, 29.6, 29.8, 30.1, 30.2, 30.5, 31.0, 32.0 ($arCH_2ar$, CH_2), 44.2 ($arCH_2NH$), 75.2, 75.5 (OCH_2), 121.0, 122.0 (*p*-ar), 123.8, 127.0, 127.3, 128.3, 128.7, 128.8 (*m*-ar, nph-CH), 130.1, 134.2, 134.6, 136.5, 136.6, 140.5, 149.6 (C_q), 155.7, 156.1, 157.5 (*ipso*-ar), 165.3 (C=O).

5-(4-Aminophenylcarbonyl)amino-11,17,23-tris(1,1-dimethylethyl)-25,26,27,28-tetrakis(1-pentyloxy)calix[4]arene (**5a**): 0.6 g (0.6 mmol) of nitro compound **16a** was dissolved in 40 ml of THF and hydrogenated at a pressure of 4 bar for 6 h in the presence of 5% PtO_2 (30 mg). The catalyst was filtered off, washed with THF and the filtrate evaporated in vacuo. The residue was recrystallized from MeOH to give 0.524 mg (90%) of **5a**, m.p. 114−116°C. − R_f = 0.43 (CH_2Cl_2/ethyl acetate, 50:1). − MALDI-TOF (2,5-DHB); *m/z* = 1030.5 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.72 [s, 9 H, $C(CH_3)_3$], 0.92−0.99 (m, 12 H, CH_3), 1.21−1.58 (m, 43 H, $CH_2CH_2CH_3$, $C(CH_3)_3$], 1.82−2.10 (m, 8 H, OCH_2CH_2), 3.10 (d, 2 H, H_{eq}, *J* = 12.8 Hz), 3.12 (d, 2 H, H_{eq}, *J* = 13.0 Hz), 3.65 (t, 2 H, OCH_2, *J* = 6.9 Hz), 3.73 (t, 2 H, OCH_2, *J* = 6.6 Hz), 4.03 (t, 4 H, OCH_2, *J* = 8.4 Hz), 4.42 (d, 2 H, H_{ax}, *J* = 12.6 Hz), 4.44 (d, 2 H, H_{ax}, *J* = 12.8 Hz), 6.23 (s, 2 H, arH), 6.60 (s, 2 H, arH), 6.64 (d, 2 H, aph-H, *J* = 7.8 Hz), 6.92 (s, 1 H, $arNHCO$), 7.03 (d, 2 H, ar-H, *J* = 2.2 Hz), 7.10 (d, 2 H, ar-H, *J* = 2.2 Hz), 7.51 (d, 2 H, aph-H, *J* = 8.0 Hz). − .^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.0, 14.1, 14.4 (CH_3), 22.8, 23.0 (CH_2CH_3), 28.2, 28.6, 28.7, 29.8, 30.2, 31.0, 31.2, 31.3, 31.6, 31.8 [$arCH_2ar$, $C(CH_3)_3$, CH_2], 33.4, 34.1 [$C(CH_3)_3$], 75.1, 75.4, 75.7 (OCH_2), 120.1, 124.4, 125.4, 126.0, 128.5 (*m*-ar, aph-CH), 131.4, 132.3, 134.1, 135.1, 136.0, 143.6, 144.7, 152.6, 153.1, 154.9 (C_q), 164.5 (C=O).

5-N-(4-Aminophenylcarbonyl)aminomethyl-25,26,27,28-tetrakis(1-octyloxy)calix[4]arene (**5b**): The preparation was analogous to **5a**, using 544 mg of compound **16b** and 30 mg of PtO_2 in 30 ml of THF. − Yield 449 mg (85%), m.p. 53−55°C. − R_f = 0.22 (CH_2Cl_2/ethyl acetate, 10:1). − MALDI-TOF (2,5-DHB); *m/z* = 1044.5 [M + Na^+]. − ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ = 0.85−0.98 (m, 12 H, CH_3), 1.22−1.58 (m, 20 H, CH_2),

1.83−2.02 (m, 8 H, OCH_2CH_2), 3.14 (d, 4 H, H_{eq}, J = 13.1 Hz), 3.70−3.82 (m, 4 H, OCH_2), 3.95−4.06 (m, 4 H, OCH_2), 4.09 (d, 2 H, $arCH_2NH$, J = 4.5 Hz), 4.45 (d, 4 H, H_{ax}, J = 13.2 Hz), 5.58 (t, NH, 1 H, $arCH_2NH$, J = 4.4 Hz), 6.21 (t, 1 H, *p*-ar-H, J = 7.5 Hz), 6.27 (s, 2 H, *m*-ar-H), 6.33 (d, 2 H, *m*-ar-H, J = 7.4 Hz), 6.72−7.00 (m, 8 H, *p*-ar-H, *m*-ar-H, aph-H), 7.46 (d, 2 H, aph-H, J = 8.5 Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 26.2, 26.5 ($CH_2CH_2CH_3$), 29.5, 29.7, 29.8, 30.0, 30.2, 30.3, 30.5, 30.9, 32.0 ($arCH_2ar$, CH_2), 43.8 ($arCH_2NH$), 75.1, 75.3 (OCH_2), 115.9 (aph-*C*H), 121.3, 122.0 (*p*-ar), 125.5, 127.0, 127.5, 128.5, 128.7 (*m*-ar, aph-*C*H), 130.9, 134.2, 134.5, 136.1, 136.2, 155.5, 156.0, 157.3 (C_q), 167.0 (C=O).

Rotaxane **7a**: The reaction was carried out using 31 mg (0.11 mmol) of **2**, 113 mg of **1a** (0.11 mmol) and 223 mg (0.22 mmol) of **5a**. − Eluent: CH_2Cl_2/ethyl acetate (20:1). − Yield 54 mg (15%), m.p. > 300°C. − R_f = 0.17 (CH_2Cl_2/ethyl acetate, 15:1). − MALDI-TOF (9-NA); *m*/*z*: 3261.6 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.71, 0.83 [s, 18 H, $C(CH_3)_3$], 0.96 (t, 24 H, CH_3, J = 7.3 Hz), 1.15−1.55 [m, 72 H, $CH_2CH_2CH_3$, $C(CH_3)_3$, ch-CH_2], 1.69 (m, 8 H, ch-CH_2), 1.80−2.10 (m, 40 H, OCH_2CH_2, ar-CH_3), 2.32 (m, 8 H, ch-CH_2), 3.12 (d, 4 H, H_{eq}, J = 12.8 Hz), 3.14 (d, 4 H, H_{eq}, J = 12.0 Hz), 3.70−4.05 (m, 16 H, OCH_2), 4.43 (d, 4 H, H_{ax}, J = 12.7 Hz), 4.46 (d, 4 H, H_{ax}, J = 12.0 Hz), 6.29, 6.62 (s, 4 H, ar-H), 6.85−7.05 (m, 24 H, *m*-ar-H, wheel-ar-H, bph-H), 7.49 (br. s, 4 H, aph-H), 7.67 (br. s, 4 H, aph-H), 8.18 (s, 6 H, iso-ar-H), 8.48 (br. s, 2 H, NH). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.1, 14.2, 14.4 (CH_3CH_2), 18.7 (ar-CH_3), 22.8, 23.0 (ch-CH_2, CH_2CH_3), 28.2, 28.6, 28.7, 29.8, 30.1, 30.3, 31.0, 31.3, 31.7 [arCH_2ar, $C(CH_3)_3$, $OCH_2CH_2CH_2$], 33.4, 34.0 [s, $C(CH_3)_3$], 35.4 (ch-CH_2), 45.3 (ch-C_q), 75.1, 75.3, 75.7 (OCH_2), 120.4, 120.8, 124.5 (*m*-ar), 124.9, 126.0, 126.7, 127.2, 127.4, 128.0 (*m*-ar, aph-CH, wheel-ar-CH, bph-CH), 128.6 (iso-CH), 131.4, 132.8, 134.4, 134.8, 135.2, 135.7, 143.6, 143.9, 144.6, 153.3, 153.6, 154.7 (C_q), 165.4, 166.3, 166.8 (C=O). − $C_{216}H_{274}N_8O_{16}$: calcd. C 80.11, H 8.53, N 3.46; found C 80.43, H 8.59, N 3.40.

Dumbbell **9a**: Formed during the preparation of rotaxane **7a** described above. − Eluent: CH_2Cl_2/ethyl acetate, 20:1. − Yield 135 mg (55%), m.p. > 300°C. − R_f = 0.35 (CH_2Cl_2/ethyl acetate, 15:1). − MALDI-TOF(9-NA); *m*/*z*: 2244.2 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.75 [s, 18 H, $C(CH_3)_3$], 0.96 (t, 24 H, CH_3 J = 7.0 Hz), 1.15−1.60 [m, 68 H, $CH_2CH_2CH_3$, $C(CH_3)_3$], 1.75−2.10 (m, 16 H, OCH_2CH_2), 3.07 (d, 4 H, H_{eq}, J = 12.5 Hz), 3.12 (d, 4 H, H_{eq}, J = 12.7 Hz), 3.55 -3.75 (m, 8 H, OCH_2), 3.95−4.05 (m, 8 H, OCH_2), 4.41 (d, 4 H, H_{ax}, J = 12.6 Hz), 4.43 (d, 4 H, H_{ax}, J = 12.6 Hz), 6.23 (s, 4 H, ar-H), 6.60 (s, 4 H, ar-H), 7.02 (s, 4 H, ar-H), 7.10 (s, 4 H, ar-H), 7.50 (br. s, 4 H, aph-H), 7.57 (br. s, 4 H, aph-H), 7.80 (br. s, 4 H, bph-H), 7.92 (br. s, 4 H, bph-H), 8.61 (br. s, 2 H, NH). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.1, 14.4 (CH_3), 22.8, 23.0 (CH_2CH_3), 28.2, 28.7, 29.8, 30.2, 30.3, 31.0, 31.2, 31.3, 31.6, 31.8 [$arCH_2ar$, $C(CH_3)_3$, CH_2], 33.4, 34.1 [$C(CH_3)_3$], 75.1, 75.5, 75.8 (OCH_2), 119.8, 120.1 124.4 (*m*-ar), 125.4, 126.0, 127.2, 127.7, 128.0 (*m*-ar, aph-CH, bph-CH), 132.4, 134.2, 135.1, 136.1, 140.6, 143.6, 144.7, 153.1, 155.0 (C_q), 165.5, 166.6 (C=O). − $C_{148}H_{194}N_4O_{12}$: calcd. C 80.03, H 8.80, N 2.52; found C 80.10, H 8.89, N 2.57.

Dumbbell **10b**: Treatment of 23 mg (0,1 mmol) of **6** and 98 mg (0.1 mmol) of **1a** with 196 mg (0.19 mmol) of **5b**. Eluent: CH_2Cl_2/ethyl acetate, 20:1. Yield 145 mg (68%) of **10b**, m.p. 133−135°C. − R_f = 0.46 (CH_2Cl_2/ethyl acetate, 5:1). − MALDI-TOF(2,5-DHB); *m*/*z*: 2232.1 [M + Na^+]. − ^{1}H NMR(400 MHz, $CDCl_3$, 25°C): δ = 0.85−0.97 (m, 24 H, CH_3), 1.22−1.56 (m, 40 H, CH_2), 1.82−1.99 (m, 16 H, OCH_2CH_2), 3.05−3.15 (m, 8 H, H_{eq}), 3.69−3.78 (m, 8 H, OCH_2), 3.94−4.05 (m, 8 H, OCH_2), 4.08 (s, 4 H, $arCH_2NH$), 6.00−6.35 (m, 10 H, ar-H), 6.68−7.00 (m, 16 H, ar-H, aph-H), 7.28−7.49 (m, 5 H, aph-H, iso-H), 7.78 (br. s, 1 H, iso-H), 8.05 (br. s, 2 H, iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.3 (CH_3), 22.9 (CH_2CH_3), 26.3, 26.7 ($CH_2CH_2CH_3$), 29.7, 29.9, 30.0, 30.2, 30.4, 30.7, 31.1, 31.4, 32.1 ($arCH_2ar$, CH_2), 44.6 ($arCH_2NH$), 75.3, 75.5 (OCH_2), 120.6, 121.4, 122.2, 127.3, 127.7, 128.8 (ar-CH, aph-CH, iso-CH), 130.3, 134.4, 134.8, 136.3, 136.5, 155.9, 156.2, 157.5 (C_q), 165.1, 167.3 (C=O). − $C_{143}H_{194}N_4O_{13}S$: calcd. C 77.75, H 8.85, N 2.54; found C 77.99, H 8.92, N 2.47.

11,17,23-Tris(1,1-dimethylethyl)-5-nitro-25,26,27,28-tetrakis(1-pentyloxy)calix[4]arene (**11**): To 1.0 g (1 mmol) of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26,27,28-tetrakis(1-pentyloxy)-calix[4]arene (**12**)[17] in 75 ml of CH_2Cl_2 were added 3.75 ml of glacial acetic acid and 2.15 ml of 60% HNO_3 (30 mmol). After stirring for about 12 h, the mixture was poured into water (100 ml) and washed twice with 50 ml saturated $NaHCO_3$ solution. The organic layer was dried with Na_2SO_4 and concentrated to afford a yellow solid which was further purified by column chromatography (cyclohexane/$CHCl_3$, 2:1) to give 751 mg (76%) of a white solid, m.p. 73−75°C. − R_f = 0.20 (cyclohexane/$CHCl_3$, 2:1). − MALDI-TOF(2,5-DHB); *m*/*z*: 941.3 [M + Na^+]. − ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ = 0.63 [s, 9 H, $C(CH_3)_3$], 0.96 (t, 12 H, CH_3, J = 7.2 Hz), 1.20−1.58 [m, 34 H, $CH_2CH_2CH_3$, $C(CH_3)_3$], 1.80−2.12 (m, 8 H, OCH_2CH_2), 3.13 (d, 2 H, H_{eq}, J = 13.0 Hz), 3.16 (d, 2 H, H_{eq}, J = 13.0 Hz), 3.63−3.78 (m, 4 H, OCH_2), 3.91−4.15 (m, 4 H, OCH_2), 4.41 (d, 2 H, H_{ax}, J = 13.3 Hz), 4.46 (d, 2 H, H_{ax}, J = 13.4 Hz), 6.20 (s, 2 H, ar-H), 7.12 (d, 2 H, ar-H, J = 2.3 Hz), 7.15 (d, 2 H, ar-H, J = 2.4 Hz), 7.26 (s, 2 H, ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ = 14.0, 14.1, 14.3 (CH_3), 22.6, 22.7, 23.0 (CH_2CH_3), 28.1, 28.4, 28.7, 29.8, 30.0, 30.3, 30.7, 31.1, 31.2, 31.7 [$arCH_2ar$, $C(CH_3)_3$], 33.1, 34.2 [$C(CH_3)_3$], 75.0, 75.5, 76.1 (OCH_2), 123.1, 124.4, 125.1, 126.7 (*m*-ar), 131.8, 134.2, 135.2, 136.3 (*o*-ar), 142.5, 144.4, 145.3 (*p*-ar), 152.7, 154.7, 160.7 (*ipso*-ar).

5-Cyano-25,26,27,28-tetrakis(1-octyloxy)calix[4]arene (**13**): A mixture of 1.54 g (1.6 mmol) of **14** in 30 ml of *N*-methyl-2-pyrrolidinone (NMP) and 289 mg (3.2 mmol) of CuCN was heated at 200°C, under nitrogen for 12 h. Then 875 mg (3.2 mmol) of $FeCl_3$ in 35 ml of 3 N HCl was added at 100°C. The reaction was stirred for another 2 h, cooled to room temperature and extracted with CH_2Cl_2. The organic layer was washed twice with H_2O, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography using CH_2Cl_2/petroleum ether (40/60), 2:1 as eluent to give 783 mg (54%) of a yellow solid, m.p. 51−53°C. − R_f = 0.45 [CH_2Cl_2/petroleum ether (40:60), 1:1]. − MALDI-TOF(2,5-DHB); *m*/*z*: 921.3 [M + Na^+]. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.90 (t, 12 H, CH_3, J = 7.2 Hz), 1.22−1.55 (m, 20 H, CH_2), 1.82−1.95 (m, 8 H, OCH_2CH_2), 3.13 (d, 2 H, H_{eq}, J = 14.0 Hz), 3.16 (d, 2 H, H_{eq}, J = 14.2 Hz), 3.74 (t, 2 H, OCH_2, J = 6.6 Hz), 3.79 (t, 2 H, OCH_2, J = 6.9 Hz), 3.88−4.05 (m, 4 H, OCH_2), 4.42 (d, 2 H, H_{ax}, J = 13.5 Hz), 4.43 (d, 2 H, H_{ax}, J = 13.8 Hz), 6.26 (d, 2 H, *m*-ar-H, J = 7.6 Hz), 6.51 (s, 2 H, *m*-ar-H), 6.52 (t, 1 H, *p*-ar-H, J = 7.9 Hz), 6.84 (dd, 2 H, *p*-ar-H, J = 7.4 Hz, J = 6.5 Hz), 6.92 (d, 2 H, *m*-ar-H, J = 6.4 Hz), 6.99 (d, 2 H, *m*-ar-H, J = 7.2 Hz). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.4, 26.6 ($CH_2CH_2CH_3$), 29.5, 29.6, 29.7, 29.8, 30.0, 30.2, 30.4, 30.5, 30.8, 31.0, 32.0 ($arCH_2ar$, CH_2), 75.1, 75.2 (OCH_2), 105.5 (*p*-ar), 119.8 (CN), 122.2, 122.3 (*p*-ar), 127.7, 128.5, 129.4, 131.7 (*m*-ar), 133.8, 135.3, 136.0, 136.9 (*o*-ar), 155.7, 157.3, 159.6 (*ipso*-ar).

5-Bromo-25,26,27,28-tetrakis(1-octyloxy)calix[4]arene (**14**): 1.29 g (2.6 mmol) of compound **15**[15] in 60 ml DMF was treated

at room temperature with 1.23 g (26 mmol) of NaH (50% suspension in oil) and 4.19 ml (26 mmol) octyl bromide. The mixture was stirred for about 12 h under nitrogen at room temperature. Then 50 ml of 2 N HCl was added cautiously and the product was extracted twice with 70 ml of CH_2Cl_2. The organic layer was washed several times with 2 N HCl, finally with water, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with hexane/$CHCl_3$ (2:1) as eluent to give 2 g (82%) of a colourless dense oil. – R_f = 0.26 (hexane/$CHCl_3$, 3:2). – MALDI-TOF(2,5-DHB); *m/z*: 975.2 [M + Na^+]. – ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ = 0.9 (t, 12 H, CH_3, *J* = 7.0 Hz), 1.20–1.48 (m, 20 H, CH_2), 1.80–1.96 (m, 8 H, OCH_2CH_2), 3.09 (d, 2 H, H_{eq}, *J* = 13.5 Hz), 3.17 (d, 2 H, H_{eq}, *J* = 13.5 Hz), 3.72–3.94 (m, 8 H, OCH_2), 4.40 (d, 2 H, H_{ax}, *J* = 13.6 Hz), 4.45 (d, 2 H, H_{ax}, *J* = 13.7 Hz), 6.42 (d, 2 H, *m*-ar-H, *J* = 7.5 Hz), 6.50 (s, 2 H, *m*-ar-H), 6.60 (t, 1 H, *p*-ar-H, *J* = 7.1 Hz), 6.71 (t, 2 H, *p*-ar-H, *J* = 7.3 Hz), 6.77 (dd, 2 H, *m*-ar-H, *J* = 7.5 Hz, *J* = 1.9 Hz), 6.82 (dd, 2 H, *m*-ar-H, *J* = 7.0 Hz, *J* = 2.1 Hz).

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[16] Crystal data: $C_{68}H_{80}N_4O_4 \cdot 3\ C_4H_8O_2 \cdot 2\ CH_2Cl_2$, M_r = 1451.5, colourless crystals, dimension 0.23 × 0.25 × 0.55 mm, triclinic, space group $P\bar{1}$ (No.2), *a* = 11.616(4), *b* = 11.941(2), *c* = 15.920(3) Å, α = 71.95(2), β = 77.37(2), γ = 80.44(2)°, *V* = 2037.2(9) Å^3, *Z* = 1, μ(Cu-K_α) = 1.77 mm^{-1}, $2\theta_{max.}$ = 120°, *T* = 200 K, 6056 unique reflections, *wR*2(F^2) = 0.426; R_1 = 0.160 [for $I > 2\sigma(I)$]; 443 parameters, 409 restraints. Due to the disordered solvent ($C_4H_8O_2$ and CH_2Cl_2) only the conformation, the nature of the inclusion and the hydrogen bond path between the host and the two included $C_4H_8O_2$ can be determined.

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