Synthesis of Rotaxane Assemblies**

Thomas Dünnwald, Ralf Jäger, and Fritz Vögtle*

Abstract: The preparative syntheses of new nano-sized rotaxane assemblies are described, namely, of the first tris[2]-rotaxane, **15**, the first bis[2]rotaxane connected at the axles, **4**, and the first [3]rotaxane with two different axles, **12** (unsymmetrical "bis[2]rotaxane"). These syntheses were made possible by the directed incorporation of a sulfonamide group into the amide-linked rotaxane building blocks. The sulfonamide moiety can be used as a functional group in alkylation reactions, allowing the further attachment of building blocks in good yields. The successful synthesis of these new rotaxane architectures demonstrates the synthetic potential of this sulfonamide strategy in the preparation of multirotaxane and dendritic rotaxane structures.

Keywords
macrocycles · rotaxanes · sulfonamides · supramolecular chemistry · template synthesis

Introduction

The first rotaxanes were reported in 1967 by Schill and Zollenkopf,[1] synthesized in a multistep synthesis, and by Harrison and Harrison,[2] who used a statistical approach. However, for a long time, these mechanically linked molecules were considered to be laboratory curiosities, only accessible in low yields. Only after Sauvage and co-workers (1983)[3] and Stoddart and co-workers (1989)[4] introduced template-supported strategies[5] for the synthesis of catenanes did the related rotaxanes became accessible on a preparative scale.

In 1995 we developed a new nonionic template synthesis (molecular recognition between electrically uncharged molecules) for amide-based [2]rotaxanes.[6, 7] Steric complementarity, π,π-interactions, and hydrogen bonding favor the inclusion of the guest (diacid dichloride/acid monoamide) in the cavity of a host macrocycle containing amide groups (threading process).[8] This strategy turned out to be surprisingly tolerant towards a great variety of diacid dichlorides,[9] and even the synthesis of the first amide-linked [3]rotaxane (**1**, Scheme 1) was carried out successfully.[10]

With the introduction of sulfonamide groups both in the axle and the wheel, further preparative chemistry with rotaxanes became possible. The higher acidity of the sulfonamide proton opened up the possibility of chemoselective deprotonation and further alkylation.[11] [2]Rotaxane **11** was dimerized to [3]rotaxane (bis[2]rotaxane) **2** (Scheme 1) by using a suitable 1,ω-diodo compound.[11]

We now present the synthesis of new rotaxane assemblies by directed integration of sulfonamide groups followed by derivatization. The promising yields achieved for [*n*]rotaxanes recommend this strategy for further investigation with the aim of preparing poly- and dendritic rotaxanes.

Results and Discussion

Synthesis of a [3]rotaxane from a [2]rotaxane: The intramolecular bridging of the wheel and the axle of a cycloenantiomeric[12] [2]rotaxane by means of 1,2-bis(2-iodoethoxy)ethane to give a "[1]rotaxane" proved that the steric demand of the wheel does not prevent the sulfonamide proton of the axle from reacting.[11] Therefore, a [3]rotaxane should be accessible by dimerization of a suitable [2]rotaxane with a sulfonamide group in its axle. [2]Rotaxane **3** was prepared in 48% yield by our published procedure.[9] Reaction of **3** and 1,2-bis(2-iodoethoxy)ethane in DMF with potassium carbonate led to [3]rotaxane **4**—the first axle-linked bis[2]rotaxane—in 48% yield (Scheme 2). The translation process of the macrocycles along the axle is not only hindered by the other macrocycle but also by the podand chain attached to the sulfonamide groups. This limits the translational movement of the macrocycles of [3]rotaxane **4** in comparison to that in [2]rotaxane **3** or [3]rotaxane **1**.[10]

Synthesis of the first unsymmetrical amide-based "bis[2]-rotaxane" (i.e., a [3]rotaxane bearing two different axles): The direct bridging of two different [2]rotaxanes leads to both the symmetrical and the unsymmetrical bis[2]rotaxanes, which are difficult to separate. We therefore decided on a two-step proce-

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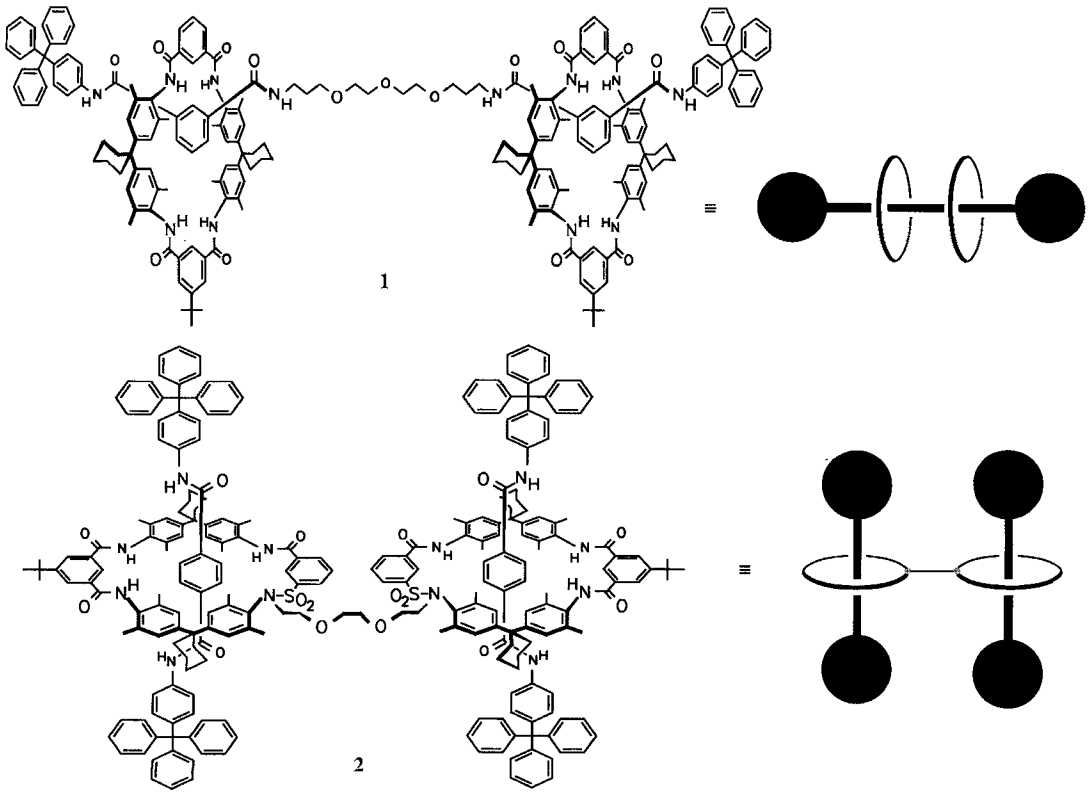
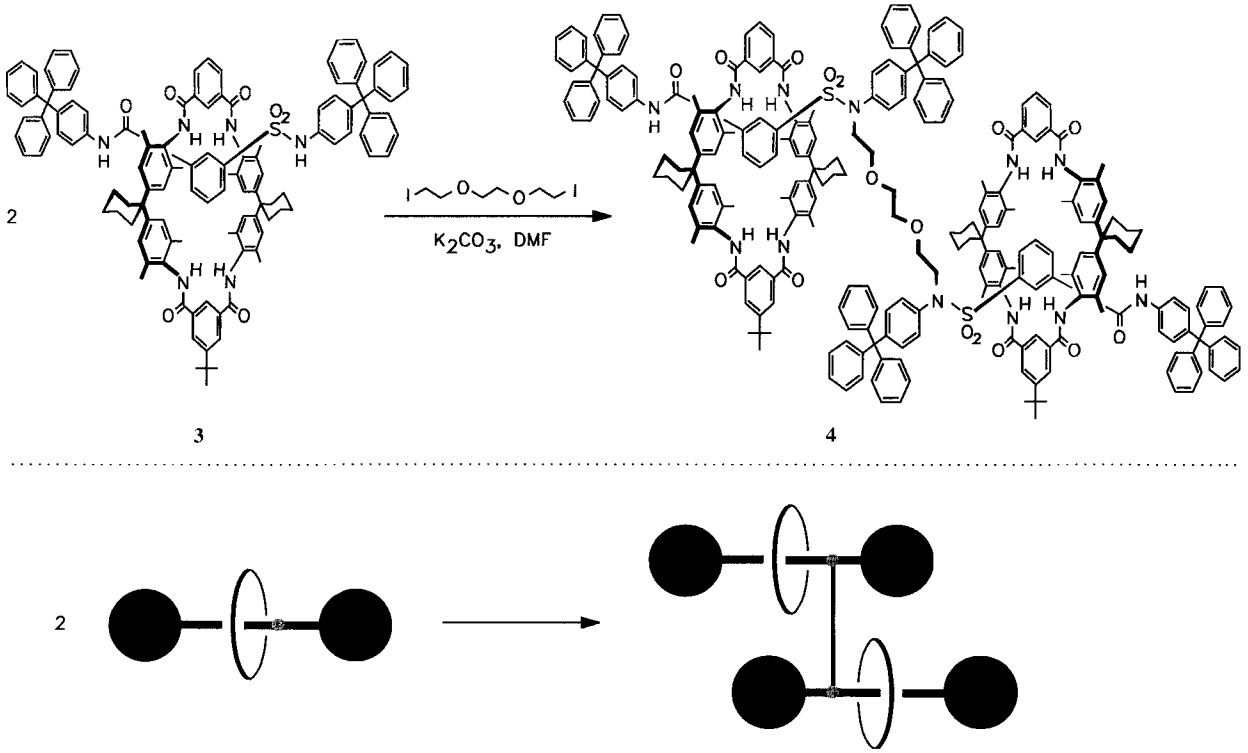


Scheme 1. Amide-based [3]rotaxane **1** and bis[2]rotaxane **2**.

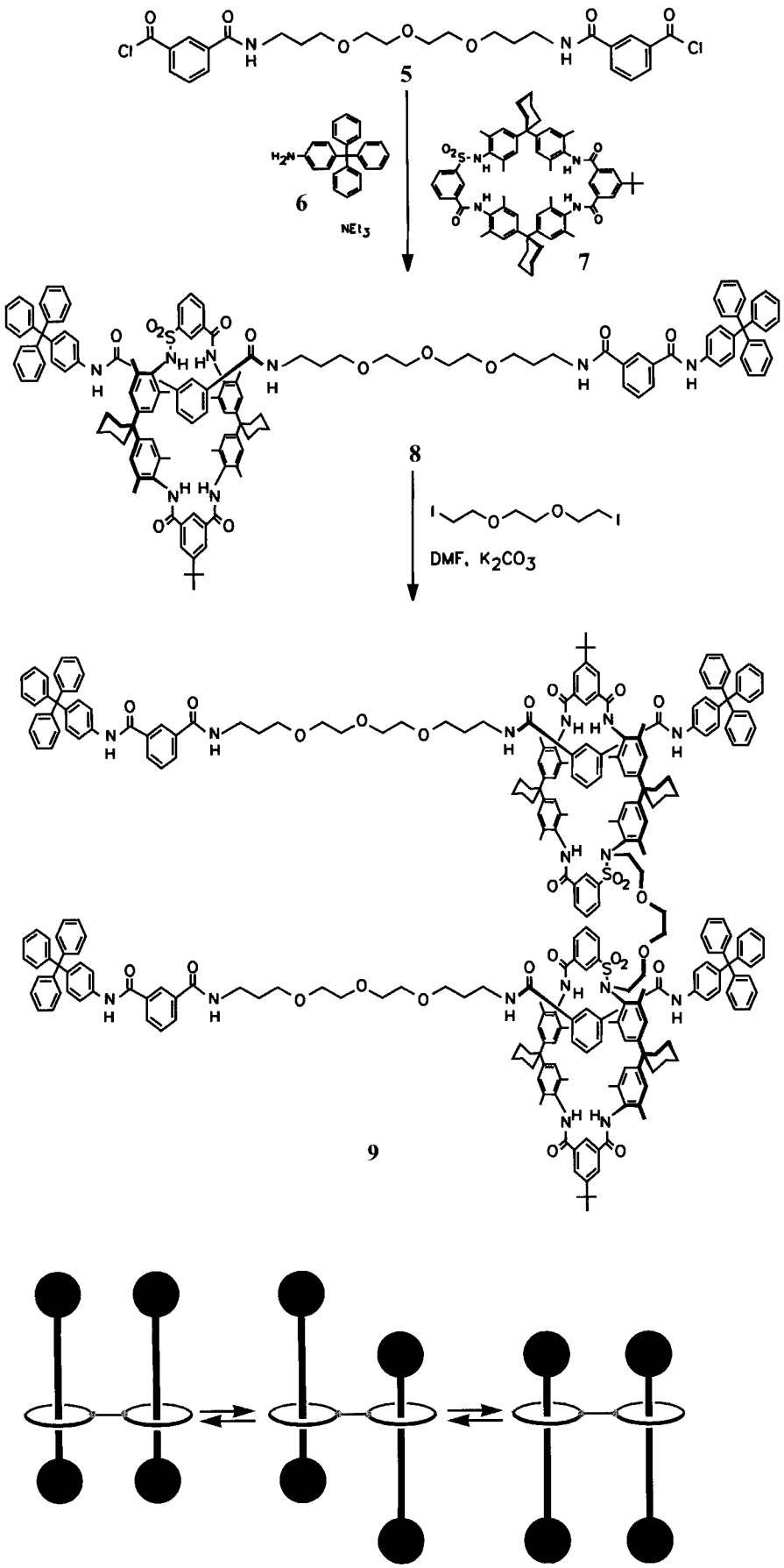


Scheme 2. "Dimerization" of [2]rotaxane **3** to give [3]rotaxane **4**.

dure consisting of the synthesis of the iodo-substituted rotaxane **10** followed by the coupling-step with rotaxane **11**.

Diacid dichloride **5** has proved to be an adequate template for the synthesis of rotaxanes in previous work.[10] Following our threading strategy, **5** was treated with the stopper component *p*-triphenylmethylaniline (**6**) in the presence of the sulfonamide macrocycle **7** (Scheme 3). After column chromatography on silica, we obtained a mixture of the [2]- and the corresponding

0947-6539/97/0312-2044 $ 17.50+.50/0 *Chem. Eur. J.* **1997**, *3*, No. 12



Scheme 3. Synthesis of [2]rotaxane **8** and [3]rotaxane **9** (bottom: dynamic translation processes).

[3]rotaxane, which were detected by mass spectrometry. However, only [2]rotaxane **8** could be seperated by HPLC in 6% yield. The [3]rotaxane could not be isolated in pure form, but proof of its existence was provided by mass spectrometry.

The iodo-substituted rotaxane **10** (Scheme 4) was obtained by treatment of sulfonamide [2]rotaxane **8** with 1,2-bis(2-iodoethoxy)ethane in presence of the mild base potassium carbonate. In fact, we obtained both the desired rotaxane **10** and the symmetrical [3]rotaxane (bis[2]rotaxane) **9** (Scheme 3). The conformational flexibility of **9** should be similiar to that of our previously published rotaxanes[10] containing elongated axles: dynamic NMR spectroscopy confirmed that the wheels are not localized at one isophthaloyl unit, but shuffle between the isophthaloyl units (Scheme 3).

Reaction of iodo rotaxane **10** with mono(sulfonamide) rotaxane **11** led to formation of [3]rotaxane **12**, which, to our knowledge, is the first [3]rotaxane bearing different axles (unsymmetrical "bis[2]rotaxane").

Synthesis of the first amide-based [4]rotaxane (tris[2]rotaxane): As a test system for the following trisrotaxane synthesis, we first tried to convert sulfonamide macrocycle **7** and 1,3,5-tris(4-bromomethylphenyl)benzene (**13**) into the corresponding trismacrocycle **14** (Scheme 5). Benzyl bromides are expected to have a similar reactivity under analogous reaction conditions (DMF/potassium carbonate) to the iodoalkanes used above; indeed, we obtained the desired trismacrocycle **14** in 71% yield.

The first amide-linked [4]rotaxane (tris[2]rotaxane) **15** was obtained by reaction of **13** with [2]rotaxane **11**. The fact that yield is lower (35%) than that for macrocycle **7** can be explained by the greater steric demand of rotaxane **11**. Compound **15** with its new topology can be viewed as a first step towards a neutral, amide-based dendritic rotaxane system.

Design of a macrocyclic blocking group for the synthesis of rotaxane networks: The next logical step in the synthesis of rotaxane assemblies was to design a macrocyclic blocking group that could also act as a host (cf. the self-assembly of an organometallic rotaxane network of Rob-

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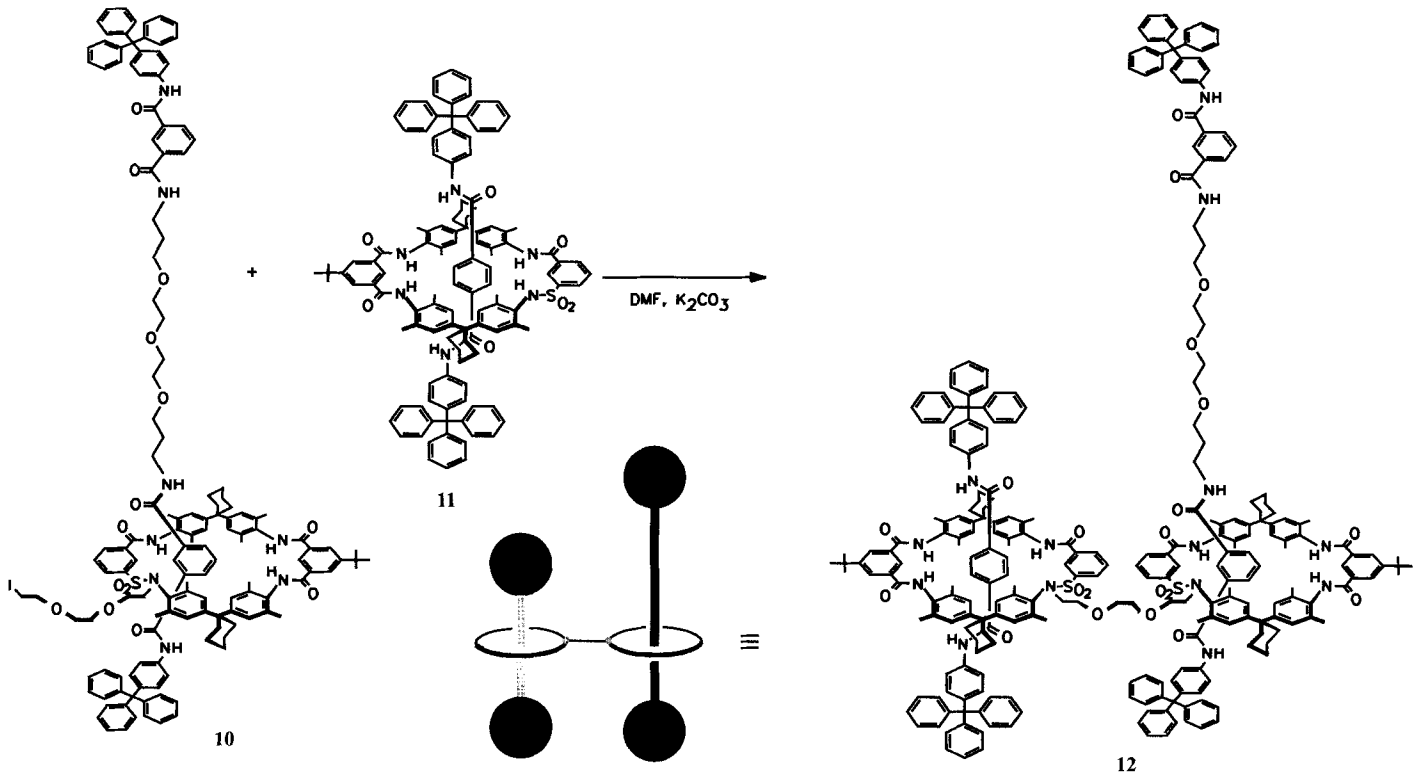


Scheme 4. Synthesis of [3]rotaxane **12**, the first amide-based, unsymmetrical "bis[2]rotaxane".

son and co-workers,[13] Scheme 6). We therefore decided to append an amino group to an amide-linked macrocycle. As the point of attachment, we used a sulfonamide group, which can readily be derivatized.

The reaction of macrocycle **7** with excess of 1,2-bis(2-iodoethoxy)ethane yielded iodo compound **16** (Scheme 7), which could be converted to amine **17** by a Gabriel synthesis.[14, 15]

Unfortunately, reaction of the blocking group **17** with terephthaloyl dichloride only resulted in the formation of bismacrocycle **18** (69% yield). No rotaxane assemblies could be detected, even in the crude product by MALDI-TOF-MS. This finding suggests that aromatic amines (e.g. *p*-triphenylmethylaniline) are more suitable for rotaxane synthesis than aliphatic ones. *p*-Triphenylmethylaniline, which we usually use, seems to possess a better complementarity with the macrocyclic host, owing to its qualities in hydrogen bonding and its steric fit.

Nevertheless, **18** could be used as a wheel in rotaxane synthesis to give compounds of new topology (bismacrocycle-[2]rotaxanes). The [2]rotaxanes **20a** and **b** were isolated in 13 and 28% yield, respectively, by using terephthaloyl dichloride (**19a**) and sulfobenzoyl dichloride (**19b**), respectively, as the axle building block (Scheme 8). The corresponding bisrotaxanes could not be detected. Especially **20b** could be used in further synthesis of rotaxane assemblies, for example, by covalent bridging of the sulfonamide groups.

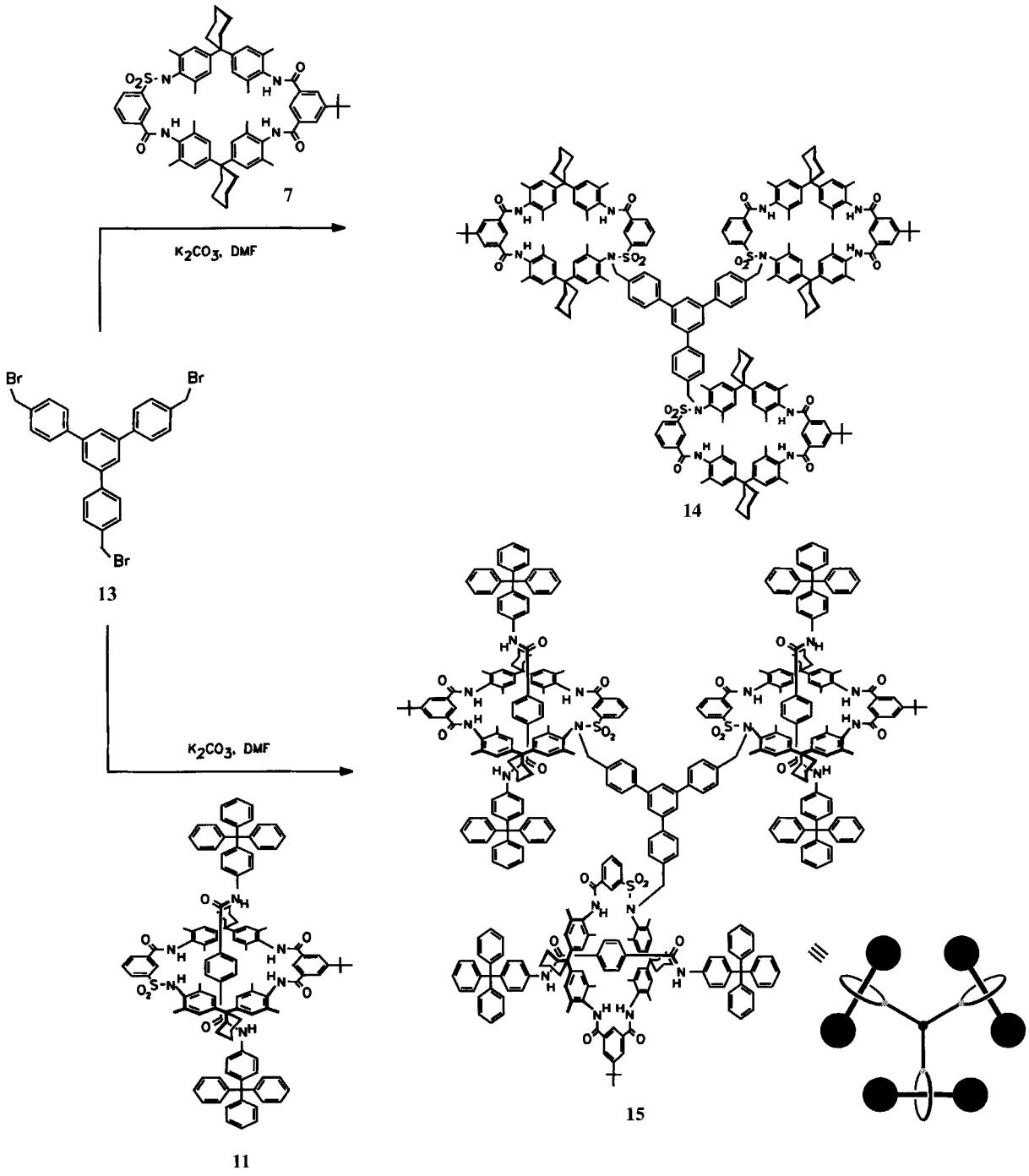
Conclusions and Outlook

The directed integration of sulfonamide[16] moieties into rotaxanes opens up a synthetic strategy for creating new assemblies. Nanoscale architectures such as polyrotaxanes[17–19] and ultimately dendritic rotaxanes[20] now appear to be a realistic goal. We have demonstrated the synthetic potential of the iodo-substituted rotaxane **10** (e.g. with the synthesis of unsymmetrical "bis[2]rotaxane" **12**). Owing to its reactivity, **10** can be used as terminal group in dendrimer synthesis and, in combination with various areas of organic chemistry, is a promising building block for the synthesis of novel molecular architectures and topologies containing mechanically bound components. These designed nanostructures are expected to provide materials with interesting properties, for example, topologically chiral[21] materials (cf. cycloenantiomeric rotaxanes[22]), structures with luminescent building blocks in the wheel or axle[23] or allowing electron transfer processes between moieties of the molecule,[24] and catenane/rotaxane polymers.[25]

Experimental Section

General Methods: Chemicals were purchased from Fluka and Aldrich and were used as received. Dichloromethane was dried over 4 Å molecular sieves, DMF was distilled before use. 3-Sulfobenzoic acid dichloride (**19b**),[26] bis[2-(3′-aminopropyloxy)ethyl] ether **5**,[10] macrocycle **7**,[11] [2]rotaxane **3**,[9] [2]rotaxane **11**,[11] and 1,3,5-tris(4-bromomethylphenyl)benzene (**13**)[27] were prepared according to published procedures. Thin-layer chromatography was carried out on aluminum sheets precoated with silica gel $60\,F_{254}$ (Merck 1.05554). The sheets were inspected by UV light ($\lambda = 254$ nm). Column chromatography was carried out on silica gel 60 (Merck 15101) and high-performance liquid chromatography on a Gilson Serie Abimed fitted with a UV detector. The column was packed with Lichrosorb RP18-5[28] or Eurospher 100-C18.[29] Melting points were determined on a Kofler microscope heater (Reichert, Wien) and are not corrected. Microanalyses were performed by the Microanalytical Department at the "Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn". Fast-atom bombardment mass spec-

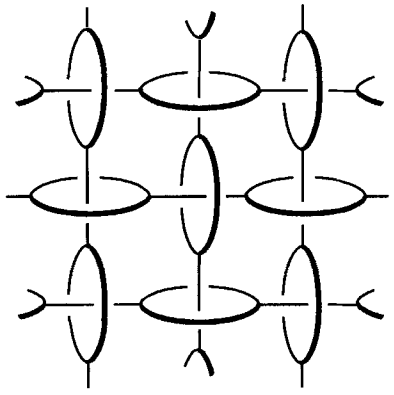
0947-6539/97/0312-2046 $ 17.50+.50/0 *Chem. Eur. J.* **1997**, *3*, No. 12



Scheme 5. Synthesis of trismacrocycle **14** and the first amide-linked [4]rotaxane **15**.

tra (FABMS) were obtained on an Kratos Concept 1 H spectrometer (Kratos, Manchester, UK). The matrix used was *m*-nitrobenzyl alcohol. MALDI-TOF spectra were recorded on a Micromass TOF spec E (Micromass, Manchester, UK); the matrices used were 9-nitroanthracene (9-NA) and 2,5-dihydroxybenzoic acid (2,5-DHB). The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 250 (250 MHz (^1H), 62.9 MHz (^{13}C)) or a Bruker AM 400 (400 MHz (^1H), 100.6 MHz (^{13}C)) spectrometer. Abbreviations: ar.: aromatic; cy: cyclohexyliden; *t*Bu: *tert*-butyl; iso: isophthaloyl; 3sb: 3-sulfobenzoyl; ter: terephthaloyl.

[3]Rotaxane 4: Potassium carbonate (30 mg, 0.22 mmol) was suspended in a solution of [2]rotaxane **3** (254 mg, 0.14 mmol) in dry DMF (15 mL). 1,2-Bis(2-iodoethoxy)ethane (26 mg, 70 µmol) dissolved in dry DMF (10 mL) was added to this suspension at room temperature. The reaction mixture was



Scheme 6. Part of a proposed rotaxane network (cf. the organometallic rotaxane network of Robson and co-workers [13]).

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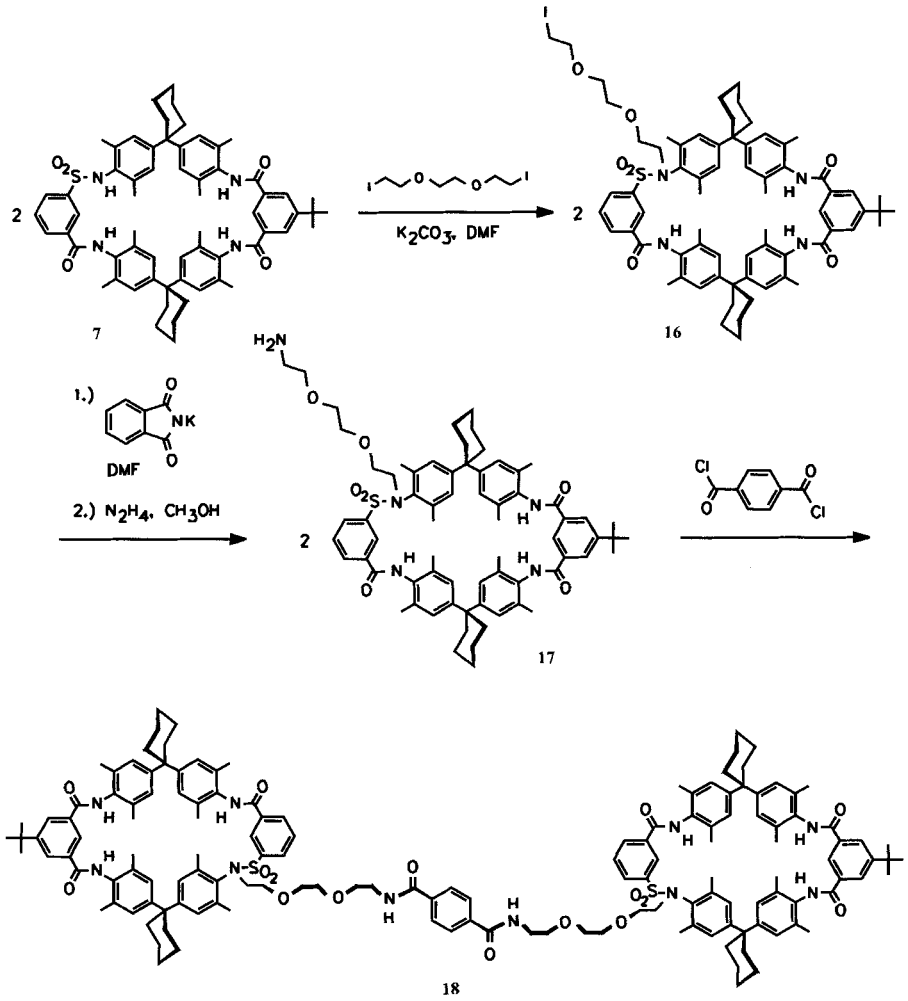
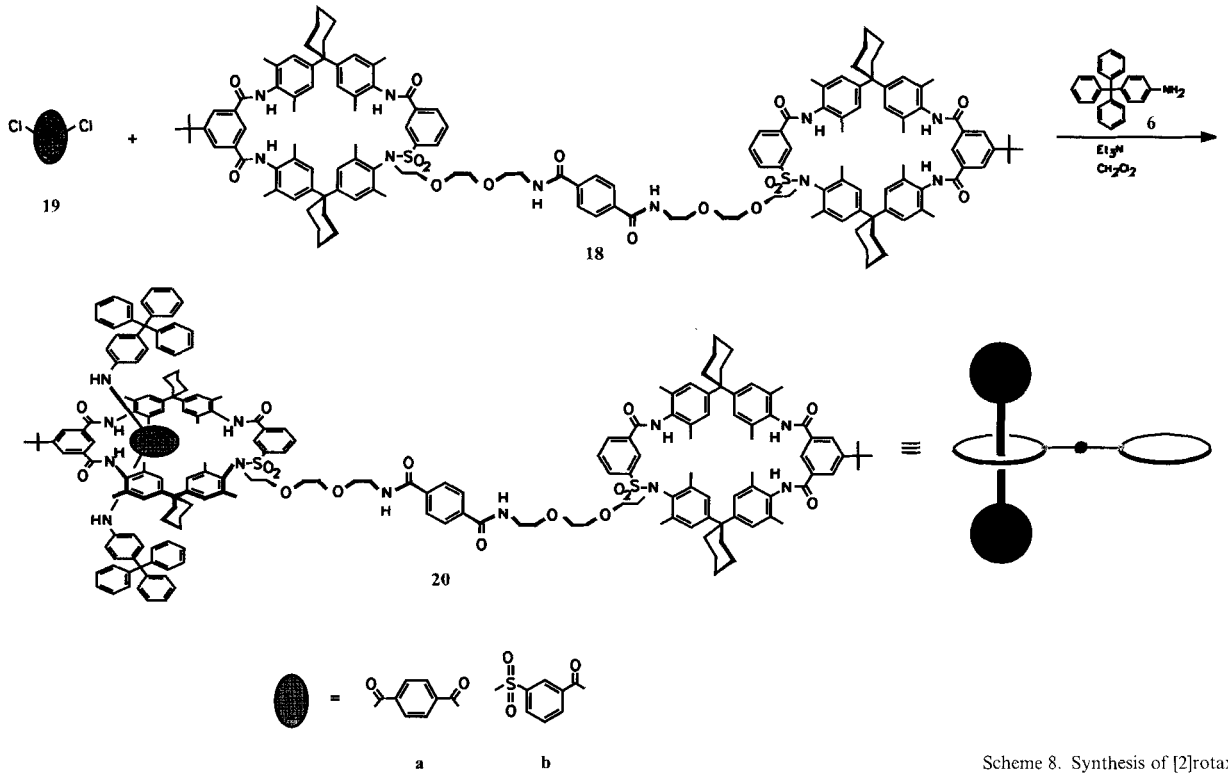


Scheme 7. Synthesis of the macrocyclic blocking group **17** and bismacrocycle **18**.

stirred for 2 d, the solvent removed in vacuo, and the remaining residue purified by column chromatography (SiO_2, dichloromethane/ethyl acetate/diethyl ether 20:1:1; $R_f = 0.67$). 126 mg (48% yield). M.p. 239 °C; MALDI-TOF (2,5-DHB): $m/z = 3709.9$ $[M+H]^+$; ^{1}H NMR (250 MHz, $CDCl_3 + CD_3OD$, 20 °C): $\delta = 0.94$ (s, 18H; CH_3-*t*Bu), 1.10–1.39 (br, 24H; CH_2), 1.44 (s, 24H; CH_3), 1.47 (s, 24H; CH_3), 1.97 (br, 16H; CH_2), 2.89–2.95 (br, 8H; CH_2N, CH_2O), 3.63 (br, 4H; CH_2O), 6.00 (d, 4H, ^3J(H,H) = 7.7 Hz; stopper), 6.18 (d, 2H, ^3J(H,H) = 7.8 Hz; 3sb-axle), 6.41 (d, 4H, ^3J(H,H) = 8.7 Hz; stopper), 6.57 (s, 8H; wheel), 6.62 (s, 8H; wheel), 6.71 (d, 4H, ^3J(H,H) = 7.7 Hz; stopper), 6.75–6.95 (signal group, 66H; 64H stopper, 2H 3sb-axle), 7.06 (d, 2H, ^3J(H,H) = 7.8 Hz; 3sb-axle), 7.14 (t, 2H, ^3J(H,H) = 7.6 Hz; iso-wheel), 7.68 (d, 4H, ^3J(H,H) = 7.6 Hz; iso-wheel), 7.70 (s, 2H; 3sb-axle), 7.83 (s, 4H; *t*Bu-iso-wheel), 7.97 (s, 2H; *t*Bu-iso-wheel), 8.03 (s, 2H; iso-wheel).

[2]Rotaxane 8: A solution of **7** (4.9 g, 4.9 mmol) and **5** (518 mg, 0.94 mmol) in dry dichloromethane (150 mL) was added at room temperature over a period of 5 h to *p*-triphenylmethylaniline (**6**) (631 mg, 1.88 mmol) and triethylamine (0.26 mL, 1.88 mmol) in dry dichloromethane (100 mL). After removal of the solvent the remaining residue was purified by column chromatography (SiO_2, dichloromethane/methanol/diethyl ether 30:1:5, $R_f = 0.35$). The resulting product was a mixture of [2]- and [3]rotaxane. [2]Rotaxane **8** was isolated by HPLC on Lichrosorb RP18-5 (liquid phase: CH_3OH); the [3]rotaxane could not be isolated in a pure form. 122 mg (6% yield). M.p. 205–207 °C; FABMS: $m/z = 2148.0$ $[M+H]^+$, 997.5 $[M+H$ (wheel **7**)$]^+$; MALDI-TOF (9-NA): $m/z = 2148.1$ $[M+H]^+$; ^{1}H NMR (400 MHz,



Scheme 8. Synthesis of [2]rotaxanes **20a** and **b**.

0947-6539/97/0312-2048 $ 17.50+.50/0 *Chem. Eur. J.* **1997**, *3*, No. 12

[D$_7$]DMF, 20 °C) = 1.37 (s, 9H; CH$_3$-*t*Bu), 1.48 (br, 8H; CH$_2$), 1.58 (br, 8H; CH$_2$), 1.80 (s, 12H; CH$_3$), 2.20 (s, 6H; CH$_3$), 2.22 (s, 6H; CH$_3$), 2.33–2.47 (br, 8H; CH$_2$), 3.15 (br, 4H; CH$_2$N), 3.38 (t, 4H, ^3J(H,H) = 6.3 Hz; CH$_2$O), 3.50 (m, 8H; CH$_2$O), 7.09 (s, 2H; wheel), 7.14 (s, 2H; wheel), 7.20 (d, 4H, ^3J(H,H) = 8.6 Hz; stopper), 7.22–7.38 (signal group, 30H; stopper), 7.42 (m, 8H; 4H iso-axle, 4H wheel), 7.68 (d, 4H, ^3J(H,H) = 8.6 Hz; stopper), 7.85 ("t", 1H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 7.90 (d, 2H, ^3J(H,H) = 7.8 Hz; iso-axle), 8.03 (s, 1H; 3sb-wheel), 8.15 (s, 1H; *t*Bu-iso-wheel), 8.22 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.28 (s, 1H; *t*Bu-iso-wheel), 8.31 (s, 2H; NH-aliph.), 8.34 (s, 2H; iso-axle), 8.46 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.60 (s, 1H; NH-wheel), 9.04 (s, 1H; *t*Bu-iso-wheel), 9.25 (br, 1H; SO$_2$NH-wheel), 9.43 (s, 1H; NH-wheel), 10.32 (s, 2H; NH-axle), 10.33 (s, 1H; NH-wheel); ^{13}C NMR (100.6 MHz, CDCl$_3$ + CD$_3$OD, 20 °C) = 18.14, 18.23, 18.46, 18.80 (CH$_3$), 22.53, 22.70, 26.01, 27.17, 28.76 (CH$_2$), 30.92 (CH$_3$-*t*Bu), 34.32 (CH$_2$N), 35.06 (C$_q$-*t*Bu), 36.70, 37.53 (CH$_2$), 44.68, 44.75 (C$_q$-cy), 64.44 (C$_q$-trityl), 69.15, 69.79, 70.06 (CH$_2$O), 120.46, 122.72, 125.33, 125.49, 125.61, 125.84, 126.58, 126.86, 127.31, 128.49, 129.13, 129.58, 129.88, 130.06 (CH), 130.17, 130.70 (C$_q$), 130.92, 131.27 (CH), 133.26, 133.78, 134.41, 134.63, 134.89, 134.91, 135.13, 135.30, 135.38, 137.68, 143.30, 143.80, 146.01, 146.51, 147.11, 148.53, 149.47, 153.31 (C$_q$), 164.58, 165.64, 166.04, 166.66, 167.64 (CO); $C_{139}H_{142}N_8O_{12}S \cdot 5H_2O$: calcd C 74.57, H 6.84, N 5.00, S 1.43; found C 74.80, H 6.74, N 4.80, S 1.62.

[3]Rotaxane 9 and iodide 10: Potassium carbonate (7 mg, 51 μmol) was suspended in a solution of 1,2-bis(2-iodoethoxy)ethane (27 mg, 73 μmol) in dry DMF (5 mL). [2]Rotaxane **8** (110 mg, 51 μmol) dissolved in dry DMF (8 mL) was added at room temperature to this suspension. The reaction mixture was stirred for 12 h, the solvent removed in vacuo, and the remaining residue purified by column chromatography (SiO$_2$, dichloromethane/methanol/diethyl ether 20:1:5).

9: R_f = 0.39; 12 mg (10% yield). M.p. 197 °C; MALDI-TOF (2,5-DHB) m/z = 4413.3 $[M+H]^+$, 4433.6 $[M+Na]^+$, 4450.6 $[M+K]^+$; ^{1}H NMR (400 MHz, [D$_7$]DMF, 20 °C): δ = 1.38 (s, 18H; CH$_3$-*t*Bu), 1.50 (br, 8H; CH$_2$), 1.62 (br, 24H; CH$_2$), 1.81 (s, 12H; CH$_3$), 2.22 (s, 36H; CH$_3$), 2.44 (br, 16H; CH$_2$), 3.14–3.53 (signal group, 44H; CH$_2$N, CH$_2$O), 7.08 (s, 8H; wheel), 7.18–7.38 (signal group, 80H; 76H stopper, 4H iso-axle), 7.42 (s, 8H; wheel), 7.84 ("t", 2H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.05 (s, 2H; 3sb-wheel), 8.16 (s, 2H; *t*Bu-iso-wheel), 8.17 (s, 4H; iso-axle), 8.23–8.38 (signal group, 16H; 2H 3sb-wheel, 2H *t*Bu-iso-wheel, 8H iso-axle, 4H NH-axle), 8.54 (d, 2H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.59 (s, 4H; NH-axle), 9.03 (s, 2H; H *t*Bu-iso-wheel), 9.44 (s, 2H; NH-wheel), 10.30 (s, 2H; NH-wheel), 10.33 (s, 2H; NH-wheel); $C_{284}H_{294}N_{16}O_{26}S_2 \cdot 9H_2O$: calcd C 74.58, H 6.88, N 4.90; found C 74.25, H 6.66, N 4.45.

10: R_f = 0.67; 87 mg (71% yield). M.p. 169 °C; MALDI-TOF (2,5-DHB): m/z = 2390.6 $[M+H]^+$, 2412.6 $[M+Na]^+$, 2428.5 $[M+K]^+$; ^{1}H NMR (250 MHz, [D$_7$]DMF, 20 °C): δ = 1.39 (s, 9H; CH$_3$-*t*Bu), 1.53 (br, 4H; CH$_2$), 1.61 (br, 12H; CH$_2$), 1.83 (s, 12H; CH$_3$), 2.24 (s, 12H; CH$_3$), 2.48 (br, 8H; CH$_2$), 3.35–3.75 (signal group, 28H; CH$_2$I, CH$_2$N, CH$_2$O), 7.10 (s, 4H; wheel), 7.20 (d, 4H, ^3J(H,H) = 8.6 Hz; stopper), 7.25–7.38 (signal group, 38H; 30H stopper, 8H iso-axle), 7.42 (s, 4H; wheel), 7.67 (d, 4H, ^3J(H,H) = 8.6 Hz; stopper), 7.88 ("t", 1H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.08 (s, 1H; 3sb-wheel), 8.18 (s, 1H; *t*Bu-iso-wheel), 8.28 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.29 (s, 1H; *t*Bu-iso-wheel), 8.34 (s, 2H; NH-axle), 8.55 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.60 (s, 2H; NH-axle), 9.03 (s, 1H; *t*Bu-iso-wheel), 9.43 (s, 1H; NH-wheel), 10.28 (s, 1H; NH-wheel), 10.33 (s, 1H; NH-wheel); ^{13}C NMR (100.6 MHz, CDCl$_3$, 20 °C): δ = 2.83 (CH$_2$I), 18.42, 18.72, 18.93 (CH$_3$), 22.91, 23.02, 23.75, 28.94, 30.40 (CH$_2$), 31.28 (CH$_3$-*t*Bu), 35.28 (C$_q$-*t*Bu), 38.73 (CH$_2$), 44.92, 45.19 (C$_q$-cy), 64.62 (C$_q$-trityl), 68.13, 68.19, 69.84, 69.99, 70.07, 70.24, 71.89 (CH$_2$N, CH$_2$O), 125.60, 126.06, 126.14, 127.55, 127.63, 127.92, 128.79, 128.83, 128.86, 129.10, 129.84, 129.86, 130.79, 130.96, 131.13, 131.46 (CH), 131.87, 132.43, 133.66, 134.13, 134.18, 134.39, 135.10, 135.13, 135.50, 141.50, 146.69, 153.33, 153.50 (C$_q$), 164.16, 164.41, 165.41, 165.43, 165.87 (CO); $C_{145}H_{153}IN_8O_{14}S \cdot 6H_2O$: calcd C 69.69, H 6.66, N 4.48, S 1.28; found C 69.56, H 6.99, N 3.48, S 1.88.

[3]Rotaxane 12: Potassium carbonate (1.5 mg, 11.1 μmol) was suspended in a solution of [2]rotaxane **11** (18 mg, 10.4 μmol) in dry DMF (10 mL). Iodide **10** (35 mg, 14.6 μmol) dissolved in dry DMF (5 mL) was added to this suspension at room temperature. The reaction mixture was stirred for an additional 12 h, the solvent removed in vacuo, and the remaining residue purified by column chromatography (SiO$_2$, dichloromethane/methanol/diethyl ether 5:0.1:1; R_f = 0.36). 11 mg (27% yield). M.p. 229 °C; MALDI-TOF (2,5-DHB): m/z = 4061.0 $[M+H]^+$, 4083.8 $[M+Na]^+$, 4098.9 $[M+K]^+$; ^{1}H NMR (400 MHz, [D$_7$]DMF, 20 °C): δ = 1.38 (s, 9H; CH$_3$-*t*Bu), 1.39 (s, 9H; CH$_3$-*t*Bu), 1.50 (br, 8H; CH$_2$), 1.59 (br, 20H; CH$_2$), 1.81 (s, 12H; CH$_3$), 2.11 (s, 12H; CH$_3$), 2.23 (s, 24H; CH$_3$), 2.45 (br, 16H; CH$_2$), 3.10–3.55 (signal group, 28H; CH$_2$N, CH$_2$O), 7.04 (s, 4H; wheel), 7.08 (s, 4H; wheel), 7.10 (s, 4H; wheel), 7.18–7.38 (signal group, 82H; 76H stopper, 2H iso-axle, 4H ter-axle), 7.41 (s, 4H; wheel), 7.85 (m, 2H; 3sb-wheel), 8.07 (s, 2H; 3sb-wheel), 8.15 (s, 2H; *t*Bu-iso-wheel), 8.16 (s, 2H; iso-axle), 8.23–8.35 (signal group, 10H; 2H 3sb-wheel, 2H *t*Bu-iso-wheel, 4H iso-axle, 2H NH-axle), 8.54 (d, 2H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.58 (s, 2H; NH-axle), 8.59 (s, 2H; NH-axle), 8.95 (s, 2H; *t*Bu-iso-wheel), 9.03 (s, 1H; NH-wheel), 9.20 (s, 1H; NH-wheel), 9.43 (s, 1H; NH-wheel), 10.32 (s, 1H; NH-wheel), 10.33 (s, 1H; NH-wheel), 10.41 (s, 1H; NH-wheel).

Trismacrocycle 14: Macrocycle **7** (637 mg, 0.64 mmol) and 1,3,5-tris(4-bromomethylphenyl)benzene (**13**) (125 mg, 0.21 mmol) were dissolved in DMF (15 mL). After addition of potassium carbonate (88 mg, 0.64 mmol) the resulting mixture was stirred for 48 h at 50 °C. After removal of the solvent, the remaining residue was purified by column chromatography (SiO$_2$, dichloromethane/ethyl acetate/diethyl ether 20:1:1; R_f = 0.21). 504 mg (71% yield). M.p. > 300 °C; FABMS: m/z = 3334.7 $[M+H]^+$; MALDI-TOF: m/z = 3334.5 $[M+H]^+$; ^{1}H NMR (250 MHz, CDCl$_3$ + CD$_3$OD, 20 °C): δ = 1.12–1.65 (br, 36H; CH$_2$), 1.25 (s, 27H; CH$_3$-*t*Bu), 1.91 (s, 36H; CH$_3$), 1.92–2.38 (br, 24H; CH$_2$), 2.02 (s, 36H; CH$_3$), 4.38 (s, 6H; CH$_2$N), 6.60 (s, 6H; ar-H), 6.75 (s, 6H; ar-H), 6.85 (s, 12H; ar-H), 6.89 (d, 6H, ^3J(H,H) = 7.8 Hz; *ter*-H), 7.32 (d, 6H, ^3J(H,H) = 7.8 Hz; *ter*-H), 7.49 (s, 3H; ar-H), 7.52 (dd, 3H, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 7.6 Hz; 3sb-H), 7.99 (d, 3H, ^3J(H,H) = 7.6 Hz; 3sb-H), 8.02 (s, 6H; *t*Bu-iso-H), 8.08 (s, 3H; *t*Bu-iso-H), 8.09 (d, 3H, ^3J(H,H) = 7.6 Hz; 3sb-H) 8.11 (s, 3H; 3sb-H); ^{13}C NMR (62.9 MHz, CDCl$_3$ + CD$_3$OD): δ = 17.94, 18.17, 18.33, 18.82 (CH$_3$), 22.53, 22.62, 25.98, 26.32 (CH$_2$), 30.99 (CH$_3$-*t*Bu), 34.78 (CH$_2$), 34.90 (C$_q$-*t*Bu), 36.65 (CH$_2$), 44.65, 44.75 (C$_q$-cy), 53.48 (CH$_2$N), 123.03, 124.71, 125.43, 126.05, 126.55, 126.72, 127.03, 127.34, 128.49, 128.71, 129.08, 130.01, 130.55, 130.68, 130.83, 131.14, 131.21 (CH), 133.00, 133.40, 133.67, 133.73, 134.81, 134.99, 135.10, 140.40, 141.52, 142.33, 146.01, 146.86, 148.48, 149.18, 153.18 (C$_q$), 165.16, 166.28, 166.53 (CO).

[4]Rotaxane 15: [2]Rotaxane **11** (210 mg, 0.12 mmol) and 1,3,5-tris(4-bromomethylphenyl)benzene (**13**) (23 mg, 0.04 mmol) were dissolved in DMF (12 mL). After addition of potassium carbonate (30 mg, 0.22 mmol), the resulting mixture was stirred for 48 h at 50 °C. After removal of the solvent, the remaining residue was purified by column chromatography (SiO$_2$, dichloromethane/ethyl acetate 25:1; R_f = 0.08). 79 mg (35% yield). M.p. > 300 °C; MALDI-TOF (2,5-DHB): m/z = 5759.4 $[M+Na]^+$; ^{1}H NMR (250 MHz, CDCl$_3$ + CD$_3$OD): δ = 1.12–1.65 (br, 36H; CH$_2$), 1.30 (s, 27H; CH$_3$-*t*Bu), 1.75–2.38 (br, 24H; CH$_2$), 1.91 (s, 36H; CH$_3$), 1.93 (s, 36H; CH$_3$), 4.58 (s, 6H; CH$_2$N), 6.68–7.62 (signal group, 168H; ar-H), 8.03–8.21 (signal group, 15H; ar-H), 8.70 (s, 3H; ar-H); ^{13}C NMR: (62.9 MHz, CDCl$_3$ + CD$_3$OD): δ = 18.29, 18.42, 18.61, 18.88 (CH$_3$), 22.78, 26.29 (CH$_2$), 31.00 (CH$_3$-*t*Bu), 34.45 (CH$_2$), 35.16 (C$_q$-*t*Bu), 44.79, 44.87 (C$_q$-cy), 53.45 (CH$_2$N), 121.29, 122.42, 125.16, 125.58, 125.92, 126.74, 127.05, 127.20, 127.42, 127.63, 127.79, 128.70, 128.97, 129.51, 130.06, 130.19, 130.48, 130.60, 130.76, 130.97, 131.09 (CH), 131.28, 131.90, 133.06, 133.14, 133.64, 133.75, 134.87, 135.01, 135.24, 135.38, 137.36, 140.54, 141.61, 141.89, 141.95, 143.70, 143.78, 146.17, 146.37, 146.58, 147.25, 148.58, 150.19, 153.50 (C$_q$), 164.21, 165.33, 165.74 (CO).

Iodide 16: Potassium carbonate (91 mg, 0.66 mmol) was suspended in a solution of 1,2-bis(2-iodoethoxy)ethane (407 mg, 1.1 mmol) in dry DMF (10 mL). Macrocycle **7** (658 mg, 0.66 mmol) dissolved in dry DMF (20 mL) was added to this suspension at room temperature within a period of 3 h. The reaction mixture was stirred for an additional 12 h, the solvent removed in vacuo, and the remaining residue purified by column chromatography (SiO$_2$, trichloromethane/ethyl acetate 4:1; R_f = 0.50). 507 mg (62% yield). M.p. 197–198 °C (decomp.); FABMS: m/z = 1239.6 $[M+H]^+$; ^{1}H NMR (250 MHz, [D$_7$]DMF, 20 °C) = 1.43 (s, 9H; CH$_3$-*t*Bu), 1.50–1.70 (br, 12H; CH$_2$), 2.18 (s, 6H; CH$_3$), 2.23 (s, 12H; CH$_3$), 2.25 (s, 6H; CH$_3$), 2.40–2.55 (br, 8H; CH$_2$), 3.35–3.65 (signal group, 12H; CH$_2$I, CH$_2$N, CH$_2$O), 7.25 (s, 2H; ar-H), 7.26 (s, 4H; ar-H), 7.29 (s, 2H; ar-H), 7.88 ("t", 1H, ^3J(H,H) = 7.8 Hz; 3sb-H), 8.19 (s, 1H; *t*Bu-iso-H), 8.26 (s, 1H; *t*Bu-iso-H), 8.28 (s, 1H; *t*Bu-iso-H), 8.30 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-H), 8.50 (d, 1H,

^3J(H,H) = 7.8 Hz; 3sb-H), 8.80 (s, 1H; 3-sb-H), 9.15 (s, 1H; NH), 9.85 (s, 1H; NH), 10.05 (s, 1H; NH); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20 °C): δ = 2.83 (CH_2I), 18.47, 19.07, 19.25, 19.41 (CH_3), 22.84, 23.02, 26.33, 26.40 (CH_2), 31.25 (CH_3-*t*Bu), 35.39 (CH_2), 36.23 (C_q-*t*Bu), 37.25 (CH_2), 44.95, 45.48 (C_q-cy), 49.54 (CH_2N), 68.20, 70.01, 70.26, 71.93 (CH_2O), 121.42, 125.88, 126.42, 127.19, 127.82, 128.21, 128.83, 129.40, 129.65 (CH), 130.60 (C_q), 130.94, 131.31 (CH), 132.45, 134.29, 134.47, 134.74, 134.89, 135.35, 137.89, 141.82, 144.80, 146.89, 148.75, 150.63, 154.10 (C_q), 164.28, 165.08, 165.48 (CO); $C_{69}H_{83}IN_4O_7S \cdot 3H_2O$: calcd C 64.07, H 6.94, N 4.33, S 2.48; found C 63.70, H 6.58, N 3.86, S 3.75.

Amine 17: Potassium phthalimide (302 mg, 1.63 mmol) was added to a solution of iodide **16** (832 mg, 0.67 mmol) in dry DMF (20 mL). The reaction mixture was heated to 90 °C for 7 h and stirred gently. After cooling, trichloromethane (80 mL) was added, and the organic phase was extracted three times with water (50 mL) and dried over magnesium sulfate. The solvent was removed in vacuo and the remaining residue purified by column chromatography to give the corresponding phthalimide (m.p. 195–9 °C) (SiO_2, dichloromethane/ethyl acetate 4:1; R_f = 0.67). 596 mg (70% yield). The phthalimide (188 mg, 0.15 mmol) was dissolved in methanol (10 mL). After addition of hydrazine hydrate (0.3 mL), the solution was refluxed for 2 h. Finally the solvent was removed in vacuo, and the remaining residue purified by column chromatography (SiO_2, dichloromethane/methanol/ammonia 20:1.6:0.4; R_f = 0.20). 163 mg (93% yield). M.p. 257 °C; FABMS: *m/z* = 1128.3 $[M+H]^+$; ^{1}H NMR (250 MHz, [D$_7$]DMF, 20 °C): δ = 1.40 (s, 9H; CH_3-*t*Bu), 1.55 (br, 8H; CH_2), 1.62 (br, 4H; CH_2), 2.15 (s, 6H; CH_3), 2.22 (s, 12H; CH_3), 2.25 (s, 6H; CH_3), 2.38–2.65 (br, 8H; CH_2), 3.20–3.65 (signal group, 12H; CH_2N, CH_2O), 5.82 (m, 2H; NH_2), 7.25 (s, 4H; ar-H), 7.29 (s, 4H; ar-H), 7.88 ("t", 1H, ^3J(H,H) = 7.8 Hz; 3sb-H), 8.20 (s, 1H; *t*Bu-iso-H), 8.27 (s, 1H; *t*Bu-iso-H), 8.29 (br, 2H; 3sb-H), 8.52 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-H), 8.85 (s, 1H; *t*Bu-iso-H), 9.23 (s, 1H; NH), 9.85 (s, 1H; NH), 10.05 (s, 1H; NH); ^{13}C NMR (62.9 MHz, [D$_7$]DMF, 20 °C): δ = 18.69, 18.85, 18.97, 19.42 (CH_3), 23.44, 23.57, 26.73, 28.92 (CH_2), 31.40 (CH_3-*t*Bu), 37.50 (CH_2), 42.23 (C_q-*t*Bu), 45.41, 45.89 (CH_2N), 50.43, 55.43 (C_q-cy), 68.73, 70.46, 70.51, 73.34 (CH_2O), 125.44, 126.27, 126.55, 127.76, 128.44, 128.62, 129.97, 130.13, 131.29, 131.69 (CH), 133.28, 133.70, 134.03, 135.25, 135.68, 135.80, 135.89, 135.89, 135.93, 142.55, 145.17, 147.36, 148.20, 150.86, 153.10 (C_q), 164.59, 165.44, 165.99 (CO).

Bismacrocycle 18: A solution of terephthaloyl dichloride (**19a**) (26 mg, 0.13 mmol) in dry dichloromethane (15 mL) was added at room temperature to amine **17** (298 mg, 0.26 mmol) and triethylamine (0.04 mL, 0.26 mmol) dissolved in dry dichloromethane (100 mL) over a period of 2 h. After removal of the solvent the remaining residue was purified by column chromatography (SiO_2, dichloromethane/methanol/diethyl ether 30:1:5, R_f = 0.49). 216 mg (69% yield). M.p. 270–275 °C; FABMS: *m/z* = 2387.4 $[M+H]^+$; ^{1}H NMR (250 MHz, [D$_7$]DMF, 20 °C): δ = 1.40 (s, 18H; CH_3-*t*Bu), 1.50 (br, 16H; CH_2), 1.58 (br, 8H; CH_2), 2.18 (s, 24H; CH_3), 2.20 (s, 12H; CH_3), 2.21 (s, 12H; CH_3), 2.35–2.60 (br, 16H; CH_2), 3.30–3.70 (signal group, 24H; CH_2N, CH_2O), 7.25 (s, 8H; ar-H), 7.28 (s, 8H; ar-H), 7.87 ("t", 2H, ^3J(H,H) = 7.9 Hz; 3sb-H), 8.20 (s, 2H; *t*Bu-iso-H), 8.28 (m, 8H; 4H ter-H, 2H 3sb-H, 2H *t*Bu-iso-H), 8.38 (s, 2H; 3-sb-H), 8.50 (d, 2H, ^3J(H,H) = 7.9 Hz; 3-sb-H), 8.65 (s, 2H; *t*Bu-iso-H), 8.80 (s, 2H; NH), 9.15 (s, 2H; NH), 9.80 (s, 2H; NH), 10.00 (s, 2H; NH); ^{13}C NMR (62.9 MHz, [D$_7$]DMF, 20 °C): δ = 18.69, 18.83, 18.95, 19.43 (CH_3), 23.45, 23.57, 26.72, 26.92 (CH_2), 31.40 (CH_3-*t*Bu), 35.23 (CH_2), 37.24 (C_q-*t*Bu), 40.23 (CH_2N), 45.41, 45.88 (C_q-cy), 50.40 (CH_2N), 68.75, 69.90, 70.72, 70.74 (CH_2O), 125.28, 126.28, 126.55, 127.78, 127.91, 128.48, 128.65, 130.13, 131.25, 131.67 (CH), 133.26, 133.66, 133.98, 135.24, 135.69, 135.80, 135.88, 135.92, 137.75, 142.56, 145.22, 147.40, 148.21, 150.86, 153.14 (C_q), 164.63, 165.38, 165.96, 166.61 (CO); $C_{146}H_{172}N_{10}O_{16}S_2 \cdot 7H_2O$: calcd C 69.77, H 7.46, N 5.57, S 2.55; found C 69.43, H 7.33, N 6.76, S 2.86.

[2]Rotaxane 20a: A solution of **18** (179 mg, 75 μmol) and terephthaloyl dichloride (**19a**) (203 mg, 1 mmol) in dry dichloromethane (15 mL) was added at room temperature over a period of 2 h to *p*-triphenylmethylaniline (**6**) (671 mg, 2 mmol) and triethylamine (0.28 mL, 2 mmol) in dry dichloromethane (30 mL). After removal of the solvent the remaining residue was purified by column chromatography (SiO_2, trichloromethane/methanol/diethyl ether 30:1:2; R_f = 0.10). The resulting product was a mixture of **20a** and unconverted **18**. [2]Rotaxane **20a** could be separated by HPLC on Eurospher 100-C18 (liquid phase: CH_3OH). 32 mg (13% yield). M.p. 260–262 °C; FABMS: *m/z* = 3186.5 $[M+H]^+$, 2386.3 $[M$ + H (bismacrocycle)$]^+$; ^{1}H NMR (400 MHz, [D$_7$]DMF, 20 °C): δ = 1.40 (s, 9H; CH_3), 1.41 (s, 9H; CH_3), 1.50 (br, 8H; CH_2), 1.60 (br, 16H; CH_2), 2.12 (s, 12H; CH_3), 2.17 (s, 12H; CH_3), 2.21 (s, 12H; CH_3), 2.24 (s, 12H; CH_3), 2.43 (br, 16H; CH_2), 3.50–3.68 (signal group, 24H; CH_2N, CH_2O), 7.19–7.36 (signal group, 58H; 38H stopper, 16H wheel, 4H ter-axle), 7.45 (br, 2H; NH-axle), 7.87 ("t", 2H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.04 (s, 4H; ter-spacer), 8.07 (s, 1H; 3sb-wheel), 8.16 (s, 1H; *t*Bu-iso-wheel), 8.19 (s, 1H; *t*Bu-iso-wheel), 8.22–8.31 (signal group, 5H; 3H 3sb-wheel, 2H *t*Bu-iso-wheel), 8.38 (s, 1H; NH wheel), 8.50 (d, 1H, ^3J(H,H) = 8.7 Hz; 3sb-wheel), 8.60 (d, 1H, ^3J(H,H) = 8.7 Hz; 3sb-wheel), 8.65 (br, 2H; NH-aliph.), 8.81 (s, 1H; H *t*Bu-iso-wheel), 8.96 (s, 1H; *t*Bu-iso-wheel), 9.18 (s, 1H; NH-wheel), 9.21 (s, 1H; NH-wheel), 9.84 (s, 1H; NH-wheel), 10.05 (s, 1H; NH-wheel), 10.43 (s, 1H; NH-wheel); ^{13}C NMR (100.6 MHz, $CDCl_3$ + CD_3OD, 20 °C): δ = 17.88, 17.98, 18.20, 18.24, 18.40 (CH_3), 22.46, 22.61, 25.93, 26.11 (CH_2), 30.78 (CH_3-*t*Bu), 34.75 (CH_2), 34.99 (C_q-*t*Bu), 36.69 (CH_2), 39.54 (CH_2N), 44.70, 44.79 (C_q-cy), 49.33 (CH_2N), 64.39 (C_q-trityl), 68.02, 69.37, 69.70, 69.87 (CH_2O), 125.37, 125.45, 125.76, 126.04, 126.95, 127.13, 127.25, 128.50, 128.56, 128.65, 128.75, 128.80, 128.85, 130.22, 130.82, 131.10 (CH), 132.96, 133.40, 133.60, 133.88, 134.47, 134.84, 134.91, 135.05, 135.26, 136.64, 136.67, 140.75, 141.44, 146.42, 153.25, 153.37 (C_q), 164.03, 165.29, 165.74, 166.54, 167.44 (CO); $C_{204}H_{216}N_{12}O_{18}S_2 \cdot 8H_2O$: calcd C 73.53, H 7.02, N 5.04, S 1.92; found C 73.25, H 6.62, N 4.67, S 2.47.

[2]Rotaxane 20b: A solution of **18** (57 mg, 23.9 μmol) and sulfobenzoyl dichloride (**19b**) (239 mg, 1 mmol) in dry dichloromethane (8 mL) was added at room temperature over a period of 2 h to *p*-triphenylmethylaniline (**6**) (671 mg, 2 mmol) and triethylamine (0.28 mL, 2 mmol) in dry dichloromethane (25 mL). After removal of the solvent the remaining residue was purified by column chromatography (SiO_2, dichloromethane/methanol/diethyl ether 30:1:5; R_f = 0.29). The resulting product was a mixture of **20b** and unconverted **18**. [2]Rotaxane **20b** could be separated by HPLC on Eurospher 100-C18 (liquid phase: CH_3OH). 22 mg (28% yield). M.p. 253–256 °C; FABMS: *m/z* = 3223.1 $[M+H]^+$, 2387.1 $[M+H$ (bismacrocycle)$]^+$; MALDI-TOF (9-NA): *m/z* = 3221.8 $[M+H]^+$, 3260.7 $[M+K]^+$; (9-NA + Ag^+): *m/z* = 3329.2 $[M+Ag]^+$; ^{1}H NMR (400 MHz, [D$_7$]DMF, 20 °C): δ = 1.44 (s, 18H; CH_3-*t*Bu), 1.53 (br, 16H; CH_2), 1.64 (br, 8H; CH_2), 2.19 (s, 12H; CH_3), 2.24 (s, 24H; CH_3), 2.26 (s, 12H; CH_3), 2.35–2.58 (br, 16H; CH_2), 3.30–3.69 (signal group, 24H; CH_2N, CH_2O), 7.05 (s, 8H; wheel), 7.09 (s, 4H; wheel), 7.11 (s, 4H; wheel), 7.18–7.37 (m, 38H; stopper), 7.58 ("t", 1H, ^3J(H,H) = 7.8 Hz; 3sb-axle), 7.88 (m, 2H; 3sb-wheel), 7.95 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-axle), 8.08 (s, 4H; ter-spacer), 8.21 (s, 1H; *t*Bu-iso-wheel), 8.21 (s, 1H; *t*Bu-iso-wheel), 8.23–8.33 (signal group, 7H; 2H 3sb-axle, 2H *t*Bu-iso-wheel, 3H 3sb-wheel), 8.55 (d, 1H, ^3J(H,H) = 7.8 Hz; 3sb-wheel), 8.59 (br, 5H; 2H NH-aliph., 1H NH, 2H 3sb-wheel), 8.85 (s, 1H; *t*Bu-iso-wheel), 8.88 (s, 1H; *t*Bu-iso-wheel), 9.15 (s, 1H; NH), 9.27 (s, 1H; NH), 9.32 (br, 1H; NH), 9.91 (s, 1H; NH), 10.09 (s, 1H; NH), 10.41 (s, 1H; NH), 10.47 (s, 1H; NH); ^{13}C NMR (100.6 MHz, $CDCl_3$ + CD_3OD, 20 °C): δ = 18.31, 18.40, 18.83 (CH_3), 22.71, 22.86, 26.19, 26.34 (CH_2), 31.16 (CH_3-*t*Bu), 35.27 (CH_2), 39.84 (C_q-*t*Bu), 40.26 (CH_2N), 44.84, 45.24 (C_q-cy), 64.34, 64.55 (C_q-trityl), 69.21, 69.72, 69.99, 70.13 (CH_2O), 118.93, 122.25, 125.58, 125.61, 125.74, 125.77, 125.94, 126.12, 127.37, 127.44, 127.48, 127.67, 128.43, 128.45, 128.80, 128.92, 128.94, 129.09, 130.91, 131.04, 131.19, 131.20, 131.75 (CH), 133.45, 133.72, 134.01, 134.76, 135.08, 135.34, 135.66, 136.88, 138.47, 140.13, 140.72, 142.96, 144.32, 145.19, 146.43, 146.48, 147.14, 148.89, 149.09, 150.22, 151.06, 153.56 (C_q), 164.13, 165.23, 165.47, 165.58, 165.88 (CO).

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