Amide-Based [3]Catenanes and [2]Catenanes with Aliphatic Chains

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[3]Catenanes of the amide type were synthesized preparatively for the first time. Large macrocycles bearing two guest-binding sites were used to synthesize these amide-linked [3]catenanes in yields of 4%, either by formation of rigid macrocyclic boxes, or with macrocycles consisting of flexible long-chained aliphatic diamines. Furthermore, the systematic introduction of 1,ω-alkane diamines as building blocks for catenanes is described. The synthesis of a series of [2]catenanes by varying the ring size of one of the two macrocycles was also achieved in yields of 10%.

Introduction

The syntheses of oligo- or polycatenanes[1] with mechanically-connected units is a fascinating challenge for preparative chemistry. So far, [3]catenanes of the amide type have been detected only in trace amounts.[2] Since the first syntheses of amide-linked catenanes[3] of type **1** in 1992, rigid angular arene building blocks were considered to be essential for the formation of these interlocked molecules. Although [2]catenanes **2** containing 1,12-diaminododecane building blocks were reported by us,[4] supramolecular synthesized catenanes containing flexible aliphatic chains are very rare.[5] In 1996, Leigh et al. introduced one aliphatic ester-bridge into both macrocycles, which were cyclized by a tin oxide intermediate in order to yield symmetrical catenanes of type **3**.[6]

The postulated mechanism of formation in the template synthesis of catenane of type **1**, is based on the orthogonal host/guest-incorporation of an amide group into the cavity of a predominantly-formed macrocycle (cf. **4** in Figure 2) due to hydrogen bonding between the amide groups of the isophthalamide macrocycle (host) and the guest′s carbonyl oxygen.[7]

NMR titrations revealed the selective host/guest inclusion of amide guests in the cavity of lactam macrocycles such as **4** having 32 ring member atoms.[8] Additionally, our syntheses of rotaxanes containing aliphatic axles[9] indicate that π,π-interactions between guest and host are not essential. Employing chains longer than in catenanes **2**, a [3]catenane **10** (n = 14, Figure 3) was not detected. Whereas oligo-catenanes (based on donor/acceptor complexes and coordination-complexes with a "polymerisation"-grade up to seven) have been reported,[1] higher amide-linked catenanes have not been isolated as yet, but have only been detected in mass spectra.[2] In the new approach to build up [3]catenanes described here, we employ a large "tetrameric" macrocyclic host **5** which is able to incorporate two other macrocycles. The design of this 64-membered macrocycle **5** (Figure 2) containing two complexation sites and its efficient synthesis made the preparative isolation of the first

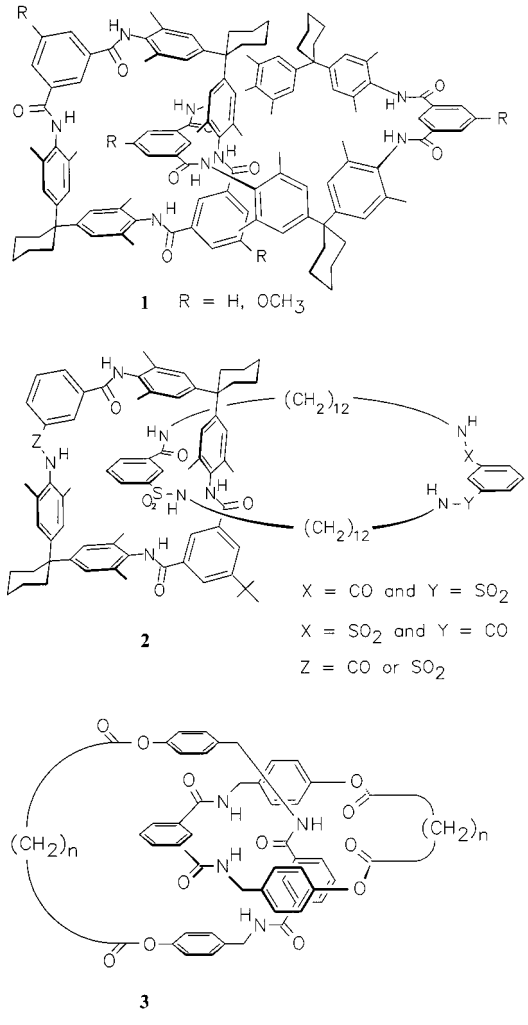

Figure 1. Amide-based [2]catenanes

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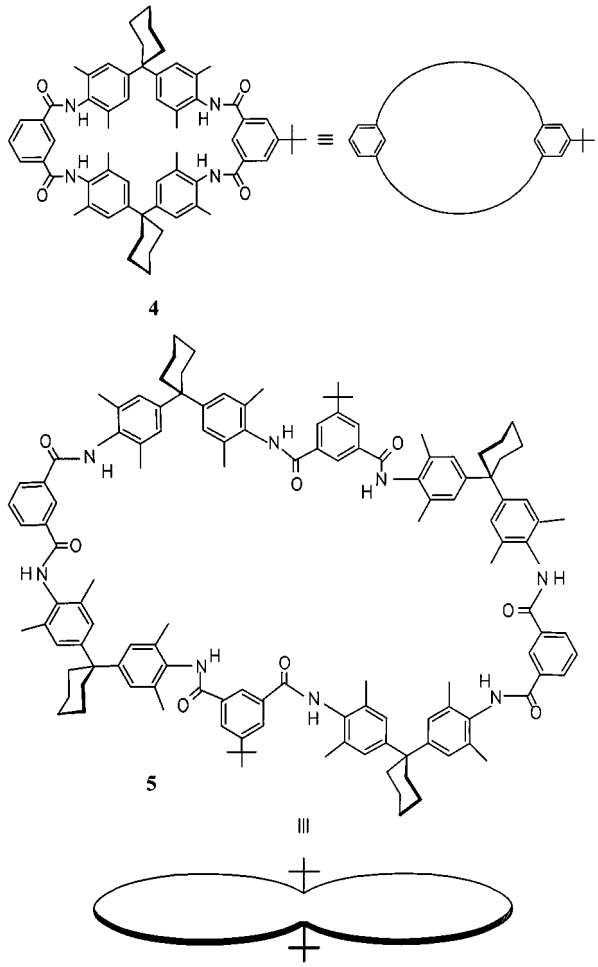


Figure 2. Host macrocycles for the catenane syntheses

amide-linked [3]catenanes **29** and **32** possible, as described below.

Results and Discussion

Synthesis of New [2]Catenanes

Starting from the catenane of type **2**, we set out to investigate the formation of catenanes depending on the size of the cycle bearing the aliphatic chains. Therefore we treated macrocycle **4** with the diacid chloride **9** and the long-chain aliphatic diamines **6**−**8** to obtain the catenanes **11**−**13** in yields of about 10% (Figure 3). These results indicate that the length of the aliphatic chains can be varied over a wide range. However, the reaction with 1,6-diaminohexane did not lead to a [2]catenane. We suppose that the "dimeric" macrocycle which is formed is not of an adequate size to form a catenane with tetralactam **4**. A corresponding [3]catenane of type **10** has not been detected in any of the reactions.

Besides the catenanes, we obtained the free "aliphatic" macrocycles **15**, **17**, and **18** as "dimers" and "monomers" **14** and **16** in about 15% yield. The expected isomers due to the orientation of X and Y in the dimeric cycles were not isolated because of the marginal differences in their properties.

For the mechanism of formation, we assume a similar template assistance is at play, as in the formation of catenanes with fixed angular building blocks. It can be seen in NMR titrations that sulfonamides, unlike carboxy amides, are not considerably bound by the lactam box **4**. Furthermore the carbonyl chloride group is more reactive than the sulfonyl chloride group. Thus we suggest that in the first reaction step, a carbonamide is formed, which is then complexed by the macrocycle **4**. Upon subsequent intramolecular formation of the sulfonamide bond, the second macrocycle, and thus the catenane, is formed. We also assume that van der Waals interactions between the aliphatic chains support the formation of these long-chain catenanes in one step.

In order to investigate whether macrocycle **21** was able to form a cavity to enclose a guest molecule and then to form a catenane, we applied an inverse route for the catenane synthesis (Figure 4).

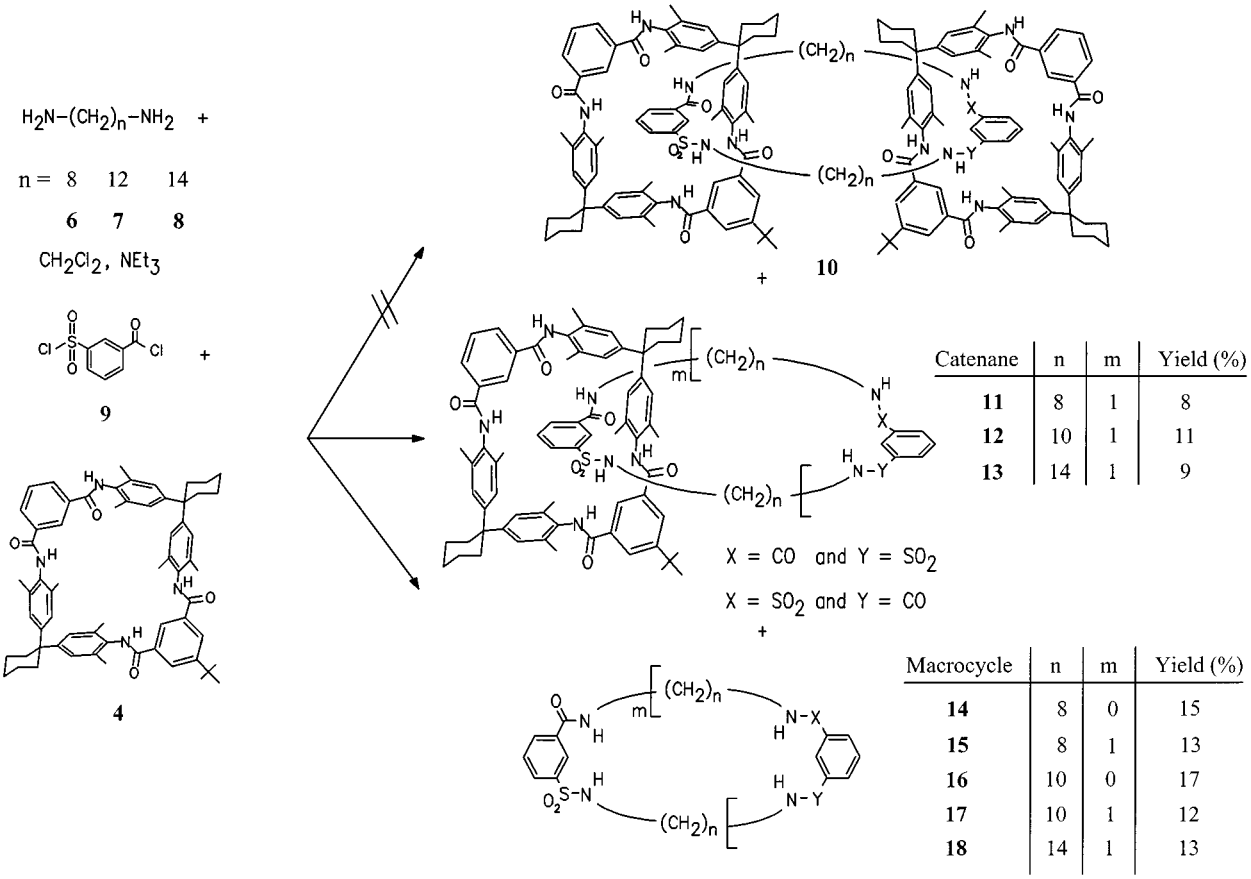
The diacid dichloride **19** was reacted with diamine **20** in the presence of the flexible macrocycle **21**. Remarkably, the formation of catenane **22** was not observed. We think that the attracting forces between the two aliphatic chains of **21** and their flexibility prevent the formation of a preshaped cavity.

Experiments with other diacid chlorides (e.g. isophthaloyl- and terephthaloyl dichloride) have thus far failed. As an alternative, we replaced the acid chlorides by activated esters in the catenane synthesis. In the presence of the macrocycle **4**, the activated ester **24** and the long-chain diamine **23** were reacted under the same conditions (Figure 5). The resulting catenane **25** was isolated in a yield of 7%, and the corresponding free macrocycle **26** in a 12% yield. This result supports the assumption that monoamide guest intermediates − and not acid chlorides − are the species which form inclusion complexes with host macrocycles of type **4**.

Synthesis of New [3]Catenanes

Since the route described in Figure 3 had failed for the syntheses of [3]catenanes, we investigated the formation of an inverse [3]catenane, i.e., a large macrocycle composed of rigid angular building blocks flanked by two flexible macrocycles of type **21**. Therefore we designed macrocycle **5** (in Figure 2) which has twice the size of **4** and possesses two docking sites for guest molecules. We transferred the successful strategy for the formation of [2]catenanes (Figure 3) and replaced the host **4** by the macrocycle **5** (Figure 6). [3]Catenane **29** was obtained in a 4% yield. The corresponding [2]catenane **28**, which seems to be preferred over **29**, could not be isolated but was detected in the mass spectra.

Furthermore, we were able to synthesize the conformationally more rigid [3]catenane **32** in 3% yield, by treating the diamine **20** with acid dichloride **30** in the presence



Catenane	n	m	Yield (%)
11	8	1	8
12	10	1	11
13	14	1	9

Macrocycle	n	m	Yield (%)
14	8	0	15
15	8	1	13
16	10	0	17
17	10	1	12
18	14	1	13

Figure 3. Syntheses of "unsymmetrical" catenanes employing long-chain aliphatic diamines

of macrocycle **5**. The corresponding [2]catenane **31** could not be isolated either, but was detected in the mass spectra. An explanation for the low yield in catenation reactions with **5** could be that its poor solubility allowed only for suspensions, even under dilute conditions.

Conclusion and Outlook

This amide catenane system demonstrated a remarkable tolerance towards variation of the length of the aliphatic chains. In this case, commercially-available diamines were sufficient and the number of reaction steps was low, which was a great advantage towards catenane syntheses, with rigid angular building blocks used so far. These catenanes have two sulfonamide protons, and therefore offer the required functionalities for the syntheses of oligo- and poly-[2]catenanes.[10] Moreover, the alternative route developed here by using activated esters allows for the replacement of the acid dichlorides. We are optimistic that in the near future the yields of these types of [2]catenanes with two different intertwining macrocycles can be raised.

The first step in the synthesis of amide-based oligo-catenanes (which differ from oligo-[2]catenanes) was carried out. If the routes in Figures 3 and 6 can be combined, it is possible to synthesize higher catenanes in one reaction step. Therefore it seems advantageous for future development to raise the yield of the catenanes **29** and **32**, and to design a large ditopic macrocyclic box of type **5** (for two guests) which is more soluble.

Experimental Section

General Remarks: Solvents were purified by standard methods and dried if necessary. – Commercial quality reagents were used. – TLC was carried out on silica gel 60 F 254 and column chromatography on silica gel 60, mesh size 63–100 μm (Merck, Darmstadt, Germany). – Melting points were determined on a microscope heating unit of Reichert, Vienna and are not corrected. – The NMR spectra were measured on AM-250 (^{1}H: 250 MHz, ^{13}C: 62.9 MHz) or on AM-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) spectrometers of Bruker Physik AG, Karlsruhe, Germany. All chemical shifts are quoted in ppm and the coupling constants are expressed in Hertz. – (Abbreviations: Iso: **iso**phthaloyl, 3Sb: **3**-**s**ulfonyl**b**enzoyl, *t*Bi: 5-*tert*-**b**utyl**i**sophthaloyl, Ar: Aryl). – Microanalyses: Microanalytical department of Kekulé-Instiut für Organische Chemie und Biochemie der Universität Bonn. FAB-MS: Concept 1 H, Kratos Analytical Ltd. (matrix: *m*-nitrobenzyl alcohol). MALDI-MS: MALDI-Tof-Spec-E, Micromass, UK (matrix: 9-nitroanthracene, 2,5-dihydroxybenzoic acid).

Macrocycle 5: A solution of 5-*tert*-butylisophthaloyl dichloride **28** (0.80 g, 3 mmol) dissolved in dichloromethane (50 mL) and a solution of *N,N′*-Bis{4-[1-(4-amino-3,5-dimethylphenyl)cyclohexyl]-2,6-dimethylphenyl}isophthaloyl diamide[11] **21** (2.40 g, 3 mmol with 2 equiv. of triethylamine) in dichloromethane (50 mL) were added at

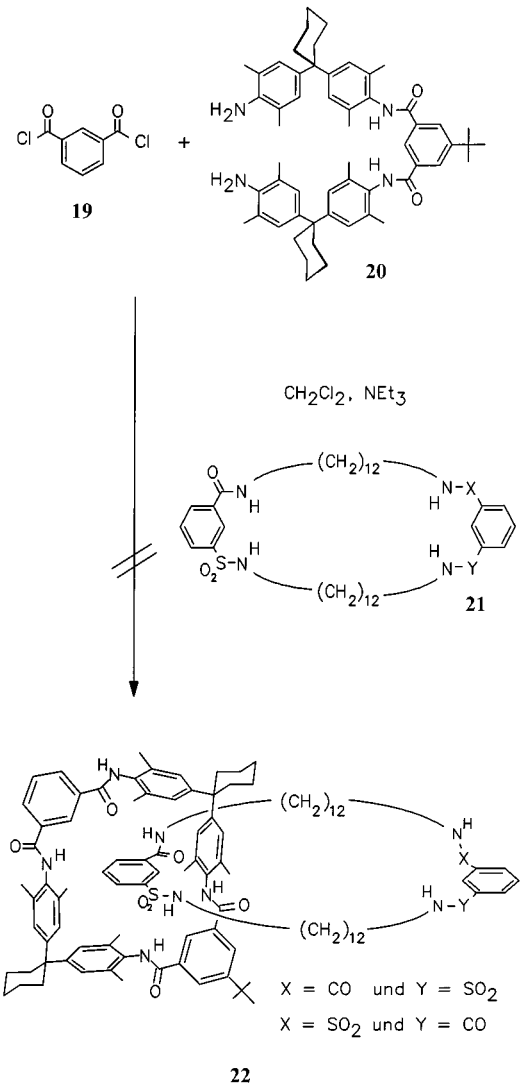


Figure 4. Inverse reaction path to build up catenane **22**

room temperature simultaneously by means of a motor-driven syringe pump to dichloromethane (2000 mL) over 18 h. After stirring for another 24 h, the solvent was evaporated and the residue was dissolved in trichloromethane (200 mL). After 2 d, macrocycle **5** was collected by filtration. The product was recrystallized in dichloromethane/ethyl acetate = 2:1. M.p. > 300°C. − R_f 0.16 (CH_2Cl_2/CH_3OH = 20:1). − Yield 310 mg (10%). − ^{1}H NMR (400 MHz, [D_6]DMSO, 25°C): δ = 1.34 (s, 18 H, *t*Bu), 1.45 (m, 8 H, CH_2), 1.52 (m, 16 H, CH_2), 2.14 (s, 48 H, Ar-CH_3), 2.28 (m, 16 H, CH_2), 7.07 (s, 8 H, Ar-H), 7.08 (s, 8 H, Ar-H), 7.64 [t, ^3J(H,H) = 7.71 Hz, 2 H, Ar-H], 8.11 [d, ^3J(H,H) = 7.71 Hz, 4 H, Ar-H], 8.14 (s, 4 H, Ar-H), 8.41 (s, 2 H, Ar-H), 8.55 (s, 2 H, Ar-H), 9.81 (s, 4 H, amide-NH). − ^{13}C NMR (100.6 MHz, [D_6]DMSO, 25°C): δ = 18.5, 18.6 (CH_3), 22.1, 22.7, 25.9, 26.6 (CH_2), 31.0 (Ar-CH_3), 34.9, 36.0, 44.8, 45.5 (Cq), 124.3, 126.1, 126.9, 127.1, 128.8, 130.2, 132.4, 132.5, (CH), 134.6, 134.8, 135.0, 135.1, 146.7, 146.9, 150.6, 151.6, (Cq), 164.7, 164.9 (C=O). − FAB-MS: *m/z* = 1923.2 $[M + H]^+$, MALDI-MS: *m/z* = 1945.3 $[M + Na]^+$. − $C_{128}H_{144}N_8O_8 \cdot 3\,C_4H_8O_2$: calcd. C 76.88, H 7.75, N 5.13, found C 76.64, H 7.77, N 5.31.

General Procedure for Catenanes 11−13 and the Corresponding Macrocycles: The corresponding 1,ω-diaminoalkane (0.5 mmol)

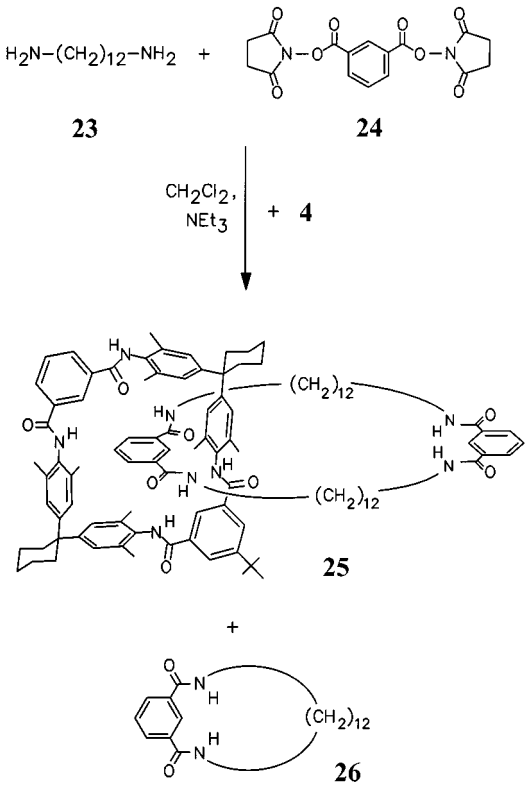


Figure 5. Synthesis of the unsymmetrical catenane **25** employing the active ester **24**

and triethylamine (0.14 mL, 1.0 mmol) were dissolved in dry dichloromethane (250 mL). Macrocycle **4** (480 mg, 0.5 mmol) and 3-chlorosulfonylbenzoyl dichloride **9** (119 mg, 0.5 mmol) were dissolved accordingly. Both solutions were added dropwise at room temperature over a period of 8 h to a stirred solution of dry dichloromethane (1000 mL). After stirring for a further 12 h and removal of the solvent, the remaining residue was purified by column chromatography.

Catenane 11: M.p. > 300°C. − R_f = 0.09 (CH_2Cl_2/CH_3OH = 50:1). − Yield 34 mg (8%). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 0.75−1.43 (m, 32 H, CH_2), 1.24 (s, 9 H, *t*Bu), 1.75−2.15 (m, 12 H, CH_2), 2.21 (s, 24 H, Ar-CH_3), 2.46 (m, 4 H, CH_2), 2.82 [t, ^3J(H,H) = 7.1 Hz, 4 H, CH_2], 3.34 [t, ^3J(H,H) = 7.0 Hz, 4 H, CH_2], 7.03 (s, 8 H, Ar-H), 7.56 (dd, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 7.8 Hz, 2 H, 3Sb-H), 7.58 [t, ^3J(H,H) = 8.0 Hz, 1 H, Iso-H], 7.96 [d, ^3J(H,H) = 8.0 Hz, 2 H, 3Sb-H], 8.00 [d, ^3J(H,H) = 7.8 Hz, 2 H, 3Sb-H], 8.03 (s, 2 H, Iso-H), 8.05 (s, 2 H, *t*Bi-H), 8.11 (s, 2 H, 3Sb-H), 8.42 (s, 1 H, *t*Bi-H), 8.55 (s, 1 H, Iso-H). − ^{13}C NMR (62.9 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 17.6, 18.1, 18.2, 18.5 (Ar-CH_3), 22.7, 26.2, 26.4, 26.5, 28.6, 28.8, 28.9, 29.1, 29.2 (CH_2), 30.8 [C(CH_3)$_3$], 34.8 (CH_2), 34.9 [*C*(CH_3)$_3$], 39.9, 42.8 (CH_2), 44.8 (Cq), 121.8, 125.1, 125.7, 126.8, 128.4, 128.8, 129.2, 129.3, 130.8, 130.9, 131.0 (CH), 131.2, 133.7, 134.1, 134.7, 134.9, 135.0, 135.4, 140.6, 147.6, 147.7, 153.0 (Cq), 166.4, 166.6, 167.1 (CO). − MALDI-MS: *m/z* = 1582.0 $[M]^+$, 1605.0 $[M + Na]^+$, 1621.0 $[M + K]^+$.

Monomeric Macrocycle 14: M.p. 196°C. − R_f = 0.38 (CH_2Cl_2/CH_3OH = 20:1). − Yield 23 mg (15%). − ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 1.12 (m, 8 H, CH_2), 1.26 [t, ^3J(H,H) = 5.9 Hz, 2 H, CH_2], 1.47 [t, ^3J(H,H) = 5.9 Hz, 2 H, CH_2], 2.99 [t, ^3J(H,H) = 5.9 Hz, 2 H, CH_2], 3.27 [t, ^3J(H,H) = 5.9 Hz, 2 H, CH_2], 7.43 [t, ^3J(H,H) = 7.9 Hz, 1 H, 3Sb-H], 7.81 [d, ^3J(H,H) = 7.9 Hz, 1 H, 3Sb-H], 7.95 [d, ^3J(H,H) = 7.9 Hz, 1 H, 3Sb-H], 8.01

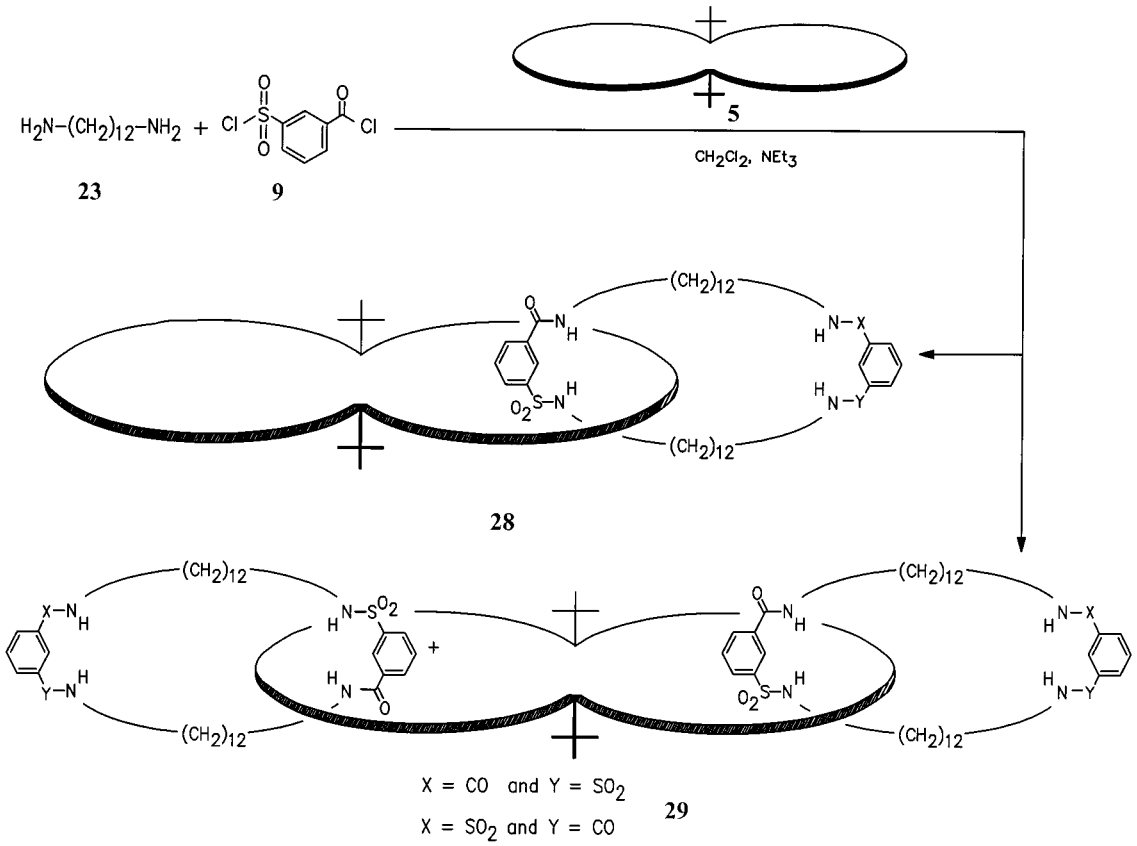


Figure 6. Synthesis of [3]catenane **29**

(s, 1 H, 3Sb-H). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 24.5, 25.0, 26.5, 26.6, 27.4, 27.7, 39.4, 42.6 (CH_2), 124.2, 128.6, 129.2, 131.1 (CH), 135.1, 141.5, (Cq), 166.6 (C=O). − FAB-MS: *m/z* = 311.1 $[M + H]^+$.

Dimeric Macrocycle 15: M.p. 216°C. − R_f = 0.32 (CH_2Cl_2/CH_3OH = 20:1). − Yield 20 mg (13%). − ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 0.84 (m, 4 H, CH_2), 1.12 (m, 16 H, CH_2), 1.36 (m, 4 H, CH_2), 2.58 [t, ^3J(H,H) = 7.1 Hz, 4 H, CH_2], 3.14 [t, ^3J(H,H) = 6.9 Hz, 4 H, CH_2], 7.34 [t, ^3J(H,H) = 7.9 Hz, 2 H, 3Sb-H], 7.70 [d, ^3J(H,H) = 7.9 Hz, 2 H, 3Sb-H], 7.77 [d, ^3J(H,H) = 7.9 Hz, 2 H, 3Sb-H], 7.95 (s, 2 H, 3Sb-H). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 25.4, 25.6, 27.8, 27.9, 28.3, 28.5, 39.3, 42.2 (CH_2), 124.9, 128.8, 128.9, 130.6 (CH), 135.0, 140.4 (Cq), 166.4 (C=O). − MALDI-MS: *m/z* = 621.9 $[M + H]^+$, 644.0 $[M + Na]^+$.

Catenane 12: M.p. > 300°C. − R_f = 0.09 (CH_2Cl_2/CH_3OH = 50:1). − Yield 44 mg (11%). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 0.75−1.43 (m, 40 H, CH_2), 1.17 (s, 9 H, *t*Bu), 1.80−2.15 (m, 12 H, CH_2), 1.99 (s, 24 H, Ar-CH_3), 2.46 (m, 4 H, CH_2), 2.65 [t, ^3J(H,H) = 7.1 Hz, 4 H, CH_2], 3.11 [t, ^3J(H,H) = 6.8 Hz, 4 H, CH_2], 6.85 (s, 8 H, Ar-H), 7.37 [t, ^3J(H,H) = 6.5 Hz, 1 H, Iso-H], 7.70 [d, ^3J(H,H) = 7.8 Hz, 2 H, 3Sb-H], 7.75 [d, ^3J(H,H) = 7.9 Hz, 2 H, 3Sb-H], 7.87 [d, 2 H, ^3J(H,H) = 7.8 Hz, Iso-H], 8.01 [d, ^4J(H,H) = 1.7 Hz, 2 H, *t*Bi-H], 8.04 (s, 2 H, 3Sb-H), 8.20 (s, 1 H, *t*Bi-H); 8.32 (s, 1 H, Iso-H). − ^{13}C NMR (62.9 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 17.7, 18.1, 18.3, 18.5 (Ar-CH_3), 22.5, 26.2, 26.5, 28.6, 28.9, 29.1, 29.3 (CH_2), 30.9 [C(CH_3)$_3$], 34.8 (CH_2), 35.0 [C(CH_3)$_3$], 40.0, 42.8 (CH_2), 44.8 (Cq), 121.8, 125.8, 126.9, 128.4, 128.8, 129.1, 129.6, 130.8, 130.9, 131.2 (CH), 131.3, 133.7, 134.3, 134.9, 135.0, 135.4, 140.9, 147.6, 147.7, 153.5 (Cq), 166.4, 166.6, 167.3 (C=O). − MALDI-MS: *m/z* = 1638.0 $[M]^+$, 1661.0 $[M + Na]^+$, 1677.0 $[M + K]^+$.

Monomeric Macrocycle 16: M.p. 199°C. − R_f = 0.34 (CH_2Cl_2/CH_3OH = 20:1). − Yield 28 mg (17%). − ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 0.95 (m, 9 H, CH_2), 1.18 (m, 9 H, CH_2), 1.47 (m, 2 H, CH_2), 2.72 [t, ^3J(H,H) = 7.1 Hz, 2 H, CH_2], 3.31 [t, ^3J(H,H) = 5.7 Hz, 2 H, CH_2], 7.45 [t, ^3J(H,H) = 7.9 Hz, 1 H, 3Sb-H], 7.81 [d, 1 H, ^3J(H,H) = 7.9 Hz, 3Sb-H], 7.92 [d, ^3J(H,H) = 7.9 Hz, 1 H, 3Sb-H], 8.10 (s, 1 H, 3Sb-H). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 26.7, 27.1, 28.7, 29.5, 29.9, 30.0, 41.1, 43.9 (CH_2), 126.7, 130.9, 131.1, 132.7 (CH), 136.6, 142.5, (Cq), 167.8 (C=O). − FAB-MS: *m/z* = 339.3 $[M + H]^+$.

Dimeric Macrocycle 17: M.p. 220°C. − R_f = 0.30 (CH_2Cl_2/CH_3OH = 20:1). − Yield 21 mg (12%). − ^{1}H NMR (400 MHz, [D_6]DMSO, 25°C): δ = 0.90−1.35 (m, 32 H, CH_2), 1.55 (m, 4 H, CH_2), 2.90 [t, ^3J(H,H) = 7.4 Hz, 4 H, CH_2], 7.63 (s, 2 H, amide-NH), 7.70 [t, ^3J(H,H) = 7.9 Hz, 2 H, Ar-H], 7.91 [d, ^3J(H,H) = 7.9 Hz, 2 H, Ar-H], 8.09 [d, ^3J(H,H) = 7.9 Hz, 2 H, Ar-H], 8.34 (s, 2 H, Ar-H). − ^{13}C NMR (100.6 MHz, [D_6]DMSO, 25°C): δ = 25.2, 25.3, 27.0, 27.3, 27.4, 27.7, 38.7, 42.4 (CH_2), 127.1, 128.6, 129.5, 130.6 (CH), 135.3, 141.8 (Cq), 166.6 (C=O). − MALDI-MS: *m/z* = 677.4 $[M + H]^+$, 699.3 $[M + Na]^+$.

Catenane 13: M.p. > 300°C. − R_f = 0.09 (CH_2Cl_2/CH_3OH = 50:1). − Yield 66 mg (9%). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 0.75−1.43 (m, 52 H, CH_2), 1.30 (s, 9 H, *t*Bu), 2.00−2.30 (m, 12 H, CH_2), 2.13 (s, 24 H, Ar-CH_3), 2.56 (m, 4 H, CH_2), 2.76 [t, ^3J(H,H) = 6.1 Hz, 4 H, CH_2], 2.90 [t, ^3J(H,H) = 8.1 Hz, 4 H, CH_2], 7.03 (s, 8 H, Ar-H), 7.37 [t, ^3J(H,H) = 6.5 Hz, 1 H, Iso-H], 7.90 (s, 2 H, 3Sb-H), 7.92 [d, ^3J(H,H) = 7.1 Hz, 2 H, 3Sb-H], 8.11

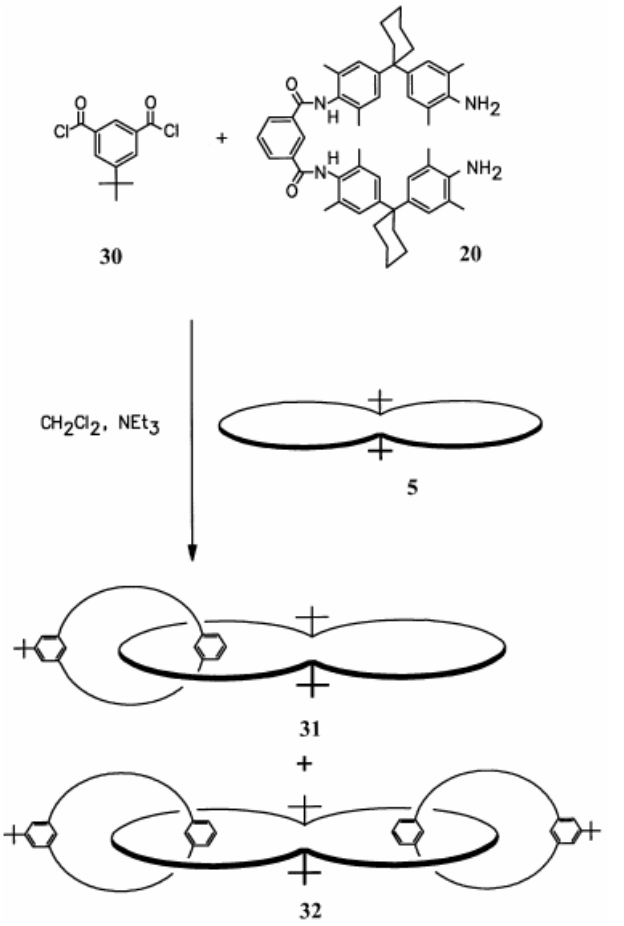


Figure 7. Synthesis of [3]catenane **32**

[d, ^4J(H,H) = 1.7 Hz, 2 H, Iso-H], 8.16 [d, ^4J(H,H) = 1.6 Hz, 2 H, *t*Bi-H], 8.04 (s, 2 H, 3Sb-H), 8.28 (s, 1 H, *t*Bi-H); 8.42 (s, 1 H, Iso-H). − ^{13}C NMR (62.9 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 14.2, 18.5, 18.6 (Ar-CH_3), 22.7, 26.2, 29.0, 29.4 (CH_2), 31.0 [C(CH_3)$_3$], 35.0 [C(CH_3)$_3$], 45.1 (Cq), 125.1, 126.4, 129.4, 129.8 (CH), 131.2, 134.3, 135.2, 147.4, 152.5 (Cq), 166.6 (C=O). − MALDI-MS: *m*/*z* = 1750.0 $[M]^+$.

Dimeric Macrocycle 18: M.p. 195°C. − R_f = 0.30 (CH_2Cl_2/CH_3OH = 20:1). − Yield 17 mg (13%). − ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 0.98 (m, 20 H, CH_2), 1.05−1.30 (m, 24 H, CH_2) 1.44 (m, 4 H, CH_2), 2.69 [t, ^3J(H,H) = 7.4 Hz, 4 H, CH_2], 3.22 [t, ^3J(H,H) = 7.1 Hz, 4 H, CH_2], 7.42 [t, ^3J(H,H) = 7.9 Hz, 2 H, 3Sb-H], 7.79 [d, ^3J(H,H) = 7.9 Hz, 2 H, 3Sb-H], 7.86 [d, ^3J(H,H) = 7.9 Hz, 2 H, 3Sb-H], 8.05 (s, 2 H, 3Sb-H). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 25.8, 26.1, 28.2, 28.5, 28.6, 28.7, 39.6, 42.4 (CH_2), 124.8, 128.8, 128.9, 130.6 (CH), 140.2 (Cq), 174.3 (C=O). − MALDI-MS: *m*/*z* = 790.4 $[M + H]^+$.

[2]Catenane 25 and Macrocycle 26: 1,12-Diaminododecane **23** (120 mg, 0.6 mmol) and triethylamine (0.14 mL, 1.0 mmol) were dissolved in dry dichloromethane (250 mL). Macrocycle **4** (570 mg, 0.6 mmol) and bis-*N*-succinyl isophthalate **24** (215 mg, 0.6 mmol) were dissolved accordingly. Both solutions were added dropwise at room temperature over a period of 8 h to a stirred solution of dry dichloromethane (1000 mL). After stirring for a further 12 h and removal of the solvent, the remaining residue was purified by column chromatography.

Catenane 25: M.p. > 300°C. − R_f = 0.51 ($CHCl_3/CH_3OH$ = 20:1). − Yield 30 mg (7%). − ^{1}H NMR (400 MHz, CF_3COOD, 25°C): δ = 1.30−1.60 (m, 36 H, CH_2), 1.42 (s, 9 H, *t*Bu), 1.67 (m, 4 H, CH_2), 1.78 (m, 8 H, CH_2), 1.96 (m, 2 H, CH_2), 1.99 (m, 2 H, CH_2), 2.16 (s, 24 H, Ar−CH_3), 2.25 (m, 4 H, CH_2), 2.31 (m, 4 H, CH_2), 2.68 [t, ^3J(H,H) = 5.5 Hz, 8 H, CH_2], 7.05 (s, 8 H, Ar-H), 7.09 [d, ^3J(H,H) = 6.1 Hz, 2 H, Ar-H] 7.68 [t, ^3J(H,H) = 6.5 Hz, 2 H, Iso-H], 7.82 [t, ^3J(H,H) = 6.5 Hz, 2 H, Iso-H], 7.99 [d, ^3J(H,H) = 7.1 Hz, 2 H, Iso-H], 8.28 (s, 1 H, *t*Bi-H), 8.31 [d, ^4J(H,H) = 1.6 Hz, 2 H, *t*Bi-H], 8.42 (s, 2 H, Iso-H). − ^{13}C NMR (62.9 MHz, CF_3COOD, 25°C): δ = 19.4, 20.6, 21.2 (Ar-CH_3), 22.9, 26.4, 26.8, 29.8, 30.0 (CH_2), 30.6 [C(CH_3)$_3$], 35.0 [C(CH_3)$_3$], 36.5, 39.8, 46.4 (Cq), 48.8 (CH_2), 125.1, 126.4, 130.3 (CH), 131.2 (Cq), 131.8, 134.9 (CH), 135.2, 136.8, 139.6, 152.5 (Cq), 160.5, 165.3 (C=O). − MALDI-MS: *m*/*z* = 1622.5 $[M]^+$. − $C_{104}H_{132}N_8O_8 \cdot CHCl_3 \cdot 2\,H_2O$: calcd. C 70.94, H 7.76, N 6.30; found C 70.57, H 7.67, N 6.39.

Monomeric Macrocycle 26: M.p: 221°C. − R_f = 0.48 (CH_2Cl_2/CH_3OH = 20:1). − Yield 23 mg (12%). − ^{1}H NMR (400 MHz, [D_6]DMSO, 25°C): δ = 1.2−1.4 (m, 16 H, CH_2), 1.50−1.60 (m, 4 H, CH_2), 3.31 (m, 4 H, CH_2), 7.54 [t, ^3J(H,H) = 7.6 Hz, 1 H, Ar-H], 7.82 [d, ^3J(H,H) = 7.6 Hz, 2 H, Ar-H], 8.04 (s, 1 H, Ar-H), 8.32 (s, 2 H, amide-NH). − FAB-MS: *m*/*z* = 331.3 $[M + H]^+$.

[3]Catenane 29: 1,12-Diaminododecane **23** (120 mg, 0.6 mmol) and triethylamine (0.14 mL, 1.0 mmol) were dissolved in dry dichloromethane (250 mL). Macrocycle **5** (460 mg, 0.24 mmol) and 3-chlorosulfonylbenzoyl chloride **9** (150 mg, 0.6 mmol) were dissolved accordingly. Both solutions were added dropwise at room temperature over a period of 8 h to a stirred solution of dry dichloromethane (1000 mL). After stirring for further 12 h and removal of the solvent, the remaining residue was purified by column chromatography. M.p: > 300°C. − R_f = 0.24 (CH_2Cl_2/ethyl acetate = 4:1). − Yield 30 mg (6%). − ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 0.80−1.42 (m, 90 H, CH_2), 1.18 (s, 18 H, *t*Bu), 1.95−2.15 (m, 64 H, CH_2), 2.39 (m, 16 H, CH_2), 2.71 (m, 18 H, CH_2), 6.85 (s, 16 H, Ar-H), 7.30−7.50 (m, 8 H, Ar-H), 7.90−8.05 (m, 16 H, Ar-H), 8.22 (s, 4 H, Ar-H), 8.28 (s, 4 H, Ar-H), 8.39 (s, 4 H, amide-NH), 8.47 (s, 4 H, amide-NH), 9.15 (s, 4 H, amide-NH), 9.21 (s, 4 H, amide-NH). − FAB-MS: *m*/*z* = 3388.6 $[M]^+$, 2656 [M − 1 aliph. cycle]$^+$, 1922 [M − 2 aliph. cycles]$^+$. − $C_{204}H_{264}N_{16}O_{20}S_4 \cdot 3\,C_4H_8O_2$: calcd. C 71.21, H 7.89, N 6.09, S 3.49; found C 71.38, H 7.99, N 5.65, S 3.18.

[3]Catenane 32: To a suspension of macrocycle **5** (100 mg, 0.05 mmol) and diamine **20** (80.6 mg, 0.1 mmol) with triethylamine (2 equiv.) in trichloromethane (30 mL), a solution of 5-*tert*-butylisophthaloyl chloride **30** (27 mg, 0.1 mmol) in trichloromethane (10 mL) was added dropwise over 1 h. After stirring for 1 d at room temperature and evaporating the solvent, the product was purified by column chromatography. − M.p. > 300°C. − R_f = 0.06 ($CHCl_3$/ethyl acetate = 7:1). − Yield 6 mg (3%). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 25°C): δ = 1.37 (s, 18 H, *t*Bu), 1.39 (s, 9 H, *t*Bu), 1.43 (s, 9 H, *t*Bu), 1.49−1.60 (m, 48 H, CH_2), 2.20−2.22 (s, 128 H, CH_2, Ar-CH_3), 7.01 (s, 16 H, Ar-H), 7.05 (s, 16 H, Ar-H), 7.47−7.52 (m, 4 H, Ar-H), 8.01−8.10 (m, 8 H, Ar-H), 8.15−8.16 (m, 4 H, *t*Bi-H), 8.23−8.24 (m, 4 H, *t*Bi-H), 8.28 (m, 4 H, *t*Bi-H), 8.58 (m, 4 H, Ar-H). − ^{13}C NMR: (250 MHz, $CDCl_3/CD_3OD$, 25°C) δ = 14.4, 18.8, 18.9, 22.9, 26.4, 29.7, 30.7 (CH_2), 31.2 (CH_3), 35.1 (CH_2), 35.5, 37.0, 45.1, 45.4, 52.4 (Cq), 124.9, 126.3, 127.1, 129.3, 129.,5 130.0, 130.4, 130.6, 130.7, 131.1 (CH), 134.0, 135.1, 147.6, 152.7 (Cq), 165.7, 166.3, 166.7 (C=O). − MALDI-MS: *m*/*z* = 3848.6 $[M + H]^+$, 3871.3 $[M + Na]^+$, 3886.6 $[M + K]^+$, 2886.5 [M − 1 cycle]$^+$, 1950.1 [M − 2 cycles+Na]$^+$, 1965.0 [M − 2 cycles+K]$^+$. − $C_{256}H_{288}N_{16}O_{16} \cdot 3\,C_4H_8O_2$ calcd. C 76.88, H 7.74, N 5.13; found C 76.14, H 7.72, N 5.23.

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