Amide-Based Oligocatenanes by an Iterative Template Strategy

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A new pathway for the supramolecular synthesis of oligocatenanes is developed. It is based on a combination of most suitable macrocyclic structural units, obtained from *tert*-butyl-substituted isophthalic acid and terephthalic acid building blocks. These structural parts guarantee, on the one hand, the solubility of the catenanes and their intermediates, and, on the other hand, the preferred formation of larger ring sizes of the macrocycles to be intertwined. Acting as monotopic and ditopic concave templates, the tetra- and octalactam macrocycles were submitted to threading procedures to yield higher-order catenanes of the amide type. By repetition of the threading steps, it was possible to isolate multiply mechanically connected [*n*]catenanes up to $n = 4$ composed of various macrocyclic units.

1. Introduction. – The synthesis of mechanically interlocked supramolecular compounds such as catenanes or rotaxanes is a fascinating challenge for preparative chemistry [1]. While the synthesis of higher-order [*n*]rotaxanes of certain structural types has been described [2], more general pathways to oligo- or polycatenanes with mechanically connected units are rare hitherto. So far, oligocatenanes have been synthesized *via* donor/acceptor complexes [3] or by formation of coordination complexes [4]. In some systems, the assembly of seven mechanically connected macrocyclic units has been achieved [3]. In the amide-type system, so far only up to [3]catenanes have been synthesized by non-ionic template assistance in a 4% yield [5][6].

2. Results. – A prerequisite for the formation of oligocatenanes is to find qualified (ditopic) host macrocycles **II** which are supplied with two binding sites (*Fig.*).

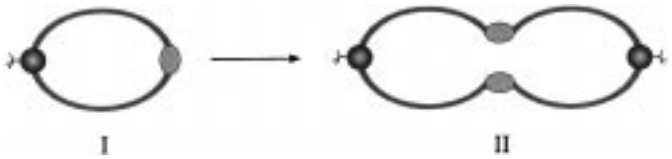


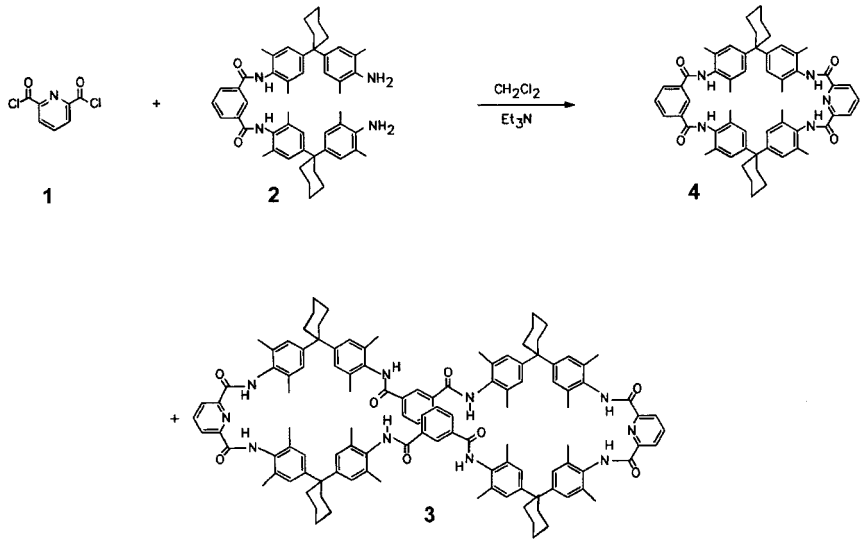
Figure. *Mono-* (**I**) *and ditopic* (**II**) *host macrocycles as templates for threading reactions* (schematic). For the meaning of symbols, see *Scheme 3*.

A step to improve the earlier routes [5] to amide-based oligocatenanes is to increase the solubility of octalactam cycles of type **II** like **3**. This could be achieved by using pyridine-2,6-dicarbonyl dichloride (**1**) [5b] in the macrocyclization reaction with the diamine **2** (*Scheme 1*). The desired octalactam **3** was obtained in a 23% yield, the tetralactam cycle **4** in a 15% yield[1]) [7]. To synthesize oligocatenanes, we tried to

[1]) Surprisingly, a molecular knot was found to be formed in this reaction, too [7].

thread the octalactam **3** with various carboxylic acid dichlorides and diamines. But none of the reactions produced the desired higher [*n*]catenanes[2]).

Scheme 1. *Synthesis of Macrocycles* **3** *and* **4**



As a more successful strategy to obtain more suitable ditopic octalactam cycles, we decided to switch from *meta*- to *para*-substituted (terephthalic acid) building blocks (*Scheme 2*), hoping that the 'rigid-group principle' [8] and the wider 180° (*para*) *vs.* 120° (*meta*) angle would favor larger (oligotopic) macrocycles [9]. We anticipated that during the synthesis, an intermediate product **8** containing two *para*-units is formed, which allows a more stretched preorganization that preferentially would lead the reaction to the 70-membered octalactam **9**, offering two binding sites for amide guests.

Indeed, in the reaction of *tert*-butylisophthaloyl dichloride **5** with the terephthalamide building block **6** under dilute conditions, we observed – apart from the large [2]catenane **13** in a 13% yield and other products **10**–**12** shown in *Scheme 3* – the desired macrocycle **9** in a 30% yield. Here, the formation of the 70-membered octalactam **9** seems to be preferred over the 35-membered tetralactam cycle **10**. Although the intermediate product **7** – with its presumably *transoid* amide groups – looks quite linear, it does not tend to react further to polycondensed material. Even dodecalactam macrocycles were not detected. We assume that the formation of **9** takes place similarly to a mechanism described by *Hunter* and co-workers for the *meta*-series [5b]. The terephthalamide moieties might form intramolecular H-bonds in order to build intermediate **8**.

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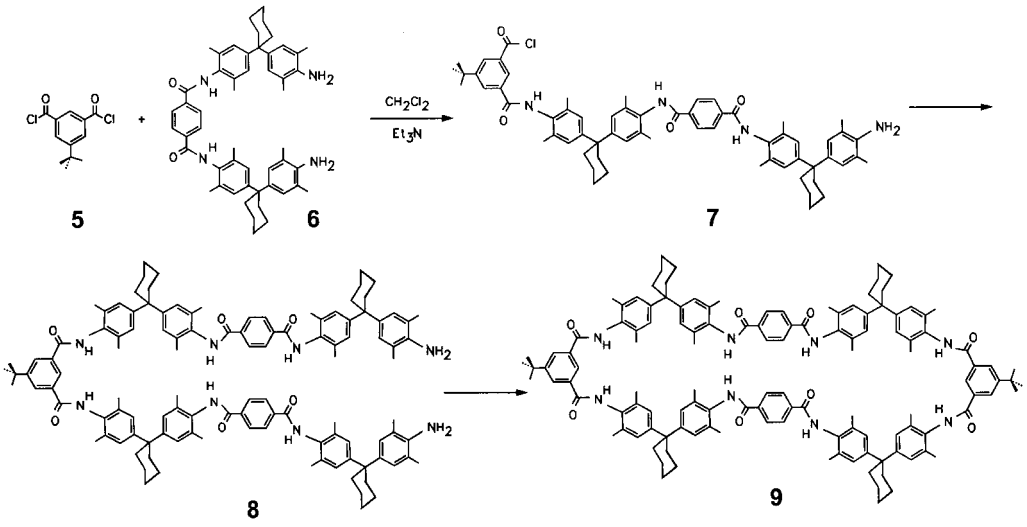
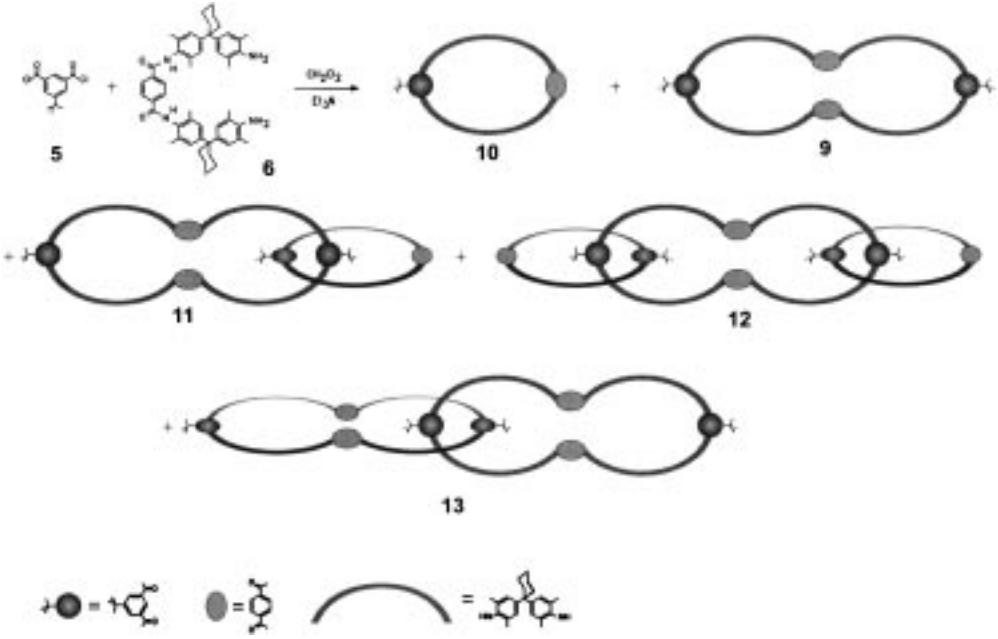
[2]) Octalactam **3** seems not to be very suitable as a concave template for the synthesis of catenanes. One reason for this fact could lie in its conformation, for it is folded, so that there might not remain enough space for guests being incorporated. Another point is the intramolecular H-bondings between the pyridinecarboxamide NH group and the pyridine N-atom itself, which causes the 'saturation' of the host cycle, so that there may not be an effective docking site left.

Scheme 2. *Possible Formation of the* para-*Substituted Building Block* **9**



Scheme 3. *Synthesis of Macrocycles* **9** *and* **10**, *and Catenanes* **11** – **13**



The catenanes' structures can be derived from the well-known fragmentation pattern in mass spectra [6]. They show the typical fragment peaks of the corresponding lower catenanes and macrocycles studied earlier. Genuine mixtures of various tetra- and octalactam cycles were studied spectroscopically under the same conditions. These

did not show mass peaks of any catenane. Furthermore, ^{1}H-NMR spectra of **11** show different signals for the tetralactam and the octalactam cycle in a ratio of 1:2 as only expected for a catenane [5a].

To achieve the synthesis of [*n*]catenanes with $n > 3$, we checked the new octalactam cycle **9** and the new [2]catenane **13** for their ability towards morefold intertwining. Because the macrocycle **9** is only sparingly soluble in organic solvents, the [2]catenane **13**, which is more easily soluble in nonpolar solvents, appeared to be the most interesting concave template. Its two docking sites should be well-suited to elongate the chain of macrocycles[3]). To verify these strategic considerations based on previous expertise [5][6], we reacted the [2]catenane **13** again with the compounds used in the first reaction step in an iterative synthesis (*Scheme 4*) [10]. Indeed, under the same conditions as before, the [3]catenane **14**, composed of three octalactam rings, was obtained in a relatively high yield of 10%[4]). In addition, the first amide-type [4]catenane **16** with two inner octalactam and two peripheric tetralactam rings could be isolated by HPLC[5]) in a yield of $< 1\%$, apart from the [3]catenanes **14** and **15**. Even if both [3]- and [4]catenanes **14** and **16** are isomers possessing the same mass, they could be distinguished by their fragmentation pattern in the MS and by comparison of the HPLC retention times.

Furthermore, in the mixture obtained from **5**, **6**, and **13**, the masses 7714.7, 9635.0, 11537.6 could be detected by MALDI-TOF mass spectrometry, which most probably belong to the [4]-, [5]-, and [6]catenanes **17**–**19**, considering the synthetic pathway. The [5]catenane **18** that we will try to prepare in larger amounts in the future would be the first amide-type 'olympiadane' [3].

The decisive finding that emerges from these syntheses is that the pyridine-2,6-carboxylic acid building block **1** as well as the terephthalic acid building block **6** are responsible for prefering the octalactam cycle **II** over the tetralactam cycle **I** during cyclization reactions (*Scheme 1*) [10d]. This finding stimulated us to use both units in one system to gain from both advantageous effects. Under standard conditions, we therefore reacted pyridine-2,6-dicarbonyl dichloride (**1**) with terephthalamide **6** (*Scheme 5*). In this reaction, seven new macrocyclic and mechanically connected compounds **20**–**26** could be isolated, while the total yield of cyclic products was 57%. In this system, the formation of catenanes seems not to be restricted like in the previous system with pyridine-2,6-dicarbonyl dichloride (**1**) and isophthalic acid building block **2** (see above, *Scheme 1*). It is remarkable that, in one step, five new catenanes and two macrocycles are obtained. Their characterization again was based on the combination of NMR and MS: for example, the NMR spectra of **25** and **26** show a specific pattern. In **25**, which contains two octalactam and one tetralactam cycle, the aromatic region shows different signals for each of the cycles in a corresponding intensity (2:2:1). Due to their different position in the centre or at the periphery of this [3]catenane, the octalactam macrocycles exhibit different chemical shifts. Regarding the more sym-

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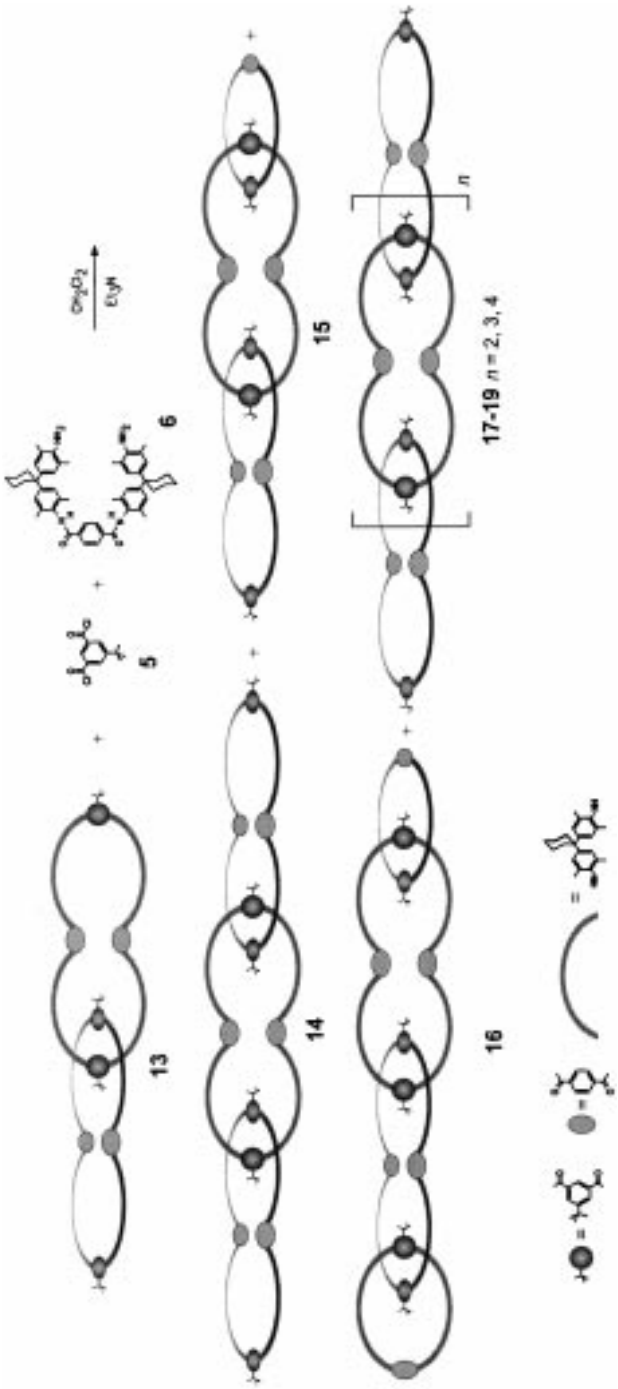
[3]) The ^{1}H-NMR ($CDCl_3/CD_3OD$) of the [2]catenane **13** has the same shape as the one of the octalactam monocycle **9** which indicates that the cavity in both cycles permit relatively free circumrotation.

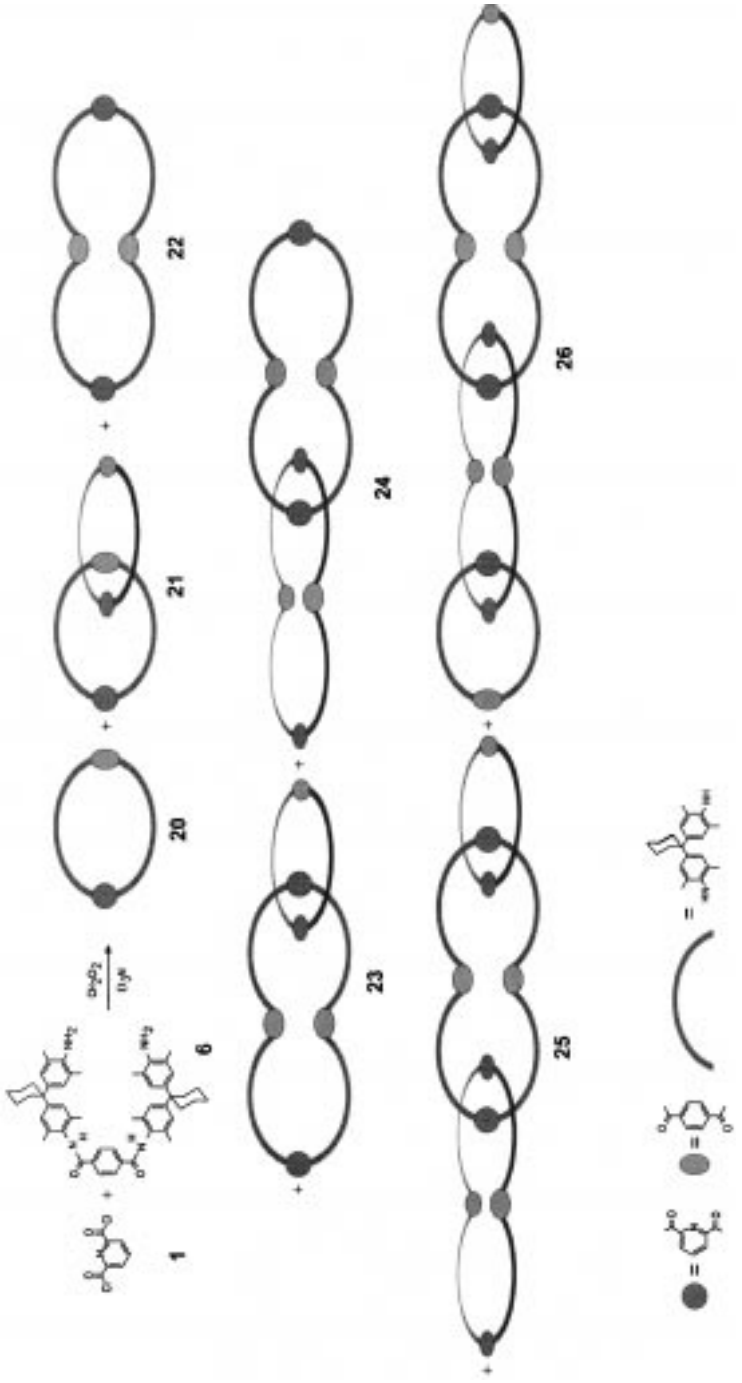
[4]) The ^{1}H-NMR Spectrum ($CDCl_3/CD_3OD$) of the [3]catenane **14** is much more complex than that of the [2]catenane **13**. This shows that the cycles are no longer equivalent in **14**; the free circumrotation of the peripheric cycles is restricted.

[5]) Semi-preparative HPLC column (silica gel, *Lichrosorb S 60* (7 μ), 11 × 2 cm).



Scheme 4. *[n]Catenanes from Solubility Increasing* (see **5**) *and* para*-Phenylene-Derived* (see **6**) *Starting Materials*

Scheme 5. *[n]Catenanes Emerging from Pyridine-2,6-dicarbonyl Dichloride* (**1**) *and* para-*Phenylene Building Blocks* **6**



metrical catenane **26**, the octalactam as well as the tetralactam cycles do not differ here in the ^{1}H-NMR spectra. The intensity of the octalactam and tetralactam protons show the expected ratio of 2:1.

The intermediate octalactam cycle **22** here seems not to be folded like octalactam cycle (see above, *Scheme 1*), for the terephthalic units are projecting in approximately perpendicular directions as shown by MM$^+$ force-field calculations [11]. Besides this, the octalactam cycle **22** should contain two docking sites, which are able to complex suitable guests (ditopic concave template), so that there would be no 'saturation' of all amide groups by H-bonding like in cycle **3**. The use of the terephthalic building block **6** causes also a formal increase of size of the octalactam cycle **22**, for now its number of atoms forming the ring is 66 compared with 64 in cycle **3** (counting the participation of 3 atoms as members of the macrocycle in the case of *meta*-substituted aromatic rings). This might additionally facilitate the uptake of guests in the cavity.

3. Conclusions. – While other types of catenanes were synthesized under high pressure (several kilobars), we resigned here to atmospheric pressure. All catenanes mentioned here were obtained by self organization at room temperature.

The matching combinations of (*tert*-butyl)isophthalic acid or pyridine-2,6-dicarboxylic acid with terephthalic acid allow to obtain higher [*n*]catenanes; as in the cyclization step, the formation of the ditopic octalactam cycle **II** is preferred over the tetralactam cycle **I**. By extension of such iterative template strategies of synthesis, it should in the future be possible to achieve oligocatenanes even with a longer chain than reached in this study.

Experimental Part

General. All solvents were distilled prior to use and all other chemicals were of the best commercial quality available and used as received. ^{1}H- and ^{13}C-NMR: *AM-400-MHz* or *DRX-500-MHz instrument*, *Bruker, Analytische Messtechnik GmbH*, Karlsruhe; solvent peak as reference, δ in ppm, J in Hz; abbreviations: cy = cyclohexane moiety, py = pyridine moiety, *t*bi = (5-(*tert*-butyl)isophthaloyl, ter = terephthaloyl. FAB-MS: *Concept 1 H, Kratos Analytical Ltd.*, Manchester; matrix 3-nitrobenzyl alcohol. MALDI-TOF-MS: *MALDI-TofSpecE*, *Micromass*, Manchester; matrix: 9-nitroanthracene or 2,5-dihydroxybenzoic acid. Elemental analysis: analytical facilities of the 'Kekulé-Institut für Organische Chemie und Biochemie' of the University of Bonn.

Macrocycles **9** *and* **10**, *and Catenanes* **11**–**13**. A soln. of 5-(*tert*-butyl)isophthaloyl dichloride (**5**; 1.54 mmol) in CH_2Cl_2 (250 ml) and a soln. of terephthalamide (**6**; 1.54 mmol) in CH_2Cl_2 (250 ml) with Et_3N (0.5 ml) are dropped synchronously into CH_2Cl_2 (1000 ml) within 8 h at r.t. After stirring for 1 d more, the solvent is evaporated and the crude product purified by column chromatography (SiO_2 (40–63 μm), CH_2Cl_2/MeOH 50:1).

*28′-(*tert*-Butyl)-5′,16′,22′,34′,37′,39′,42′,45′-octamethyldispiro[cyclohexane-1,2′-[7,14,24,32]tetraazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone* (**10**). 79 mg (11%). Colorless solid. M.p. >300°, R_f (CH_2Cl_2/MeOH 30:1) 0.13. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°: 1.31 (*s*, 9 H, ^{t}Bu); 1.36–1.49 (br., 12 H, CH_2); 2.00 (*s*, 12 H, Me); 2.08 (*s*, 12 H, Me); 2.16 (br., 8 H, CH_2); 6.83 (*s*, 4 arom. H); 6.89 (*s*, 4 arom. H); 7.18 (*s*, 4 H, ter); 8.14 (*d*, ^4J = 1.6, 2 H, *t*bi); 8.22 (*t*, ^4J = 1.6, 1 H, *t*bi). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 18.3, 18.5 (Me); 22.7, 26.2, 36.0 (CH_2); 31.0, 44.1, 46.6 (cy); 122.5, 126.1, 126.4, 128.9, 130.4 (CH); 131.6, 133.4, 133.7, 134.6, 135.1, 147.0, 148.2, 153.3 (cy); 166.0, 169.7 (C=O). FAB-MS: 961.5 (M^+). Anal. calc. for $C_{64}H_{72}N_4O_4 \cdot 2\,H_2O$: C 77.07, H 7.68, N 5.62; found: C 76.74, H 7.63, N 5.74.

28,63-Di(tert-*butyl)-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42,49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,*

9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (**9**): 173 mg (12%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.01. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.24 (*s*, 18 H, ^{t}Bu); 1.41 (br., 8 H, CH_2); 1.49 (br., 16 H, CH_2); 2.02 (*s*, 48 H, arom. Me); 2.12 (*m*, 16 H, CH_2); 6.75 (*s*, 8 arom. H; 6.77 (*s*, 8 arom. H); 7.08 (*s*, 8 arom. H); 8.14 (*s*, 4 arom. H); 8.41 (*s*, 2 arom. H); 8.55 (*s*, 2 arom. H); 9.81 (*s*, 4 H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 17.5, 17.6 (Me); 30.2 (Me); 20.8, 21.4, 24.3, 25.2 (CH_2); 121.2, 122.0, 124.9, 126.8, 127.3, 129.2, 132.3; 133.5 (CH); 33.9, 34.1, 43.5, 44.9, 134.6, 135.2, 136.1, 136.5, 145.9, 146.9, 150.6, 151.6 (cy); 165.8, 166.2 (C=O). MALDI-TOF-MS: 1945.6 ($[M+Na]^+$, $[C_{128}H_{144}N_8O_8$ (1922.6) $+Na]^+$).

*28′-(*tert*-Butyl)-5′,16′,22′,34′,37′,39′,42′,45′-octamethyldispiro[cyclohexane-1,2′-[7,14,24,32]tetraazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone – 28,63-Di*(tert*-butyl)-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42,49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (1:1) [2^{35,70}]Catenane*[6]) (**11**). 77 mg (8%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.06. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.21 (br., 8 H, CH_2); 1.25 (*s*, 9 H, ^{t}Bu); 1.26 (*s*, 18 H, ^{t}Bu); 1.33 (br., 14 H, CH_2); 1.40 (br., 26 H, CH_2); 2.05 (*s*, 30 H, arom. Me); 2.07 (*s*, 12 H, arom. Me); 2.08 (*s*, 30 H, arom. Me); 2.05–2.12 (br., 12 H, CH_2); 6.87 (*s*, 6 arom. H); 6.88 (*s*, 12 arom. H); 6.90 (*s*, 6 arom. H); 7.85 (*s*, 8 H, ter); 7.86 (*s*, 4 H, ter-H); 8.03 (*s*, 2 H, *t*bi); 8.06 (*s*, 4 H, *t*bi); 8.16 (*s*, 1 H, *t*bi); 8.17 (*s*, 2 H, *t*bi). FAB-MS: 2883.8 (M^+, $C_{192}H_{216}N_{12}O_{12}^+$ (2883.9)).

*28′-(*tert*-Butyl)-5′,16′,22′,34′,37′,39′,42′,45′-octamethyldispiro[cyclohexane-1,2′-[7,14,24,32]tetraazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,18,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone – 28,63-Di*(tert*-butyl)-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42,49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (2:1) [3^{35,70,35}]Catenane*[6]) (**12**): 20 mg (2%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.10. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.19 (*s*, 36 H); 1.24 (br., 18 H, CH_2); 1.34 (br., 36 H, CH_2); 1.80–2.00 (br., 26 H, CH_2); 1.98 (*s*, 48 H, arom. Me); 2.02 (*s*, 48 H, arom. Me); 6.80 (*s*, 16 arom. H); 6.83 (*s*, 16 arom. H); 7.75 (*s*, 2 H, *t*bi); 7.80 (*s*, 8 H, ter); 8.00 (*d*, ^3J = 1.7, 8 H, *t*bi); 8.12 (*t*, ^3J = 1.7, 2 H, *t*bi). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 19.8, 19.9, 20.4 (Me); 21.0, 24.2, 27.7, 30.1, 32.1, 32.5, 32.6 (CH_2); 35.3, 36.5, 38.0, 38.2, 38.3, 46.5, 46.6 (cy); 121.5, 123.8, 126.5, 127.6, 127.9, 128.1, 129.0 (CH); 130.2, 132.3, 132.35, 132.4, 132.7, 132.8, 135.5, 136.4, 136.6, 136.7, 138.6 (cy); 166.9, 167.9 (C=O). FAB-MS: 3845.1 (M^+, $C_{256}H_{288}N_{16}O_{16}^+$ (3845.2)).

28,63-Di(tert*-butyl)-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42,49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone [2^{70,70}]Catenane*[6]) (**13**): 180 mg (13%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.19. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.03 (*s*, 36 H, *t*Bu); 1.16 (br., 30 H, CH_2); 1.32 (br., 20 H, CH_2); 1.54 (br., 30 H, CH_2); 1.70 (*s*, 60 H, arom. Me); 1.88 (*s*, 18 H, arom. Me); 1.98 (*s*, 18 H, arom. Me); 6.65 (*s*, 16 arom. H); 6.68 (*s*, 16 arom. H); 6.95 (*s*, 16 H, ter); 7.91 (*d*, ^4J = 1.5, 8 H, *t*bi); 8.27 (*d*, ^4J = 1.5, 4 H, *t*bi). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 19.3, 19.8 (Me); 24.1, 24.2, 24.3, 24.5, 27.6, 27.7, 27.8 (CH_2); 36.4, 37.4, 37.6, 39.2, 39.3, 46.4, 46.6 (cy); 123.9, 128.1, 128.5, 130.5, 132.5, 132.8 (CH); 134.9, 136.6, 138.5, 149.6, 154.3 (cy); 168.0, 168.9 (C=O). FAB-MS: 3843.2 ($[M-2H]^+$). MALDI-TOF-MS: 3845.2 (M^+, $C_{256}H_{288}N_{16}O_{16}^+$ (3845.2)), 3866.8 ($[M+Na]^+$), 3883.6 ($[M+K]^+$).

Catenanes **14**–**19**: A soln. of 5-(*tert*-butyl)isophthaloyl dichloride (**5**; 1.54 mmol) in CH_2Cl_2 (250 ml) and a soln. of terephthaloyl diamide (**6**; 1.54 mmol) in CH_2Cl_2 (250 ml) with Et_3N (0.5 ml) and catenane **13** (0.07 mmol) are dropped synchronously to CH_2Cl_2 (1000 ml) within 8 h at r.t. After stirring for 1 d more, the solvent is evaporated and the crude product purified by column chromatography (SiO_2 (40–63 μm), CH_2Cl_2/MeOH 40:1).

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[6]) The superscripts *x*, *y*,… in the brackets [$n^{x,y,\cdots}$] indicate the maximal number of ring members of each link of the catenane, in sequential order of the catena.

28,63-Di(tert-*butyl*)*-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42, 49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone [3^{70,70,70}]Catenane* (**14**[6])): 79 mg (10%). Colorless solid. M.p. > 300°. R_f (CH_2Cl_2/MeOH 30:1) 0.22. HPLC (CH_2Cl_2/MeOH 120:1, semi-prep. silica gel column, *Lichrosorb S 60* (7 μm), 11 × 2 cm): t_R 37 min. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.18 (*s*, 27 H, Me); 1.19 (*s*, 27 H, Me); 1.00–1.50 (br., 45 H, CH_2); 1.70–2.20 (br., 75 H, CH_2); 1.97, 1.99, 2.02, 2.06 (4*s*, 144 H, Me); 6.70–7.00 (*m*, 72 arom. H); 7.90–8.20 (*m*, 18 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 15.5, 19.5, 19.9, 20.0 (Me); 20.1, 22.4, 24.3, 24.4, 25.2, 27.7, 28.3, 30.4, 30.8, 31.1, 32.1, 32.5, 32.6, 36.5 (CH_2); 37.6, 39.3, 40.2, 46.5, 46.7 (cy); 127.1, 128.3, 128.5, 129.1, 129.3, 130.2, 130.6, 134.9, 136.5 (CH); 136.6, 136.9, 137.0, 138.5, 149.0, 149.6, 154.3, 154.5, 154.9, 155.0 (cy); 166.0, 167.5, 167.6, 173.3 (C=O). MALDI-TOF-MS: 5768.7 ([M+H]$^+$), 5792.7 ([M+Na]$^+$), 5807.6 ([M+K]$^+$). Anal. calc. for $C_{384}H_{432}N_{24}O_{24}\cdot 2\ CHCl_3$: C 77.18, H 7.28, N 5.60; found: C 77.11, H 7.70, N 5.78.

28′-(tert-*Butyl*)*-5′,16′,22′,34′,37′,39′,42′,45′-octamethyldispiro[cyclohexane-1,2′-[7,14,24,32]tetraazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone – 28,63-Di*(tert-*butyl*)*-5,16,22,34,40,51,57,69,72,74,77,80,83, 85,88,91-hexadecamethyltetraspiro[7,14,24,32,42,49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}. 2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61, 63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (1:2) [3^{35,70,70}]Catenane*[6]) (**15**): 3 mg (<1%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.17. HPLC (CH_2Cl_2/MeOH 120:1, semi-prep. silica gel column, *Lichrosorb S 60* (7 μm), 11 × 2 cm): t_R 48.5 min. MALDI-TOF-MS: 4804 ([M−2H]$^+$), 4829 ([M+Na]$^+$, [$C_{320}H_{360}N_{20}O_{20}$ (4806.5)+Na]$^+$).

28′-(tert-*Butyl*)*-5′,16′,22′,34′,37′,39′,42′,45′-octamethyldispiro[cyclohexane-1,2′-[7,14,24,32]tetraazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone – 28,63-Di*(tert-*butyl*)*-5,16,22,34,40,51,57,69,72,74,77,80,83, 85,88,91-hexadecamethyltetraspiro[7,14,24,32,42,49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}. 2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63, 65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (1:1) [4^{35,70,70,35}]Catenane* (**16**): 0.6 mg (<1%). Colorless solid. (M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.15. HPLC (CH_2Cl_2/MeOH 120:1, semi-prep. silica gel column, *Lichrosorb S 60* (7 μm), 11 × 2 cm: t_R 57.5 min. MALDI-TOF-MS: 5766.2 ([M−H]$^+$, [$C_{384}H_{432}N_{24}O_{24}$ (5767.8)−H]$^+$), 5787.5 ([M−2H+Na]$^+$), 5804.9 ([M−2H+K]$^+$).

28,63-Di(tert-*butyl*)*-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42, 49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone [4^{70,70,70,70}]Catenane*[6]) (**17**): MALDI-TOF-MS: 7714.7 ([M+Na]$^+$, [$C_{512}H_{576}N_{32}O_{32}$ (7690.4)+Na]$^+$).

28,63-Di(tert-*butyl*)*-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42, 49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone [5^{70,70,70,70,70}]Catenane* (**18**): MALDI-TOF-MS: 9635.0 ([M+Na]$^+$, [$C_{640}H_{720}N_{40}O_{40}$ (9613.0)+Na]$^+$).

28,63-Di(tert-*butyl*)*-5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-hexadecamethyltetraspiro[7,14,24,32,42, 49,59,67-octaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone [6^{70,70,70,70,70,70}]Catenane* (**19**): MALDI-TOF-MS: 11537.6 ([M+H]$^+$, [$C_{768}H_{864}N_{48}O_{48}$ (11535.6)+H]$^+$), 11549.7 ([M+H+Na]$^+$), 11575.2 ([M+H+K]$^+$).

Macrocycles **20** *and* **22** *and Catenanes* **21** *and* **23**–**26**. A soln. of pyridine-2,6-dicarbonyl dichloride (**1**; 1.54 mmol) in CH_2Cl_2 (250 ml) and a soln. of terephthalamide (**6**; 1.54 mmol) in CH_2Cl_2 (250 ml) with Et_3N (0.5 ml) are dropped synchronously to CH_2Cl_2 (1000 ml) within 8 h at r.t. After stirring for 1 d more, the solvent is evaporated and the crude product purified by column chromatography (SiO_2 (40–63 μm), CH_2Cl_2/MeOH 70:1).

5′,16′,22′,34′,37′,39′,42′,45′-Octamethyldispiro[cyclohexane-1,2′-[7,14,24,32,38]pentaazaheptacyclo[31.2.2.2^{3,6}. 2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cy-

clohexane]-8′,13′,25′,31′-tetrone (**20**): 50 mg (9%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.17. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 0.90–1.10 (br., 12 H, CH_2); 1.50–1.70 (br., 4 H, CH_2); 1.54 (*s*, 12 H, Me); 1.63 (*s*, 12 H, Me); 1.80–1.90 (br., 4 H, CH_2); 6.42 (*s*, 4 arom. H); 6.54 (*s*, 4 arom. H); 7.17 (*s*, 4 H, ter); 7.61 (*t*, ^3J = 7.81, 1 H, py); 7.77 (*d*, ^3J = 7.81, 2 H, py). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 17.7, 17.8 (Me); 22.2, 25.6, 28.3 (CH_2); 30.9 (Me); 35.4, 44.2 (cy); 124.1, 125.3, 125.8, 126.8, 131.0, 131.1 (CH); 134.6, 135.2, 130.0, 138.9, 146.7, 147.9, 148.0 (cy); 161.8, 165.0 (C=O). FAB-MS: 906.5 (M^+). MALDI-TOF-MS: 905.7 (M^+), 944.7 ($[M+K]^+$). Anal. calc. for $C_{59}H_{63}N_5O_4 \cdot 2\,H_2O$: C 75.21, H 7.17, N 7.43; found: C 74.83, H 7.02, N 7.28.

5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-Hexadecamethyltetraspiro[7,14,24,32,42,49,59,67,73,84-decaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (**22**): 120 mg (17%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.05. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD/(D_6)DMSO, 20°): 1.40–1.60 (br., 28 H, CH_2); 2.06 (*s*, 24 H, Me); 2.15 (*s*, 24 H, Me); 2.38 (br., 8 H, CH_2); 6.96 (*s*, 8 arom. H); 7.08 (*s*, 8 arom. H); 7.71 (*s*, 4 H, ter); 8.16 (*t*, ^3J = 7.88, 2 H, py); 8.28 (*d*, ^3J = 7.88, 4 H, py). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD/(D_6)DMSO, 20°): 17.7 (Me); 22.3, 25.6, 35.4 (CH_2); 44.2 (cy); 124.0, 125.4, 125.8, 126.8, 131.2, 131.3 (CH); 134.7, 135.2, 136.0, 146.7, 147.8, 148.0 (cy); 161.6, 164.8 (C=O). FAB-MS: 1812.8 (M^+, $C_{118}H_{126}N_{10}O_8^+$ (1812.4)).

5′,16′,22′,34′,37′,39′,42′,45′-Octamethyldispiro[cyclohexane-1,2′-[7,14,24,32,38]pentaazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone [2^{35,35}]Catenane[6]) (**21**). 15 mg (3%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.16. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.10–1.40 (br., 16 H, CH_2); 1.49 (br., 8 H, CH_2); 1.84 (*s*, 12 H, Me); 1.94 (*s*, 12 H, arom. Me); 1.97 (*s*, 12 H, arom. Me); 1.99 (*s*, 12 H, arom. Me); 1.90–2.00 (br., 12 H, CH_2); 2.19 (br., 4 H, CH_2); 6.69 (*s*, 4 arom. H); 6.74 (*s*, 4 arom. H); 6.79 (*s*, 4 arom. H); 6.87 (*s*, 4 arom. H); 7.24 (*d*, ^3J = 7.88, 4 H, ter); 7.51 (*d*, ^3J = 7.88, 4 H, ter); 7.95 (*t*, ^3J = 7.88, 2 H, py); 7.97 (*d*, ^3J = 7.88, 4 H, py). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 19.4, 19.7, 19.9, 20.2 (Me); 23.9, 24.6, 27.5, 27.9, 36.3, 38.8 (CH_2); 46.0, 46.9 (cy); 126.5, 126.9, 127.5, 127.7, 128.0, 128.8, 129.6, 132.2, 132.7 (CH); 134.8, 135.8, 136.5, 137.0, 137.5, 138.4, 140.7, 150.2, 150.3 (cy); 164.1, 164.7, 168.9, 172.5 (C=O). FAB-MS: 1813.0 (M^+). MALDI-TOF-MS: 1812.4 (M^+), 1833.7 ($[M+Na]^+$), 1850.7 ($[M+K]^+$). Anal. calc. for $C_{118}H_{126}N_{10}O_8 \cdot 2\,H_2O \cdot CHCl_3$: C 72.64, H 6.71, N 7.10; found: C 76.81, H 6.75, N 6.65.

5′,16′,22′,34′,37′,39′,42′,45′-Octamethyldispiro[cyclohexane-1,2′-[7,14,24,32,38]pentaazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone – 5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-Hexadecamethyltetraspiro-[7,14,24,32,42,49,59,67,73,84-decaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]-dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (1:1) [2^{35,70}]Catenane[6]) (**23**): 100 mg (14%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 30:1) 0.12. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.25 (br., 28 H, CH_2); 1.33 (br., 28 H, CH_2); 1.87 (*s*, 48 H, Me); 1.98 (*s*, 48 H, Me); 1.90–2.10 (br., 24 H, CH_2); 6.74 (*s*, 16 arom. H); 6.81 (*s*, 16 arom. H); 7.68 (*s*, 16 H, ter); 7.92 (*t*, ^3J = 7.88, 4 H, py); 8.17 (*d*, ^3J = 7.88, 8 H, py). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 19.6, 19.8 (Me); 24.2, 27.7, 30.2, 31.0 (CH_2); 32.9 (Me); 38.2, 46.7 (cy); 126.8, 128.0, 128.3, 129.1, 132.5, 132.7 (CH); 136.5, 136.6, 138.6, 148.7, 149.5, 150.2 (cy); 164.4, 168.2 (C=O). FAB-MS: 3625.0 (M^+). MALDI-TOF-MS: 3623 (M^+), 3646 ($[M+Na]^+$), 3662 ($[M+K]^+$). Anal. calc. for $C_{236}H_{252}N_{20}O_{16} \cdot CHCl_3$: C 76.03, H 6.81, N 7.48; found: C 76.05, H 6.78, N 7.65.

5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-Hexadecamethyltetraspiro[7,14,24,32,42,49,59,67,73,84-decaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,73}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone [2^{70,70}]Catenane[6]) (**24**): 70 mg (10%). Colorless solid. M.p. > 300°. R_f (CH_2Cl_2/MeOH 30:1) 0.09. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.47 (br., 21 H, CH_2); 1.49 (br., 21 H, CH_2); 1.88 (*s*, 18 H, Me); 1.94 (*s*, 18 H, Me); 1.99 (*s*, 36 H, Me); 1.90–2.10 (br., 18 H, CH_2); 6.74 (*s*, 12 arom. H); 6.82 (*s*, 12 arom. H); 7.68 (*s*, 12 H, ter); 7.93 (*t*, ^3J = 7.71, 4 H, py); 8.19 (*d*, ^3J = 7.71, 8 H, py). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 19.6, 19.8 (Me); 24.3, 25.7, 32.2, 32.8, 33.0, 33.5 (CH_2); 33.6 (Me); 38.5, 46.9 (cy); 126.2, 127.6, 128.3, 128.6, 129.4, 133.5, 133.2 (CH); 137.5, 138.6, 138.9, 145.7, 146.3, 152.1 (cy); 165.4, 167.1 (C=O). FAB-MS: 2718.6 (M^+). Anal. calc. for $C_{177}H_{189}N_{15}O_{12} \cdot 2\,CHCl_3$: C 72.70, H 6.51, N 7.19; found: C 73.12, H 6.88, N 7.41.

5′,16′,22′,34′,37′,39′,42′,45′-Octamethyldispiro[cyclohexane-1,2′-[7,14,24,32,38]pentaazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cy-

clohexane]-8′,13′,25′,31′-tetrone – 5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-Hexadecamethyltetraspiro-[7,14,24,32,42,49,59,67,73,84-decaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]-dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (1:2) [3^{35,70,70}]Catenane[6]) (**25**): 14 mg (2%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 20:1) 0.58. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.29 (br., 3 H, CH_2); 1.37 (br., 32 H, CH_2); 1.59 (br., 8 H, CH_2); 1.70 (br., 12 H, CH_2); 1.82 (br., 8 H, CH_2); 1.89 (br., 8 H, CH_2); 1.93 (*s*, 30 H, Me); 2.00 (*s*, 60 H, Me); 2.03 (*s*, 30 H, Me); 6.47 (br., 2 H, ter); 6.66 (br., 2 H, ter); 7.15 (br., 4 H, ter); 7.33 (br., 4 H, ter); 7.81 (br., 4 H, ter); 7.9–8.0 (*m*, 5 H, py); 8.15 (*d*, ^3J = 7.63, 3 H, py); 8.18–8.25 (*m*, 7 H, py). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 19.7, 19.8 (Me); 19.9, 24.1, 24.2, 27.6, 27.7, 32.2, 32.8, 38.6 (CH_2); 46.5 (cy); 126.8, 128.0, 128.2, 128.5, 129.2, 132.3, 132.7 (CH); 136.2, 136.6, 140.8, 150.2 (cy); 164.3 (C=O). MALDI-TOF-MS: 4529.3 (M^+), 4550.8 ([M + Na]$^+$, [$C_{295}H_{315}N_{25}O_{20}$ (4530.9) + Na]$^+$).

5′,16′,22′,34′,37′,39′,42′,45′-Octamethyldispiro[cyclohexane-1,2′-[7,14,24,32,38]pentaazaheptacyclo[31.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,23}.1^{26,30}]hexatetraconta[3,5,9,11,15,17,20,22,26,28,30(38),33,35,36,39,41,43,45]octadecaene-19′,1″-cyclohexane]-8′,13′,25′,31′-tetrone – 5,16,22,34,40,51,57,69,72,74,77,80,83,85,88,91-Hexadecamethyltetraspiro-[7,14,24,32,42,49,59,67,73,84-decaazatridecacyclo[66.2.2.2^{3,6}.2^{9,12}.2^{15,18}.2^{20,72}.2^{33,36}.2^{38,41}.2^{44,48}.2^{50,53}.2^{55,58}.1^{26,30}.1^{61,65}]-dononaconta-3,5,9,11,15,17,20,22,26,28,30(84),33,35,38,40,44,46,50,52,55,57,61,63,65(73),68,70,71,74,76,78,80,82,85,87,89,91-hexatriacontaene-2,1′:19,1″:37,1‴:54,1⁗-tetrakiscyclohexane]-8,13,25,31,43,48,60,66-octone (1:1) [4^{35,70,70,35}]Catenane (**26**): 10 mg (2%). Colorless solid. M.p. >300°. R_f (CH_2Cl_2/MeOH 20:1) 0.50. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 20°): 1.29 (br., 24 H, CH_2); 1.36 (br., 48 H, CH_2); 1.80 (*s*, 36 H, Me); 1.87 (*s*, 48 H, Me); 1.95 (*s*, 12 H, Me); 1.97 (*s*, 36 H, Me); 2.00 (*s*, 12 H, Me); 2.04 (br., 48 H, CH_2); 6.75–6.85 (br., 52 arom. H); 7.25 (*s*, 4 H, ter); 7.41 (*s*, 8 H, ter); 7.47 (br., 8 H, ter); 7.86 (*t*, ^3J = 7.87, 2 H, py); 7.94 (*t*, ^3J = 7.63, 4 H, py); 8.14 (*d*, ^3J = 7.87, 4 H, py); 8.19 (*d*, ^3J = 7.63, 8 H, py). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD, 20°): 19.6, 19.7, 19.8 (Me); 24.2, 26.8, 27.60, 27.65, 27.70, 27.71, 38.0, 38.1, 38.2 (CH_2); 46.5, 46.6 (cy); 126.7, 126.8, 128.0, 128.1, 128.2, 128.9, 129.0, 132.4, 132.7 (CH); 136.5, 136.55, 136.7, 138.2, 138.6, 148.6, 148.9, 149.7, 150.2, 150.3 (cy); 164.3, 146.4, 167.8, 168.3 (C=O). MALDI-TOF-MS: 5459.8 ([M + Na]$^+$, [$C_{354}H_{378}N_{30}O_{24}$ (5437.1) + Na]$^+$).

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