[1]Rotaxanes and Pretzelanes: Synthesis, Chirality, and Absolute Configuration

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Abstract: The synthesis of aliphatically bridged [1]⟨*n*⟩rotaxanes and ⟨*n*⟩pretzelanes in preparative yields and the dependency of their chiroptical properties on the length ⟨*n*⟩ of their bridge are reported. A cycloenantiomeric bis(sulphonamide)[2]rotaxane with a sulphonamide group in its axle and its wheel was intramolecularly dialkylated by homologous bifunctional oligomethylene reagents to form chiral [1]⟨*n*⟩rotaxanes bearing bridges of different lengths ⟨*n*⟩ between the axle and the wheel. Intramolecular dialkylation by 1,ω-dibromoalkanes of a topologically chiral bis(sulphonamide)[2]catenane with a sulphonamide group in both of the macrolactam rings leads to pretzel shaped molecules (⟨*n*⟩pretzelanes) with homologous bridges between the two macrocycles. Their yields decrease with decreasing length of the bridge. The shortest bridge isolated so far in reasonable amounts consists of six methylene groups (⟨6⟩pretzelane). Remarkably, a covalent connection of axle and wheel in a [2]rotaxane was successful even with much shorter bridges—down to only three methylene groups ([1]⟨3⟩rotaxane). The structural changes of the [1]⟨*n*⟩rotaxanes with decreasing bridge length is expressed by an increasing high-field shift in the ^{1}H NMR spectra. Enantiomeric resolution of the racemates of both series was achieved in seven cases for the [1]⟨*n*⟩rotaxanes and two for the ⟨*n*⟩pretzelanes by use of chiral HPLC columns. The circular dichrograms of both compound families show a strong dependency on the length of the bridge. However, the shortest bridges displayed some additional unexpected deviations. A new specification of the absolute configuration of supramolecules, such as [*n*]catenanes, [*n*]rotaxanes and ⟨*n*⟩pretzelanes is introduced together with some nomenclature additions.

Keywords: catenanes · chirality · cycloenantiomerism · enantiomeric resolution · rotaxanes · supramolecular chemistry

Introduction

Cycloenantiomerism of mechanically connected molecules was foreseen theoretically by Frisch and Wassermann in 1961.[1] Topological chirality of catenanes can be determined by a difference in the segment sequence of one macrocycle with respect to the other macrocyle of a catenane. In order to show that difference, each ring of a catenane must consist of at least three different segments, even though every segment may appear in both rings.[2] In 1971, Schill described the stereochemistry of rotaxanes as being closely related to the chirality of catenanes.[3] Cycloenantiomerism of rotaxanes occurs when a macrocycle with such a kind of sequence information as described above is mechanically bound to an axle with two different blocking groups. One enantiomer has a clockwise orientation with respect to the described axle, whereas the other enantiomer shows the opposite arrangement. Approximately twenty years after the theoretical description of cycloenantiomerisation of catenanes and rotaxanes, and the chirality of knots, the first synthesis of a topologically chiral catenane[2, 4] and molecular knot[5] was achieved by Sauvage et al in 1988 and 1989, respectively. Our group reported the first example of a completely enantioseparated cycloenantiomeric bis(sulphonamide)[2]rotaxane **1** in 1996,[6, 7] and a topologically chiral bis(sulphonamide)[2]catenane **2** in 1995. (Figure 1).[6, 8]

The object **1** and its mirror image result from different sequences of the sulphonamide group and the three carbonamide groups of the wheel, mechanically bound to the oriented axle. The orientation of the wheel in **1a** and **1b** differs in the sequence of its connectivities. Determined by the orientation of the sulphonamide group and the three carbonamide groups of each macrolactam, the catenane **2** also forms two enantiomers **2a** and **2b**.[2] In both cases, **1** and **2**, the macrolactams and the axles are not chiral themselves, but after the formation of the mechanical bond these supramolecules occur as cycloenantiomers.

The incorporation of sulphonamide units into the macrocycle of amide-linked rotaxanes and catenanes not only results in two stereoisomers of each compound, but also offers a rather simple approach to their preparative chemistry.[9] Owing to their stronger acidity, sulphonamide protons can be

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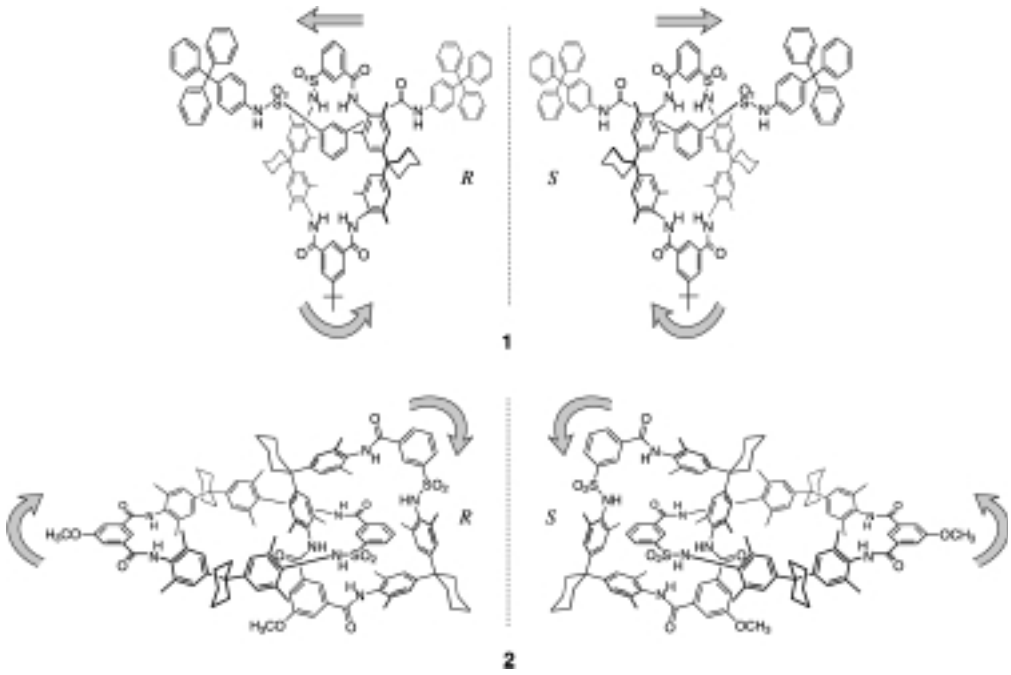

Figure 1. [2]Rotaxane **1** and [2]catenane **2**. Object and mirror image. Orientations of the sulphonamide units in the axle and the macrocycles are indicated by grey arrows.

Abstract in German: *Die Synthese aliphatisch überbrückter [1]Rotaxane und Brezelane erlaubte die Untersuchung der Abhängigkeit der chiroptischen Eigenschaften dieser Spezies von der Anzahl ihrer Brückenatome. Ein cycloenantiomeres Bis(sulfonamid)[2]rotaxan mit einer Sulfonamidgruppe in der Achse und einer weiteren im Reif wurde mit homologen Oligomethylendihalogenverbindungen intramolekular dialkyliert, wodurch chirale [1]Rotaxane mit unterschiedlich langen Brücken zwischen der Achse und dem Reif in präparativen Ausbeuten gebildet wurden. Eine intramolekulare Dialkylierung mit denselben 1,ω-Dibromalkanen des topologisch chiralen Disulfonamid[2]catenans mit je einer Sulfonamidgruppe in beiden Makrolactamcyclen führte zu Brezelanen mit homologen Brücken zwischen den beiden Makrocyclen. In der Serie der Brezelane war eine Abnahme der Ausbeuten mit kürzer werdender Kettenlänge der Brücke zu beobachten. Sechs Methylengruppen enthält die kürzeste Brücke, die bisher in einem Brezelan erhalten werden konnte. Im Gegensatz dazu war eine erfolgreiche kovalente Verknüpfung von Achse und Reif des eingesetzen [2]Rotaxans sogar mit nur einer Methylengruppe möglich, wobei ein Disulfonaminal-Rotaxan entstand. Die strukturellen Veränderungen der [1]Rotaxane durch die kontinuierliche Abnahme der Brückenlänge konnten anhand einer linearen Veränderung der auftretenden Hochfeldverschiebungen der Protonen des Achsenmittelstücks durch ^{1}H-NMR-Spektroskopie gezeigt werden. Eine Enantiomerentrennung der Racemate der [1]Rotaxane und Brezelane konnte in elf Fällen mittels chiraler HPLC-Säulen erfolgreich durchgeführt werden. Die Circulardichrogramme beider Serien von Supramolekülen zeigen eine starke und kontinuierliche Abhängigkeit von der jeweiligen Länge der Brücke im Molekül. Die Spezifikation der absoluten Konfiguration von Catenanen und Rotaxanen wird präzisiert, ebenso wie die Nomenklatur der Brezelane und [1]Rotaxane.*

removed selectively by mild bases even in the presence of carbonamide protons. This enables substitution reactions at the sulphonamide nitrogen with suitable alkylating agents.[7] A number of interesting supramolecular assemblies of some higher topological complexity have already been synthesised, such as [3]rotaxanes,[10] [4]rotaxanes,[10] bis[2]rotaxanes,[7] and dimeric [2]catenanes.[11] The first example of an oligooxapropano bridged [1]rotaxane[7, 12] and pretzelane[13] was published in 1996.[11] The enantioseparation of these last two compounds was successful, as was that of the unsubstituted compounds **1** and **2**.[14]

We were interested to see what effect a variation of the bridge length in both compound families would have on the preparation and chirality of these compounds. The syntheses of aliphatically bridged [1]⟨*n*⟩rotaxanes and ⟨*n*⟩pretzelanes with systematically varied chain lengths is reported, together with their enantioseparation and their chiroptical properties as a function of the more restricted conformational mobility forced by shorter bridges.[15]

Results and Discussion

Synthesis of [1]⟨*n*⟩rotaxanes 4a–j: The racemic mixture of the [2]rotaxane **1**, which carries sulphonamide groups in both its axle and its wheel, was prepared through a chemical-threading reaction based on non-ionic templating.[7] [1]⟨*n*⟩Rotaxanes **4a–j** were obtained by using 1,ω-dibromoalkanes that contained 1–10 methylene groups to connect the two sulphonamide nitrogens covalently. Solutions of **1** and the dibromide **3a–j** were simultaneously added to a suspension of potassium carbonate in DMF at 50 °C applying dilution conditions (Scheme 1). If the temperature rises over 50 °C a substitution reaction of the carbonamide NH protons takes

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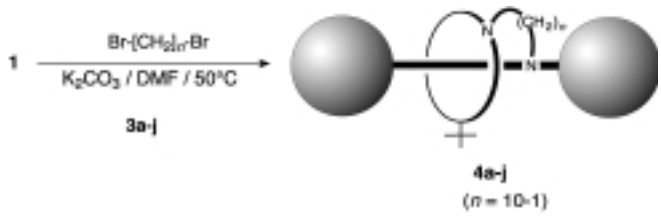

Scheme 1. Synthesis of the [1]⟨*n*⟩rotaxanes **4a–j**.

place, so a control of the reaction conditions is important for the chemoselective substitution.

The yields turned out to be remarkably high (22–64%) in some of the bridging reactions. Side products were identified as the monosubstituted monobromo[2]rotaxane and the disubstituted dibromo[2]rotaxane.[16] The chain length of the difunctionalised alkylating agents does not show distinct effects on the yields of **4a–j**. The highest yields of 52% and 64% are obtained by using 1,8-dibromooctane and 1,3-dibromopropane as bridging agents (Table 1). The lower limit of the length proved to be just one methylene group to form a [1]⟨1⟩rotaxane **4j**.[17] This reflects that the steric arrangement

Table 1. Yields of the [1]⟨*n*⟩rotaxanes **4a–j**. (**4i** and **4j** are only detected by FAB-MS).

	⟨*n*⟩	yield[%]
4a	10	21
4b	9	23
4c	8	52
4d	7	52
4e	6	39
4f	5	50
4g	4	40
4h	3	64
4i	2	–[17]
4j	1	–[17]

of the entities of the [2]rotaxane **1** is flexible and the wheel rotates and glides on the axle. The steady decrease in the length of the bridge in compounds **4a–j** leads to the question of what effect the chain length has on the rotational and translatorial flexibility of the wheel, which is mechanically and additionally covalently connected to the axle. In the ^{1}H NMR spectrum of the [2]rotaxane **1**, the H_i atom shows a high-field shift relative to the free axle due to the influence of the benzene units of the host wheel (Figure 2).[9f, 18] The H_i atom of the free axle appears as a singlet at $\delta = 8.25$, whereas the same proton of the axle incorporated in the [2]rotaxane **1** shows a singlet at $\delta = 6.47$. In the NMR spectra of the [1]⟨*n*⟩rotaxanes **4a–j** a singlet also appears at the higher field; its high-field shift increases linearly with decreasing chain length. NOE experiments show that this singlet is not assigned to the isophthalic proton H_i, but to the wheel. Due to the very short length of the bridge, only three methylene groups, in **4h** the proton appears as a singlet at $\delta = 4.95$.

A second high-field shift is obtained from the central axle proton H_a (doublet $^3J = 7.6–7.8$ Hz) of the [1]⟨*n*⟩rotaxanes with longer bridges (⟨*n*⟩ = 6–10; Figure 2). In the case of the [1]⟨*n*⟩rotaxanes with shorter bridges (⟨*n*⟩ = 3–5), this H_a proton does not show such a strong shift to the higher field, whereas the doublets of the aniline stopper protons St_1 and St_2 appear at $\delta = 6.65–6.09$ ($^3J = 8.6$ Hz). This leads to the conclusion that the rotational as well as the translatorial flexibility of the wheel on the axle is increasingly hindered with decreasing length of the bridges ⟨*n*⟩ and, therefore, the benzene units of the wheel exert a stronger influence on the chemical shift of the H_i proton (Figure 2). This effect has a different influence on the protons H_i, H_a and the aniline stopper protons of the axle with decreasing ⟨*n*⟩ due to the decreasing angle of the wheel on the axle.

Synthesis of ⟨*n*⟩pretzelanes 5a–e: Bis(sulphonamide)[2]catenane **2** was synthesised by using the chemical-threading reaction. In analogy to the known threading mechanism, the formation of an *in*/*out* and an *out*/*out* isomer is possible here, but only the *in*/*out* isomer was formed.[8a] No interconversion or equilibrium of the isomers of **2** has been observed, since the translation (circumrotation) of the rings is hindered by the large cyclohexylidene units.[8] An analogous procedure as for the [1]⟨*n*⟩rotaxanes **4a–j** was used for the syntheses of the ⟨*n*⟩pretzelanes **5a–e**. The intramolecular cyclization was achieved by the use of homologous 1,ω-dibromoalkanes **3a–e** containing 6–10 methylene groups (Scheme 2).

The yields decrease with decreasing length of the difunctionalised alkylating agent (Table 2). The low yield (5%) of **5e** suggests that the lower limit of the chain length is ⟨*n*⟩ = 6 in this series. In contrast to the [1]⟨*n*⟩rotaxanes, an intramolecular bridging of **2** down to one methylene group incorporated in the bridge was not possible. Unlike the sulphonamide units

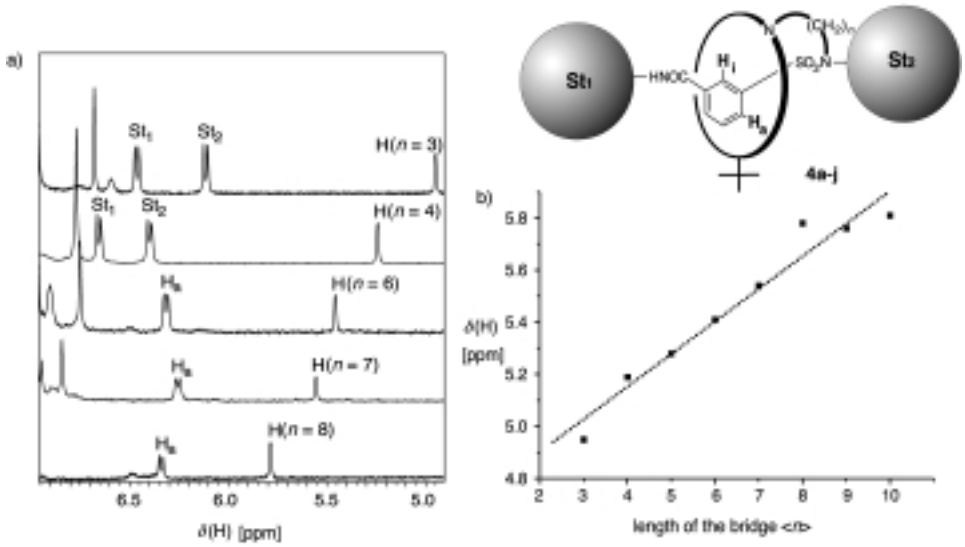

Figure 2. Linearly increasing high-field shift of the corresponding wheel proton with decreasing length ⟨*n*⟩ of the bridge. a) ^{1}H NMR spectra, b) high-field shift as a function of ⟨*n*⟩. For other absorptions see text.

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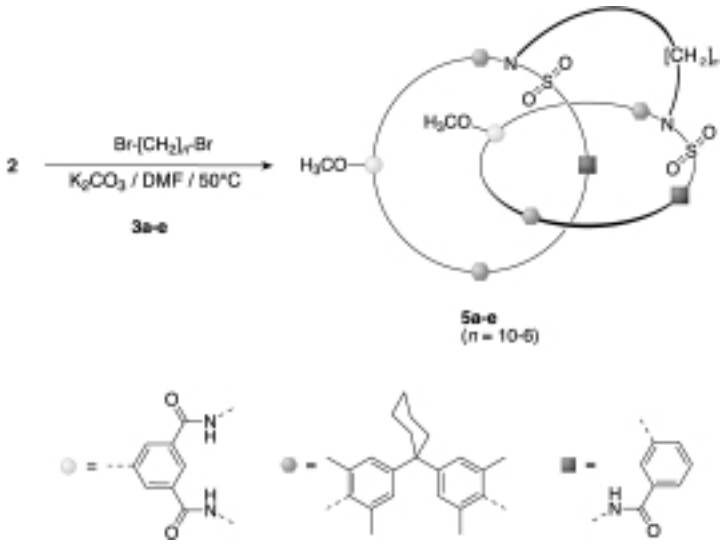

Scheme 2. Synthesis of the ⟨*n*⟩pretzelanes **5a–e**.

Table 2. Yields of the ⟨*n*⟩pretzelanes **5a–e**.

	⟨*n*⟩	yield [%]
5a	10	47
5b	9	39
5c	8	24
5d	7	8
5e	6	5

of **1**, these units in **2** have a more fixed distance to each other caused by the hindered circumrotation of the rings. We therefore obtained a strong correlation between the yields of the ⟨*n*⟩pretzelanes and the length of the dibromoalkane employed.

Enantioseparation and chiroptical properties of compounds 4a–e, 4g–h, 5a, 5c, and 2: The rotational and translatorial flexibility of the entities of the synthesised [1]⟨*n*⟩rotaxanes and the circumrotation of the rings of the ⟨*n*⟩pretzelanes decreases as the length ⟨*n*⟩ of the bridge decreases. This leads to the question as to whether there is any correlation with the chiroptical properties of the cycloenantiomers.

Therefore, the racemates of the [1]⟨*n*⟩rotaxanes **4a–e** and **4g–h** were enantioseparated by HPLC on a "Chiralcel OD" column.[19] The chromatograms of **4c–e** and **4g–h** showed a clear baseline separation. Almost complete resolution was obtained for **4a–b**. The separation factors α are higher with decreasing length of the bridges under the same conditions and were found to be $\alpha = 1.23-2.30$ (Table 3). In all separations the (−)-enantiomer was eluted first. HPLC on Chiralcel OD of the topologically chiral ⟨*n*⟩pretzelanes **5a–e** did not lead to a baseline separation, in contrast to the complete resolution of the [2]catenane **2**. Hence, the separation factors α are rather small (1.17–1.19). However, we did succeed in the enantioseparation of the ⟨10⟩pretzelane **5a** and the ⟨8⟩pretzelane **5c**. In all cases the (−)-enantiomers were eluted first.

The CD spectra of the [1]⟨*n*⟩rotaxanes were measured in 1,1,1,3,3,3-hexafluoro-2-propanol and those of the

Table 3. Cotton effects from molar circular dichroism spectra and separation factors [α] of the cycloenantiomers of **1**, **4a–d**, **4g**, **4h**, **2**, **5a** and **5c**.

	⟨*n*⟩	Cotton effect	[α]
1	–	114	1.48[14]
4a	10	68	1.23 (94:6)
4b	9	32	1.39 (94:6)
4c	8	10	1.56 (92:8)
4d	7	6	2.03 (92:8)
4e	6	–	1.48 (90:10)
4g	4	81	2.30 (90:10)
4h	3	77	1.79 (90:10)
2	–	141	2.68 (75:25)
5a	9	52	1.19 (75:25)
5c	8	13	1.17 (75:25)

⟨*n*⟩pretzelanes in 1,1,1-trifluoroethanol. The Cotton effects obtained for each of the enantiomers are mirror images over the whole region of the spectra. The molar CD spectra of the [1]⟨*n*⟩rotaxanes reach an extremum in the aromatic region at 197–212 nm. An extremum can be observed in the spectra of the ⟨*n*⟩pretzelanes at 209 nm. Remarkably, the circular dichrograms of **4a–e**, **5a** and **5c** showed Cotton effects with decreasing intensity as the length of the aliphatic bridge is decreased (Figure 3, Table 3). In comparison with the circular dichrogram of the unsubstituted enantiomers of **1** and **2**, the Cotton effects of **4a–e** and **5a** and **5c** are also smaller.[14] The Cotton effects of the [1]⟨4⟩rotaxane **4g** and the [1]⟨3⟩rotaxane **4h**, which contain very short bridges, are again higher and show a bathochromic shift of the extrema (Figure 3).

Clearly, the homologous bridges in **4a–e, 4g–h**, **5a** and **5c** have an impact on the conformation of the [1]⟨*n*⟩rotaxanes and the ⟨*n*⟩pretzelanes owing to steric and electronic factors, but so far there is neither an exact theoretical explanation for the described results, nor is a prediction of the strength of topological chirality or cycloenantiomerism possible.

Assignment of absolute configuration: Tauber[20] suggested in 1963 to determine the absolute configuration of catenanes in the following way: in each ring the atoms with highest and second highest order is chosen according to the CIP rules. These atom pairs have to be placed perpendicularly as far apart from each other as possible. Applying these rules for axial chiral compounds the absolute configuration of the schematic catenane **6** in Figure 4 is *R* if A has higher priority than B.

This formal method does not take into account the decisive and clear reason for chirality in these compounds: the clockwise/anticlockwise orientation of the macrocycles in catenanes or the wheel in rotaxanes.

Chiral compounds can be fundamentally depicted as helices, in the CIP scheme[21] also called the "steering wheel" reference system. Helices are generated using the combination of an axial and a polar vector (Figure 5). The combination of the two vectors, here generating a right handed *P* helix, is also a schematic presentation of a cycloenantiomeric [2]rotaxane (here in the *R* form), therefore dubbed the "CIP-molecule" by Mislow.[2a,b]

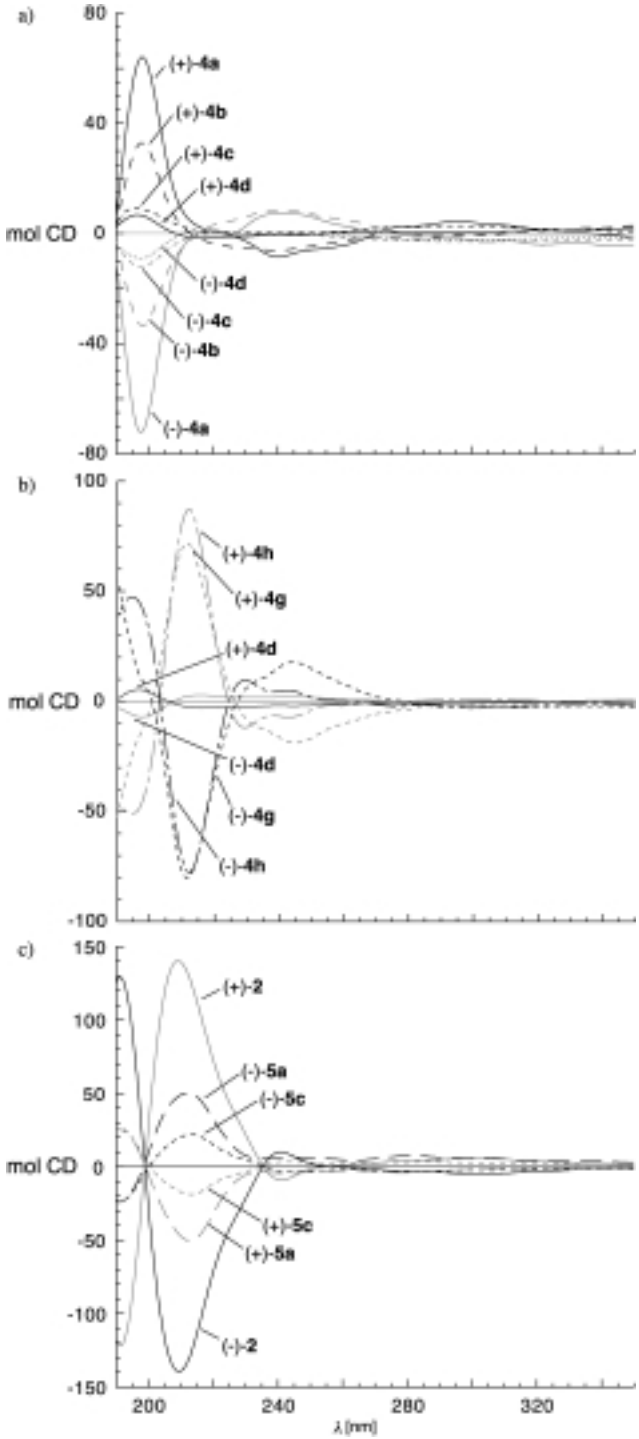

Figure 3. Circular dichrograms of: a) the [1]⟨*n*⟩rotaxanes **4a–d**, b) [1]⟨*n*⟩rotaxanes **4d,4g** and **4h**, and c) [2]catenane **2**, and the ⟨*n*⟩pretzelanes **5a** and **5c**.

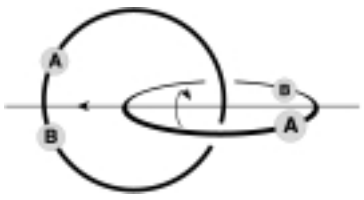

Figure 4. Assignment of the absolute configuration of the schematic catenane **6** applying the CIP rules for axial chirality.

Figure 5. Description of a helix using an axial and a polar vector.

We hereby suggest an alternative method for the assignment of the absolute configuration of topologically chiral catenanes and cycloenantiomeric rotaxanes by specifying the orientation of the macrocycles or of the wheel and axle. The CIP terminology defines the direction from atoms, or groups with higher priority to the ones with lower priority taking the shortest distance. In the sulphonamide macrolactam wheel (Figure 1), the sulphur atom has the highest priority and the neighbouring nitrogen atom the second highest priority. The same holds for the axle with the shown orientation, therfore, rotaxane **1** has the configuration assigned in Figure 1. In catenanes, one of the macrocycles can be considered as the axial vector and the orientation of the second as the polar vector; hence, catenane **2** in Figure 1 possesses the shown *R*,*S* classification. In cycloenantiomeric [3]rotaxanes with one oriented wheel (**7**; Figure 6), the orientation of the axle is given by the second not oriented wheel.

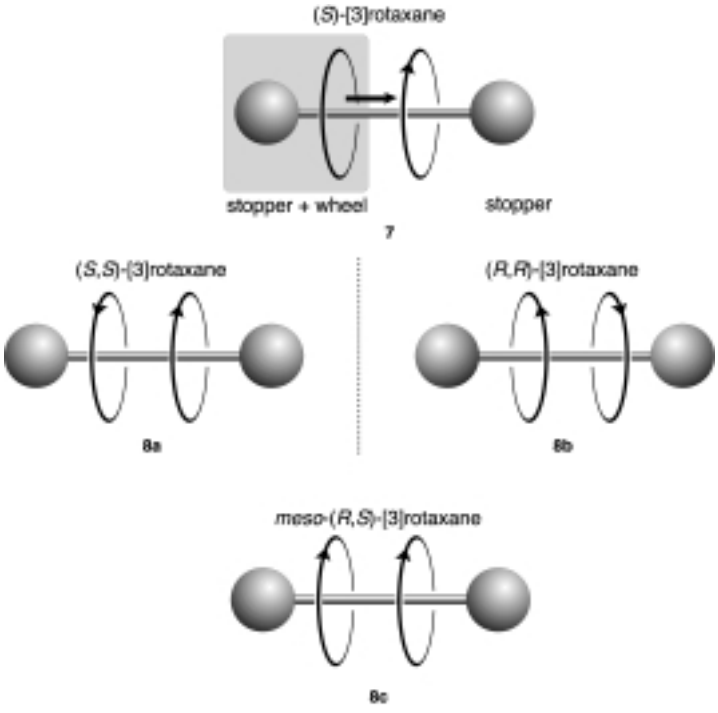

Figure 6. Assignment of the absolute configuration of cycloenantiomeric [3]rotaxanes.

Viewed from the oriented wheel, the side of axle with the second wheel has the higher priority, hence, [3]rotaxane **7** is left-handed. In our [3]rotaxanes **8** (Figure 6) with two oriented wheels (recently separated into the enantiomers),[22] from the point of view of both wheels the absolute configuration can be assigned in the above described manner, hence, we observe two stereogenic units. [3]Rotaxanes (*S*,*S*) **8a** and

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(*R*,*R*) **8b** are chiral; the (*R*,*S*) form **8c** is the *meso*-rotaxane (as in the classical covalent case of tartaric acid).

The deficiency of applying CIP rules for the assignment of absolute configurations in such molecules is that the considered two atoms are not necessarily the moieties responsible for the chirality of the molecule. The atoms with the highest and second highest order, for example, in the macrocycle **9** of Sauvages topologically chiral catenane (Figure 7) are the oxygen atoms 1 and 2. The introduction of an additional oxygen atom into the polyether chain (**10** in Figure 7) causes the change of the absolute configuration of the catenane (oxygen 1 has the highest and 2 the second highest priority) without changing the crucial substitution of the phenanthroline group.

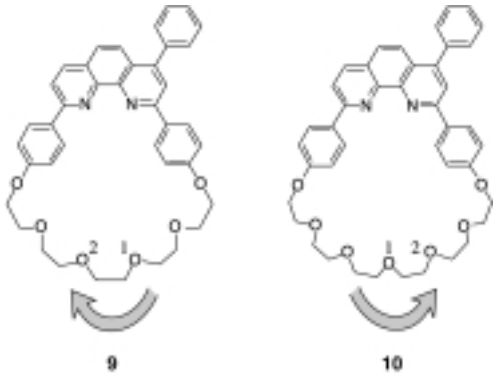

Figure 7. Macrocycle **9** of Sauvages topologically chiral catenane and macrocycle **10** with an additional oxygen atom in its polyether chain.

The existing nomenclature assigns the absolute configuration considering atoms with evidently minor influence to the chirality of the molecule. It would seem a more convincing and superior approach to use a more structure/property related nomenclature that takes into account the molecule moieties essential for chirality.

Conclusion

The results of the chiroptical properties of [1]⟨*n*⟩rotaxanes and ⟨*n*⟩pretzelanes reported here contribute to the understanding of mechanically interlocked chiral molecules, the chirality of which is determined by segment sequence information. The conformational and chiral properties are influenced by the length of the bridge and, as a consequence, lead to a linear dependency on the high-field shift in the ^{1}H NMR spectra as well as gradually modified Cotton effects. We also set an empirical limit of the length of the aliphatic bridge for the synthesis of covalently bridged [1]⟨*n*⟩rotaxanes **4** and ⟨*n*⟩pretzelanes **5**, the shortest bridge being $\langle n\rangle = 3$ (isolated) or even 2 and 1 (detected) in the first case and $\langle n\rangle = 6$ in the second case. We are currently investigating the scope for the application of other types of bridges, such as bridges that are unsaturated or contain spacer groups. The resulting [1]⟨*n*⟩rotaxanes and ⟨*n*⟩pretzelanes would then bear another chromophoric group in their bridges that might affect their CD spectra. A clear and more relevant specification of the chirality of [*n*]catenanes, [*n*]rotaxanes and ⟨*n*⟩pretzelanes has been suggested based on the existing CIP rules.

Experimental Section

All solvents were distilled prior to use and all other chemicals were of the best commercial quality available and used as received. The [2]rotaxane **1** and the [2]catenane **2** were prepared as reported previously.[7, 8] 1,10-dibromodecane (Aldrich), 1,9-dibromononane (Aldrich), 1,8-dibromooctane (Aldrich), 1,7-dibromoheptane (Aldrich), 1,6-dibromohexane (Aldrich), 1,5-dibromopentane (Aldrich), 1,4-dibromobutane (Aldrich), 1,3-dibromopropane (Fluka), 1,2-dibromoethane (Aldrich), methylenebromide (Aldrich). Elemental analysis: Analytical facilities of the Kekulé-Institut für Organische Chemie und Biochemie of the University of Bonn. FAB-MS: Concept 1H (Kratos Analytical, Manchester), matrix: *m*-nitrobenzoylalcohol. MALDI-TOF: MALDI-TofSpecE (Micromass, Manchester), matrix: 9-nitroanthracene or 2,5-dihydroxybenzoic acid. ^{1}H, ^{13}C NMR: AM 400 MHz, or DRX 500 MHz, Bruker (Analytische Messtechnik GmbH, Karlsruhe), abbreviation: sb = sulfobenzoyl. CD-Spectrometer: JASCO, J-720 Spectrometer, (Labor- und Datentechnik GmbH, Germany).

General procedure for the synthesis of the bridged [1]⟨*n*⟩rotaxanes 4a–j: [2]Rotaxane **1** (100 mg, 0.05 mmol) and dibromide **3a–j** (0.05 mmol) were dissolved separately in dry DMF (50 mL). At 50 °C both solutions were simultaneously added over a period of 2 h to a stirred suspension of potassium carbonate (25 mg, 0.18 mmol) in DMF (100 mL). Stirring was continued for another three days. Trichloromethane (100 mL) was added and the solution was extracted three times with water (70 mL). The organic layer was separated and dried over Na_2SO_4. The crude product was then purified by column chromatography (SiO_2, 63–100 μm).

General conditions for the enantioseparation of the [1]⟨*n*⟩rotaxanes: Column: Chiralcel OD (25 × 0.46 cm i.d.); eluent: hexane/ethanol (**3a–b** = 96:4, **3c–d** = 94:6, **3e**,**3g**, and **3h** = 90:10); flow rate: 1.0 mL min^{-1}; samples: 10 mL (5 mg mL^{-1}, CH_2Cl_2/methanol, 8:1).

[1]⟨10⟩rotaxane 4a: R_f = 0.69 (dichloromethane/ethyl acetate, 30:1); yield 22% (21 mg, 0.011 mmol) as a white powder, m.p. 195 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.21 (s, 9H; *t*Bu CH_3), 1.38 (s, 6H; CH_3), 1.39 (s, 6H; CH_3), 1.55 (s, 6H; CH_3), 1.56 (s, 6H; CH_3), 1.59 (br, 8H; cyclohexylidene CH_2), 1.82 (br, 8H; CH_2), 1.88 (br, 8H; cyclohexylidene CH_2), 2.28 (m, 8H; CH_2), 2.34 (s, 4H; cyclohexylidene CH_2), 3.32 (m, 4H; CH_2), 5.81 (s, 1H; aryl), 6.30 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 6.75 (s, 2H; sb, aryl), 6.76 (s, 2H; aryl), (br, 4H; aryl), 6.86 (d, ^3J(H,H) = 8.6 Hz, 2H; tritylaniline), 6.92–7.38 (m, 36H; trityl), 7.50 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.55 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.89 (s, 1H; 5-*t*Bu-isophthaloyl), 8.08 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.10 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.19 (s, 1H; sb), 8.20 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.28 (s, 1H; amide), 8.35 (s, 1H; amide), 8.56 (s, 1H; 5-*t*Bu-isophthaloyl), 8.58 (s, 1H; 5-*t*Bu-isophthaloyl), 8.74 (s, 1H; amide), 8.82 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$/CD_3OD, 25 °C): δ = 18.1, 18.4, 19.1, 20.0 (CH_3), 22.6, 22.7, 26.7, 26.9, 29.1, 29.2 (cyclohexylidene CH_2), 31.0 (*t*Bu CH_3), 32.6, 33.9 (cyclohexylidene Cq), 35.0 (*t*Bu Cq), 26.1, 26.2, 27.8, 27.9, 44.7, 45.2, 45.8, 46.6, 49.8, 49.9 (CH_2), 64.2, 64.5 (trityl Cq), 120.6, 120.8, 120.9, 122.5, 122.8, 123.2, 125.3, 125.6, 125.8, 126.0, 126.1, 126.2, 127.4, 127.5, 127.6, 128.0, 128.2, 128.6, 128.9, 130.7, 130.9, 131.0, 131.1, 131.3, 131.7 (CH), 132.4, 133.8, 134.1, 135.1, 135.4, 136.4, 139.1, 139.6, 141.3, 145.7, 146.1, 146.4, 152.4, 153.4 (Cq), 165.0, 165.1, 165.4, 165.8 (amide Cq); FAB-MS: *m*/*z*: 1972.9 $[M]^+$ (calcd 1972.7).

[1]⟨9⟩rotaxane 4b: R_f = 0.51 (dichloromethane/ethyl acetate, 40:1); yield 23% (23 mg, 0.012 mmol) as a white powder, m.p. 226 °C; ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD, 25 °C): δ = 1.72 (s, 9H; *t*Bu CH_3), 1.88 (s, 6H; CH_3), 1.89 (s, 6H; CH_3), 2.00 (s, 6H; CH_3), 2.05 (br, 8H; cyclohexylidene CH_2), 2.41 (s, 6H; CH_3), 2.43 (br, 8H; cyclohexylidene CH_2), 2.60 (m, 2H; CH_2), 2.81 (m, 2H; CH_2), 2.85 (s, 4H; cyclohexylidene CH_2), 3.66 (m, 2H; CH_2), 3.68 (m, 2H; CH_2), 3.72 (m, 4H; CH_2), 3.80 (m, 2H; CH_2), 3.84 (t, ^3J(H,H) = 6.7 Hz, 2H; CH_2), 4.03 (t, ^3J(H,H) = 6.6 Hz, 2H; CH_2), 6.10 (s, 1H; aryl), 6.72 (d, ^3J(H,H) = 6.4 Hz, 1H; sb), 7.23 (br, 6H; aryl), 7.31 (d, ^3J(H,H) = 8.4 Hz, 2H; tritylaniline), 7.47 (d, ^3J(H,H) = 8.4 Hz, 2H; tritylaniline), 7.50–7.71 (m, 38H; sb, trityl, aryl, amide), 7.72 (dd, ^3J(H,H) = 7.8,

6.4 Hz, 1H; sb), 7.99 (dd, ^3J(H,H) = 7.7, 7.8 Hz, 1H; sb), 8.35 (d, ^3J(H,H) = 7.8 Hz, 1H; sb), 8.37 (s, 1H; sb), 8.59 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.60 (s, 1H; 5-*t*Bu-isophthaloyl), 8.75 (s, 1H; 5-*t*Bu-isophthaloyl), 8.85 (s, 1H; 5-*t*Bu-isophthaloyl), 9.03 (s, 1H; amide), 9.36 (s, 1H; amide), 9.54 (s, 1H; amide); ^{13}C NMR (69.2 MHz, $CDCl_3$/CD_3OD, 25 °C): δ = 18.5, 18.9, 19.5, 20.0 (CH_3), 22.7, 23.0, 25.8, 25.9, 34.6, 34.7 (cyclohexylidene CH_2), 31.4 (*t*Bu CH_3), 35.4 (*t*Bu Cq), 45.0, 47.1 (cyclohexylidene Cq), 25.0, 26.1, 26.4, 32.7, 32.9, 34.2, 35.0, 49.1, 49.6 (CH_2), 64.8 (trityl Cq), 123.1, 123.2, 125.5, 125.9, 126.1, 126.3, 126.6, 127.2, 127.7, 127.8, 127.9, 128.5, 128.9, 128.9, 129.2, 129.4, 129.7, 130.4, 131.1, 131.2, 131.6, 131.9 (CH), 133.8, 134.2, 135.4, 135.9, 136.1, 137.0, 139.2, 139.6, 141.9, 143.1, 145.2, 146.3, 146.6, 146.7, 149.3, 152.5, 153.6 (Cq), 165.0, 165.1, 165.4, 165.8 (amide Cq); FAB-MS: *m*/*z*: 1959.0 $[M+H]^+$; elemental analysis calcd (%) for $C_{129}H_{132}N_6O_8S_2 \cdot C_2H_4Cl_4 \cdot C_8H_{16}O_4$ (1958.6): C 73.97, H 6.95, N 3.62, S 2.76; found C 73.38, H 7.06, N 3.95, S 3.00.

[1]⟨8⟩rotaxane 4c: R_f = 0.54 (dichloromethane/ethyl acetate, 40:1); yield 52% (67 mg, 0.034 mmol) as a white powder, m.p. 193 °C; ^{1}H NMR (400 MHz, [D$_7$]DMF, 25 °C): δ = 1.30 (s, 6H; CH_3) , 1.32 (s, 6H; CH_3), 1.38 (s, 9H; *t*Bu CH_3), 1.61 (s, 6H; CH_3), 1.76 (s, 6H; CH_3), 1.82 (m, 2H; CH_2), 2.18 (br, 8H; cyclohexylidene CH_2), 2.29 (br, 8H; cyclohexylidene CH_2), 2.55 (s, 4H; cyclohexylidene CH_2), 2.58 (m, 4H; CH_2), 3.21 (m, 2H; CH_2), 3.39 (m, 2H; CH_2), 3.51 (m, 2H; CH_2), 3.53 (t, ^3J(H,H) = 6.6 Hz, 2H; CH_2), 4.36 (t, ^3J(H,H) = 6.7 Hz, 2H; CH_2), 5.78 (s, 1H; aryl), 6.34 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 6.98 (d, ^3J(H,H) = 8.6 Hz, 2H; tritylaniline), 7.09 (s, 2H; aryl), 7.11 (s, 2H; aryl), 7.12 (s, 2H; aryl), 7.13 – 7.38 (m, 38H; trityl, sb, aryl), 7.45 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.56 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.84 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 7.99 (s, 1H; sb), 8.19 (d, ^3J (H,H) = 7.7 Hz, 1H; sb), 8.31 (s, 1H; 5-*t*Bu-isophthaloyl), 8.34 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.58 (s, 1H; amide), 8.79 (s, 1H; 5-*t*Bu-isophthaloyl), 8.80 (s, 1H; 5-*t*Bu-isophthaloyl), 9.29 (s, 1H; amide), 9.32 (s, 1H; amide), 10.39 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 18.4, 18.7, 19.1, 19.5 (CH_3), 23.5, 23.6, 26.6, 26.7, 33.3, 33.4 (cyclohexylidene CH_2), 26.3, 26.4 (CH_2), 31.3 (*t*Bu CH_3), 33.3, 33.6 (CH_2), 47.7 (cyclohexylidene Cq), 49.6, 50.6, 62.0 (CH_2), 65.3, 65.3 (trityl Cq), 121.8, 124.1, 125.9, 126.3, 126.7, 126.8, 126.9, 127.5, 128.3, 128.4, 128.5, 128.6, 129.4, 129.9, 130.6, 131.2, 131.3, 131.4, 131.5, 131.7, 132.0, 132.1 (CH), 132.2, 132.7, 135.1, 135.3, 135.7, 135.9, 136.0, 136.1, 137.4, 137.9, 141.8, 144.1, 147.0, 147.1, 147.2, 147.5 (Cq), 163.0, 164.6, 165.8, 167.6 (amide Cq); FAB-MS: *m*/*z*: 1945.0 $[M+H]^+$; elemental analysis calcd (%) for $C_{128}H_{130}N_6O_8S_2 \cdot C_2H_4Cl_4 \cdot H_4O_2$ (1944.6): C 71.85, H 6.54, N 3.90, S 2.97; found C 71.62, H 6.84, N 4.25, S 3.17.

[1]⟨7⟩rotaxane 4d: R_f = 0.56 (dichloromethane/ethyl acetate, 40:1); yield 52% (51 mg, 0.026 mmol) as a white powder, m.p. 252 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.40 (s, 9H; *t*Bu CH_3), 1.52 (s, 6H; CH_3), 1.57 (s, 6H; CH_3), 1.60 (s, 6H; CH_3), 1.69 (s, 6H; CH_3), 1.81 (m, 2H; CH_2), 1.92 (br, 8H; cyclohexylidene CH_2), 2.08 (m, 2H; CH_2), 2.11 (m, 2H; CH_2), 2.24 (m, 2H; CH_2), 2.31 (br, 8H; cyclohexylidene CH_2), 2.42 (s, 4H; cyclohexylidene CH_2), 2.99 (m, 1H; CH_2), 3.28 (m, 1H; CH_2), 3.40 (t, ^3J(H,H) = 6.4 Hz, 2H; CH_2), 3.62 (t, ^3J(H,H) = 6.4 Hz, 1H; CH_2), 4.03 (t, ^3J(H,H) = 6.4 Hz, 1H; CH_2), 5.56 (s, 1H; aryl), 6.23 (d, ^3J(H,H) = 7.3 Hz, 1H; sb), 6.82 (s, 2H; aryl), 6.88 (br, 4H; aryl), 6.94 (d, ^3J(H,H) = 8.6 Hz, 2H; tritylaniline), 7.05 (d, ^3J(H,H) = 8.6 Hz, 2H; tritylaniline), 7.08 – 7.23 (m, 37H; trityl, aryl, sb), 7.32 (dd, ^3J(H,H) = 7.6, 7.6 Hz, 1H; sb), 7.77 (dd, ^3J(H,H) = 7.3, 7.3 Hz, 1H; sb), 7.67 (s, 1H; 5-*t*Bu-isophthaloyl), 7.92 (s, 1H; sb), 7.94 (d, ^3J(H,H) = 7.3 Hz, 1H; sb), 8.09 (d, ^3J(H,H) = 7.3 Hz, 1H; sb), 8.24 (s, 2H; 5-*t*Bu-isophthaloyl), 8.38 (s, 1H; amide), 8.56 (s, 1H; amide), 8.88 (s, 1H; amide), 9.07 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 18.4, 19.0, 19.6, 19.7 (CH_3), 22.8, 24.5, 25.8, 26.5, 34.7, 34.9 (cyclohexylidene CH_2), 31.3 (*t*Bu CH_3), 35.9 (*t*Bu Cq), 44.9, 47.2 (cyclohexylidene Cq), 28.4, 35.9, 38.4, 48.6, 49.5, 62.9, 65.4 (CH_2), 64.6, 64.7 (trityl Cq), 121.7, 123.3, 125.8, 126.1, 126.2, 126.5, 127.2, 127.4, 127.5, 127.6, 128.3, 128.9, 129.1, 129.2, 129.3, 129.5, 130.3, 131.1, 131.4, 131.5, 131.9 (CH), 132.3, 133.7, 133.9, 134.1, 134.9, 135.4, 135.7, 136.6, 138.5, 139.7, 141.9, 143.2, 145.1, 146.3, 146.5, 146.8, 152.5, 153.4 (Cq), 164.9, 165.0, 165.3, 166.6 (amide Cq); FAB-MS: *m*/*z*: 1930.9 $[M]^+$; elemental analysis calcd (%) for $C_{127}H_{128}N_6O_8S_2 \cdot CH_2Cl_2 \cdot C_{12}H_{24}O_6$ (1930.6): C 73.76, H 6.81, N 3.67, S 2.81; found C 73.52, H 6.64, N 4.01, S 3.28.

[1]⟨6⟩rotaxane 4e: R_f = 0.39 (dichloromethane/ethyl acetate, 40:1); yield 39% (37.4 mg, 0.02 mmol) as a white powder, m.p. 258 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.43 (s, 9H; *t*Bu CH_3), 1.50 (s, 6H; CH_3), 1.57 (s, 6H; CH_3), 1.67 (br, 8H; cyclohexylidene CH_2), 1.73 (s, 6H; CH_3), 2.22 (s, 6H; CH_3), 2.30 (br, 8H; cyclohexylidene CH_2), 2.46 (s, 4H; cyclohexylidene CH_2), 2.89 (m, 2H; CH_2), 3.18 (m, 2H; CH_2), 3.35 (m, 2H; CH_2), 3.40 (t, ^3J(H,H) = 6.7 Hz, 2H; CH_2), 3.42 (m, 2H; CH_2), 3.53 (t, ^3J(H,H) = 6.7 Hz, 2H; CH_2), 5.46 (s, 1H; aryl), 6.31 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 6.75 (s, 2H; aryl), 6.90 (br, 4H; aryl), 6.96 (d, ^3J(H,H) = 8.6 Hz, 2H; tritylaniline), 7.08 (d, ^3J(H,H) = 8.6 Hz, 2H; tritylaniline), 7.10 – 7.33 (m, 36H; trityl, sb, aryl), 7.27 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 7.56 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.61 (s, 1H; 5-*t*Bu-isophthaloyl), 7.77 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.99 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.10 (s, 1H; sb), 8.12 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.53 (s, 1H; amide), 8.79 (s, 2H; 5-*t*Bu-isophthaloyl), 8.86 (s, 1H; amide), 9.09 (s, 1H; amide), 9.35 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 18.4, 19.0, 19.6 (CH_3), 22.9, 23.1, 25.0, 26.4, 34.6, 34.7 (cyclohexylidene CH_2), 31.4 (*t*Bu CH_3), 32.6 (cyclohexylidene Cq), 35.6 (*t*Bu Cq), 26.5, 26.6, 35.7, 38.2, 48.8, 50.3 (CH_2), 64.7 (trityl Cq), 121.5, 123.2, 125.6, 125.7, 126.1, 126.2, 126.6, 127.1, 127.7, 127.8, 128.7, 128.8, 128.9, 129.2, 129.3, 129.4, 130.2, 130.9, 131.0, 131.1, 131.2, 131.6, 132.0 (CH), 132.2, 133.7, 133.9, 134.2, 135.2, 135.3, 136.1, 137.0, 137.8, 140.3, 141.8, 145.0, 146.3, 146.6, 146.7, 152.4, 153.4 (Cq), 165.0, 165.1, 165.4, 165.8 (amide Cq); FAB-MS: *m*/*z*: 1916.8 $[M]^+$; elemental analysis calcd (%) for $C_{126}H_{126}N_6O_8S_2 \cdot C_7H_7ON \cdot C_8H_{16}O_4$ (1916.6): C 75.98, H 6.93, N 4.53, S 2.96; found C 75.93, H 6.60, N 4.38, S 4.46.

[1]⟨5⟩rotaxane 4f: R_f = 0.51 (dichloromethane/ethyl acetate, 40:1); yield 50% (47.5 mg, 0.02 mmol) as a white powder, m.p. 268 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.39 (s, 6H; CH_3), 1.41 (s, 9H; *t*Bu CH_3), 1.55 (s, 6H; CH_3), 1.60 (br, 8H; cyclohexylidene CH_2), 1.69 (s, 6H; CH_3), 2.05 (br, 8H; cyclohexylidene CH_2), 2.30 (s, 4H; cyclohexylidene CH_2), 2.39 (br, 4H; CH_2), 2.44 (s, 6H; CH_3), 2.82 (m, 1H; CH_2), 3.10 (m, 1H; CH_2), 3.26 (t, ^3J(H,H) = 6.8 Hz, 2H; CH_2), 3.32 (t, ^3J(H,H) = 6.8 Hz, 2H; CH_2), 5.28 (s, 1H; aryl), 6.19 (d, ^3J(H,H) = 8.5 Hz, 2H; tritylaniline), 6.79 (s, 2H; aryl), 6.85 (d, ^3J(H,H) = 8.5 Hz, 2H; tritylaniline), 6.91 – 7.28 (m, 40H; trityl, sb, aryl), 7.36 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.41 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 7.52 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.59 (s, 1H; 5-*t*Bu-isophthaloyl), 7.71 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 7.98 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.04 (s, 1H; sb), 8.11 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.19 (s, 1H; 5-*t*Bu-isophthaloyl), 8.28 (s, 1H; amide), 8.41 (s, 1H; 5-*t*Bu-isophthaloyl), 8.53 (s, 1H; amide), 8.92 (s, 1H; amide), 9.41 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 18.5, 18.6, 19.5, 21.3 (CH_3), 22.9, 24.3, 26.7, 27.4, 32.2, 33.5 (cyclohexylidene CH_2), 31.3 (*t*Bu CH_3), 34.6 (*t*Bu Cq), 35.2, 36.0, 37.7, 49.5, 50.4 (CH_2), 44.9, 45.3 (cyclohexylidene Cq), 64.6, 64.7 (trityl Cq), 121.4, 124.3, 125.4, 125.8, 126.1, 126.2, 127.2, 127.4, 127.5, 127.6, 128.4, 128.9, 129.3, 129.5, 131.1, 131.2, 131.3, 131.7, 132.0 (CH), 132.4, 133.7, 133.9, 134.6, 134.7, 135.2, 136.1, 136.6, 136.7, 138.2, 140.2, 141.9, 145.4, 146.3, 146.4, 146.5, 146.8, 152.6, 153.4 (Cq), 164.8, 165.0, 165.6, 165.9 (amide Cq); MALDI-TOF-MS: *m*/*z*: 1925.5 $[M+Na]^+$ (calcd 1902.5).

[1]⟨4⟩rotaxane 4g: R_f = 0.29 (dichloromethane/ethyl acetate, 40:1); yield 40% (37.7 mg, 0.02 mmol) as a white powder, m.p. 302 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.43 (s, 9H; *t*Bu CH_3), 1.51 (s, 6H; CH_3), 1.62 (br, 8H; cyclohexylidene CH_2), 1.69 (br, 8H; cyclohexylidene CH_2), 1.90 (s, 6H; CH_3), 2.11 (s, 6H; CH_3), 2.28 (br, 4H; CH_2), 2.31 (s, 4H; cyclohexylidene CH_2), 2.39 (s, 6H; CH_3), 2.89 (m, 1H; CH_2), 2.98 (m, 1H; CH_2), 3.21 (m, 1H; CH_2), 3.41 (m, 1H; CH_2), 5.24 (s, 1H; aryl), 6.40 (d, ^3J(H,H) = 8.2 Hz, 2H; tritylaniline), 6.67 (d, ^3J(H,H) = 8.2 Hz, 1H; tritylaniline), 6.79 (s, 2H; aryl), 7.03 – 7.30 (m, 41H; trityl, aryl, sb), 7.43 (br, 1H; sb), 7.49 (d, ^3J(H,H) = 7.8 Hz, 1H; sb), 7.52 (s, 1H; 5-*t*Bu-isophthaloyl),7.86 (br, 1H; sb), 8.00 (d, ^3J(H,H) = 7.8 Hz, 1H; sb), 8.10 (s, 1H; sb), 8.15 (d, ^3J(H,H) = 7.8 Hz, 1H; sb), 8.32 (s, 1H; 5-*t*Bu-isophthaloyl), 8.46 (s, 1H; amide), 8.51 (s, 1H; 5-*t*Bu-isophthaloyl), 8.68 (s, 1H; amide), 8.71 (s, 1H; amide), 9.15 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 18.5, 18.6, 18.8, 22.2 (CH_3), 22.9, 23.1, 25.6, 26.4, 34.2, 34.9 (cyclohexylidene CH_2), 31.3 (*t*Bu CH_3), 35.4 (*t*Bu Cq), 36.5, 36.8, 49.2, 50.3 (CH_2), 44.9, 47.7 (cyclohexylidene Cq), 64.7, 64.8 (trityl Cq), 121.2, 122.8, 125.5, 126.1, 126.3, 126.6, 126.7, 127.6, 127.7, 127.8, 128.5, 128.8, 129.1, 129.4, 129.6, 129.8, 129.9, 131.0, 131.1, 131.5, 131.6, 132.1, 132.4 (CH), 133.1, 133.6, 133.7, 134.1, 135.4, 135.6, 135.7, 137.5, 137.9, 138.6, 141.3, 143.2, 144.9, 146.2, 146.6, 147.3, 149.1, 153.0, 153.4 (Cq), 164.8, 165.0, 165.1, 165.8 (amide Cq); FAB-MS: *m*/*z*: 1888.8 $[M]^+$; $C_{124}H_{122}N_6O_8S_2 \cdot C_8H_{16}O_4 \cdot CH_2Cl_2$(1888.5): calcd C 74.31, H 6.56, N 3.91, S 2.98; found C 73.91, H 6.27, N 4.19, S 3.34.

[1]⟨3⟩rotaxane 4h: R_f = 0.44 (dichloromethane/ethyl acetate, 40:1); yield 64% (59.9 mg, 0.03 mmol) as a white powder, m.p. > 310 °C; ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD, 25 °C): δ = 1.38 (s, 9H; *t*Bu CH_3), 1.49 (s, 6H; CH_3), 1.58 (br, 8H; cyclohexylidene CH_2), 1.69 (br, 8H; cyclohexylidene CH_2), 1.77 (s, 6H; CH_3), 1.88 (s, 6H; CH_3), 2.00 (s, 4H; cyclohexylidene

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CH_2), 2.14 (br, 2H; CH_2), 2.23 (s, 6H; CH_3), 2.61 (m, 1H; CH_2), 2.69 (m, 1H; CH_2), 3.07 (m, 1H; CH_2), 3.18 (m, 1H; CH_2), 4.95 (s, 1H; aryl), 6.19 (d, ^3J(H,H) = 8.1 Hz, 2H; tritylaniline), 6.42 (d, ^3J(H,H) = 8.1 Hz, 1H; tritylaniline), 6.67 (s, 2H; aryl), 6.91–7.13 (m, 40H; trityl, sb, aryl), 7.23 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.28 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 7.58 (dd, ^3J(H,H) = 7.7, 7.7 Hz, 1H; sb), 7.70 (s, 1H; 5-*t*Bu-isophthaloyl), 7.89 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.03 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.15 (s, 1H; sb), 8.16 (d, ^3J(H,H) = 7.7 Hz, 1H; sb), 8.25 (s, 1H; 5-*t*Bu-isophthaloyl), 8.32 (s, 1H; amide), 8.48 (s, 1H; 5-*t*Bu-isophthaloyl), 8.71 (s, 1H; amide), 8.84 (s, 1H; amide), 9.49 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$/CD_3OD, 25 °C): δ = 18.2, 18.3, 19.2, 22.6 (CH_3), 22.9, 23.0, 26.2, 26.5, 34.1, 35.1 (cyclohexylidene CH_2), 31.0 (*t*Bu CH_3), 35.2 (*t*Bu Cq), 36.5, 44.7, 47.5 (CH_2), 64.5, 64.6 (trityl Cq), 121.4, 123.1, 125.1, 125.4, 126.0, 126.1, 126.6, 127.5, 127.6, 128.9, 129.4, 129.5, 129.9, 130.6, 130.7, 130.8, 130.9, 131.0, 131.1, 131.3, 131.8, 132.0, 132.5 (CH), 133.1, 133.2, 133.3, 133.8, 134.0, 135.3, 135.7, 136.3, 136.7, 137.6, 139.8, 140.6, 143.6, 144.8, 146.0, 146.4, 147.2, 152.8, 153.4 (Cq), 165.1, 165.3, 165.6 (amide Cq); MALDI-TOF-MS: *m*/*z*: 1874.2 $[M]^+$; elemental analysis calcd (%) for $C_{123}H_{120}N_6O_8S_2 \cdot C_4H_8O_2$ (1874.5): C 77.72, H 6.57, N 4.28, S 3.26; found C 77.95,H 6.54,N 4.25,S 3.38.

General procedure for the synthesis of the bridged pretzelanes 5a–e: [2]Catenane **2** (100 mg, 0.05 mmol) and dibromide **3a–e** (0.05 mmol) were dissolved separately in dry DMF (50 mL). Both solutions were simultaneously added over a period of 2 h to a stirred suspension of potassium carbonate (25 mg, 0.18 mmol) in DMF (100 mL) at 50 °C. Stirring was continued for another three days. Dichloromethane (100 mL) was added and the solution extracted three times with water (70 mL). The organic layer was separated and dried over Na_2SO_4. The crude product was then purified by column chromatography (SiO_2, 63–100 μm, chloroform/acetone, 10:1).

General conditions for the enantioseparation of the ⟨*n*⟩pretzelanes 5a and 5c and the [2]catenane 2: Column: Chiralcel OD (25 × 0.46 cm i.d.); eluent: hexane/ethanol (**2, 5a, 5c** = 75:25); flow rate: 1.0 mL min^{-1}; 10 mL (5 mg mL^{-1}, CH_2Cl_2/methanol, 8:1).

⟨10⟩pretzelane 5a: R_f = 0.51; yield: 47% (51 mg, 0.025 mmol), white powder, m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.48 (s, 3H; CH_3), 0.69 (s, 3H; CH_3), 1.06 (s, 3H; CH_3), 1.15 (s, 3H; CH_3), 1.19 (s, 3H; CH_3), 1.24 (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 1.45 (s, 3H; CH_3), 1.61 (s, 6H; CH_3), 1.84 (s, 3H; CH_3), 2.05 (s, 3H; CH_3), 2.29 (s, 3H; CH_3), 2.47 (s, 3H; CH_3), 2.49 (s, 3H; CH_3), 2.55 (s, 3H; CH_3), 1.06–2.00 (m, 34H; CH_2), 2.12–2.78 (m, 16H; CH_2), 3.03 (m, 2H; CH_2), 3.26 (m, 2H; CH_2), 3.42 (m, 2H; CH_2), 3.71 (s, 3H; OCH_3), 3.93 (s, 3H; OCH_3), 4.02 (m, 2H; NCH_2), 4.17 (m, 2H; NCH_2), 5.59 (s, 1H; aryl), 6.30 (s, 1H; aryl), 6.53–8.55 (m, 28H; aryl), 7.44 (s, 1H; amide), 8.59 (s, 1H; amide), 8.84 (s, 1H; amide), 9.01 (s, 1H; amide), 9.27 (s, 1H; amide), 9.36 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 14.4, 15.9, 17.3, 18.1, 18.3, 19.1, 19.2, 19.3, 19.4, 19.6, 20.0, 20.8, 21.1, 23.2, 23.3, 23.8, 23.6, 23.5, 26.9, 31.4, 34.7, 36.0, 36.1, 36.4, 37.9, 40.4, 45.1, 45.3, 45.5, 48.4, 50.7, 53.0, 69.6, 70.4, 123.4, 124.0, 125.2, 125.8, 125.4, 125.3, 126.9, 127.4, 127.6, 127.9, 127.3, 128.4, 128.6, 128.9, 128.5, 129.1, 129.5, 130.5, 130.8, 132.3, 132.5, 132.7, 133.2, 133.4, 133.7, 133.9, 134.3, 134.5, 134.6, 134.7, 135.2, 135.6, 135.8, 135.9, 136.1, 136.4, 136.5, 136.6, 136.8, 136.9, 137.3, 138.7, 138.9, 139.3, 140.5, 142.7, 143.1, 144.3, 147.0, 147.4, 148.3, 151.8, 152.5, 153.0, 164.6, 165.1, 165.2, 165.3, 166.8, 171.0; MALDI-TOF-MS: *m*/*z*: 2080.7 $[M]^+$; FAB-MS: *m*/*z*: 2081.0 $[M+H]^+$; elemental analysis calcd (%) for $C_{130}H_{150}O_{12}N_8S_2 \cdot C_2H_2Cl_6$ (2080.8): C 68.35, H 6.60, N 4.83, S 2.76; found C 68.10, H 6.41, N 4.91, S 3.25.

⟨9⟩pretzelane 5b: R_f = 0.43; yield: 39% (42 mg, 0.02 mmol), white powder, m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.43 (s, 3H; CH_3), 0.74 (s, 3H; CH_3), 1.03 (s, 3H; CH_3), 1.11 (s, 3H; CH_3), 1.16 (s, 3H; CH_3), 1.19 (s, 3H; CH_3), 1.21 (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.62 (s, 6H; CH_3), 1.71 (s, 3H; CH_3), 1.86 (s, 3H; CH_3), 1.98 (s, 3H; CH_3), 2.13 (s, 3H; CH_3), 2.16 (s, 3H; CH_3), 2.53 (s, 3H; CH_3), 1.08–1.87 (m, 32H; CH_2), 2.01–2.57 (m, 16H; CH_2), 3.17 (m, 2H; CH_2), 3.25 (m, 2H; CH_2), 3.51 (m, 2H; CH_2), 3.59 (s, 3H; OCH_3), 3.89 (s, 3H; OCH_3), 3.93 (m, 2H; NCH_2), 4.05 (m, 2H; NCH_2), 5.42 (s, 1H; aryl), 6.18 (s, 1H; aryl), 6.58–8.57 (m, 28H; aryl), 7.41 (s, 1H; amide), 8.42 (s, 1H; amide), 8.63 (s, 1H; amide), 8.70 (s, 1H; amide), 9.20 (s, 1H; amide), 9.34 (s, 1H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 15.3, 17.3, 18.1, 18.2, 18.7, 18.7, 19.0, 19.1, 19.2, 19.4, 19.4, 19.6, 19.6, 19.8, 19.9, 20.6, 22.7, 22.7, 22.9, 23.6, 25.0, 25.6, 25.6, 26.2, 26.3, 26.3, 26.7, 26.9, 27.3, 27.9, 28.1, 28.3, 28.5, 28.7, 28.8, 29.0, 29.0, 29.2, 29.3, 29.7, 30.9, 32.5, 32.7, 34.0, 34.1, 35.3, 35.7, 36.2, 44.4, 44.7, 44.9, 45.1, 45.2, 47.3, 49.3, 53.0, 55.4, 55.8, 115.3, 116.7, 117.0, 117.4, 117.4, 117.6, 117.9, 118.0, 118.0, 118.2, 123.8, 124.0, 124.0, 124.4, 124.4, 124.5, 124.5, 125.3, 125.8, 126.2, 126.3, 126.9, 127.0, 127.4, 127.4, 127.5, 127.6, 127.8, 128.1, 128.1, 128.2, 128.2, 128.6, 128.7, 128.8, 129.1, 129.1, 130.3, 130.6, 130.6, 130.6, 130.7, 131.3, 131.4, 131.7, 131.8, 132.3, 132.8, 132.8, 133.2, 133.3, 134.0, 134.3, 134.5, 134.6, 134.7, 134.8, 134.9, 135.0, 135.2, 135.4, 135.7, 135.7, 135.8, 135.9, 135.9, 136.1, 136.1, 136.4, 136.5, 136.7, 136.9, 137.5, 139.0,150.4, 151.4, 160.5, 160.7, 161.2, 162.8, 162.9, 164.8, 164.9, 165.1, 165.8, 166.1, 166.3; MALDI-TOF-MS: *m*/*z*: 2066.3 $[M]^+$; FAB-MS: *m*/*z*: 2066.1 $[M]^+$ (calcd 2066.8).

⟨8⟩pretzelane 5c: R_f = 0.40; yield: 24% (26 mg, 0.013 mmol), white powder, m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.48 (s, 3H; CH_3), 0.79 (s, 3H; CH_3), 0.95 (s, 3H; CH_3), 1.06 (s, 3H; CH_3), 1.14 (s, 3H; CH_3), 1.19 (s, 3H; CH_3), 1.24 (s, 3H; CH_3), 1.40 (s, 3H; CH_3), 1.63 (s, 6H; CH_3), 1.86 (s, 3H; CH_3), 1.93 (s, 3H; CH_3), 2.03 (s, 3H; CH_3), 2.30 (s, 3H; CH_3), 2.39 (s, 3H; CH_3), 2.48 (s, 3H; CH_3), 0.85–1.89 (m, 32H; CH_2), 1.95–2.73 (m, 16H; CH_2), 3.13 (m, 2H; CH_2), 3.41 (m, 2H; CH_2), 3.63 (s, 3H; OCH_3), 3.94 (s, 3H; OCH_3), 4.08 (m, 2H; NCH_2), 4.25 (m, 2H; NCH_2), 5.24 (s, 1H; aryl), 6.20 (s, 1H; aryl), 6.52–8.41 (m, 28H; aryl), 7.87 (s, 1H; amide), 8.47 (s, 1H; amide), 8.62 (s, 1H; amide), 8.71 (s, 1H; amide), 9.22 (s, 1H; amide), 9.27 (s, 1H; amide); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 11.3, 14.4, 15.6, 17.7, 17.7, 18.6, 19.1, 19.3, 19.6, 19.7, 19.8, 20.0, 20.1, 20.2, 21.0, 23.2, 23.4, 24.1, 24.8, 25.9, 26.6, 26.7, 26.8, 26.9, 27.6, 28.1, 28.8, 28.9, 29.2, 29.3, 30.1, 30.7, 31.8, 34.0, 34.3, 35.0, 35.7, 36.0, 36.1, 36.6, 39.1, 40.4, 44.9, 45.1, 45.2, 48.0, 49.4, 52.3, 55.8, 56.2, 64.9, 68.5, 115.7, 117.5, 117.8, 117.9, 118.0, 118.6, 124.3, 124.7, 124.8, 125.9, 126.4, 126.7, 127.5, 127.6, 127.8, 127.9, 128.0, 128.3, 129.2, 129.4, 129.5, 130.9, 131.0, 131.1, 131.3, 131.6, 131.8, 131.9, 132.2, 132.6, 132.8, 132.9, 133.5, 133.7, 134.5, 134.9, 135.0, 135.2, 135.4, 135.5, 135.6, 135.8, 135.8, 136.0, 136.1, 136.1, 136.3, 136.3, 136.4, 136.5, 136.9, 137.7, 137.8, 139.3, 140.5, 142.6, 142.7, 144.3, 146.4, 147.0, 147.0, 147.5, 147.5, 147.8, 149.9, 151.7, 160.9, 161.2, 165.4, 165.6, 166.3, 166.7; MALDI-TOF-MS: *m*/*z* = 2052.7 $[M]^+$; FAB-MS: *m*/*z* = 2052.0 $[M]^+$; elemental analysis calcd (%) for $C_{128}H_{146}O_{12}N_8S_2 \cdot CH_2Cl_2$(2052.8): C 72.48, H 6.98, N 5.24, S 3.00; found C 72.56, H 7.17, N 5.08, S 3.38.

⟨7⟩pretzelane 5d: R_f = 0.39; yield: 6% (6 mg, 0.003 mmol), white powder, m.p. > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.47 (s, 3H; CH_3), 0.95 (s, 3H; CH_3), 1.04 (s, 3H; CH_3), 1.09 (s, 3H; CH_3), 1.20 (s, 3H; CH_3), 1.27 (s, 3H; CH_3), 1.46 (s, 3H; CH_3), 1.53 (s, 3H; CH_3), 1.60 (s, 6H; CH_3), 1.84 (s, 3H; CH_3), 2.04 (s, 3H; CH_3), 2.08 (s, 3H; CH_3), 2.38 (s, 3H; CH_3), 2.44 (s, 3H; CH_3), 2.46 (s, 3H; CH_3), 1.12–1.89 (m, 30H; CH_2), 1.93–2.69 (m, 16H; CH_2), 3.53 (m, 2H; CH_2), 3.63 (s, 3H; OCH_3), 3.75 (m, 2H; CH_2), 3.96 (s, 3H; OCH_3), 4.08 (m, 2H; NCH_2), 4.24 (m, 2H; NCH_2), 4.95 (s, 1H; aryl), 6.22 (s, 1H; aryl), 6.55–8.31 (m, 28H; aryl), 7.73 (s, 1H; amide), 8.53 (s, 1H; amide), 8.57 (s, 1H; amide), 8.69 (s, 1H; amide), 8.88 (s, 1H; amide), 9.24 (s, 1H; amide); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 14.4, 15.5, 17.1, 17.5, 17.6, 18.1, 18.6, 19.1, 19.5, 19.6, 20.0, 20.1, 20.2, 20.6, 20.8, 21.5, 23.4, 24.1, 24.8, 26.1, 26.7, 26.8, 27.1, 28.1, 29.0, 29.3, 30.0, 30.7, 31.8, 32.3, 34.3, 34.8, 35.3, 35.6, 35.7, 35.8, 36.1, 36.4, 36.6, 36.9, 37.8, 39.1, 39.5, 44.9, 45.0, 45.1, 45.2, 45.2, 45.4, 48.4, 48.7, 53.4, 53.7, 55.8, 56.0, 56.2, 58.9, 64.3, 64.9, 65.6, 67.1, 68.5, 70.0, 112.5, 115.5, 115.6, 115.7, 115.8, 116.7, 116.8, 117.0, 117.1, 117.2, 117.6, 117.7, 117.8, 118.0, 118.1, 118.6, 118.9, 126.9, 127.5, 127.6, 127.9, 128.0, 129.2, 129.5, 131.0, 131.3, 132.3, 132.8, 133.1, 134.4, 134.8, 135.4, 135.4, 135.6, 135.8, 136.1, 136.2, 136.2, 138.2, 140.4, 142.1, 142.4, 145.0, 146.6, 146.8, 160.9, 161.2, 163.1, 164.8, 165.4, 166.7; MALDI-TOF-MS: *m*/*z*: 2039.6 $[M+H]^+$ (calcd 2038.8).

⟨6⟩pretzelane 5e: R_f = 0.38; yield: 3% (3 mg, 0.002 mmol), white powder, m.p. > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.25 (s, 3H; CH_3), 0.72 (s, 3H; CH_3), 0.82 (s, 3H; CH_3), 1.15 (s, 3H; CH_3), 1.27 (s, 3H; CH_3), 1.36 (s, 3H; CH_3), 1.48 (s, 3H; CH_3), 1.59 (s, 6H; CH_3), 1.63 (s, 3H; CH_3), 2.07 (s, 3H; CH_3), 2.11 (s, 3H; CH_3), 2.24 (s, 3H; CH_3), 2.27 (s, 3H; CH_3), 2.35 (s, 3H; CH_3), 2.48 (s, 3H; CH_3), 1.08–1.98 (m, 28H; CH_2), 2.01–2.55 (m, 16H; CH_2), 2.70 (m, 2H; CH_2), 2.92 (m, 2H; CH_2), 3.63 (m, 2H; CH_2), 3.77 (s, 3H; OCH_3), 3.95 (s, 3H; OCH_3), 4.00 (m, 2H; NCH_2), 4.12 (m, 2H; NCH_2), 6.62 (s, 1H; aryl), 6.69 (s, 1H; aryl), 6.71–8.32 (m, 28H; aryl), 7.71 (s, 1H; amide), 7.78 (s, 1H; amide), 8.02 (s, 1H; amide), 8.20 (s, 1H; amide), 9.05 (s, 1H; amide), 9.34 (s, 1H; amide); MALDI-TOF-MS: *m*/*z*: 2039.6 $[M+H]^+$ (calcd 2038.8).

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[13] In a ⟨*n*⟩pretzelane the two mechanically bound macrocycles of a catenane are connected covalently. This leads to molecules with a topology of a pretzel, which we call "pretzelane".

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[15] ⟨*n*⟩ describes the number of methylene groups in the bridge of the pretzelane or the [1]rotaxane. This prefix was used by us formally in the field of ⟨*n*⟩phanes, ⟨*n*⟩beltanes and ⟨*n*⟩tubes to define the number of benzene and arene units; see: W. Boomgaarden, F. Vögtle, M. Nieger, H. Hupfer, *Chem. Eur. J.* **1999**, *5*, 345 – 355.

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