Chiral Dendrophanes, Dendro[2]rotaxanes, and Dendro[2]catenanes: Synthesis and Chiroptical Phenomena

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New chiral dendrimers with planar-chiral, cycloenantiomeric and topologically chiral cores were prepared in yields of up to 90% starting from a racemic 4-hydroxy[2.2]paracyclophane, a [2]rotaxane with sulfonamide groups in the wheel and axle positions and [2]catenane with a sulfonamide group in both of its macrocycles. The separation of the racemic mixture of these dendrimers was possible by HPLC on chiral stationary phases. The CD spectra of the dendro[2.2]phanes showed a hitherto unknown influence of the dendritic part on the intensities of the Cotton effects. The chirality of these dendrimers is dependent not only on its chiral elements but also on its dendritic wedges and their generation.

Introduction

New chiral dendrimers based on planar-chiral, cycloenantiomeric, and topologically chiral cores are reported. The enantioseparation and the investigation of the chiroptical properties of these molecules showed a hitherto unknown relationship between the intensities of the Cotton effects and the generation of the dendrimers: the intensities increase with increasing generation.

In recent years, the synthesis of dendritic molecules in general and the investigation of the chiroptical properties of chiral dendrimers in particular have received much attention.[1] Numerous works have been published that demonstrate the varied ways in which chiral moieties can be introduced into a dendrimer. Mostly substances from the pool of optically active natural compounds have been used as chiral moieties, such as amino acids and carbohydrates. Before one can employ dendrimers as chiral catalysts in asymmetric synthesis,[2] as chiral chromatography materials or for similar applications, the relationship between the molecular chirality of the dendritic building blocks and the macroscopic chirality of the compound should be known. The stereogenic information of these dendrimers is mainly located either at the core or the periphery of dendritic molecules.[3] This chiral information is based on stereogenic centres incorporated into the structure of the dendrimers. In contrast, examples of chiral dendrimers based on axial-[4] or planar-chiral[5] architectures are rare. In 1996 the first polyamine dendrimers with planar-chiral [2.2]paracyclophane units at their periphery were synthesised.[5] The investigation of the chiroptical properties of different generations of this type of dendrimer revealed no significant difference between their circular dichrograms. Two questions arose: What would be the consequences of the introduction of different elements of chirality in the dendrimer and how would the chiroptical properties change along with higher generations? In 1977 Mislow coined the terms ''cryptochirality'' or ''accidental degeneracy''.[6] Both terms are used to describe the lack of any detectable optical rotation from enantiomerically pure molecules. In 1998 Meijer presented the synthesis and characterisation of the first examples of enantiomerically pure dendrimers with Euclidean cryptochirality in the centre of the dendrimer.[7] Using the triol derivative, *S*-(+)-2,2-dimethyl-1,3-dioxolane-4-methanol as the chiral starting material the dendrimer **1** was synthesised (Figure 1). No optical activity was found for **1** with circular dichroism in combination with ultraviolet and optical rotatory dispersion measurements, which were performed to gain information on the optical activity of this dendrimer.

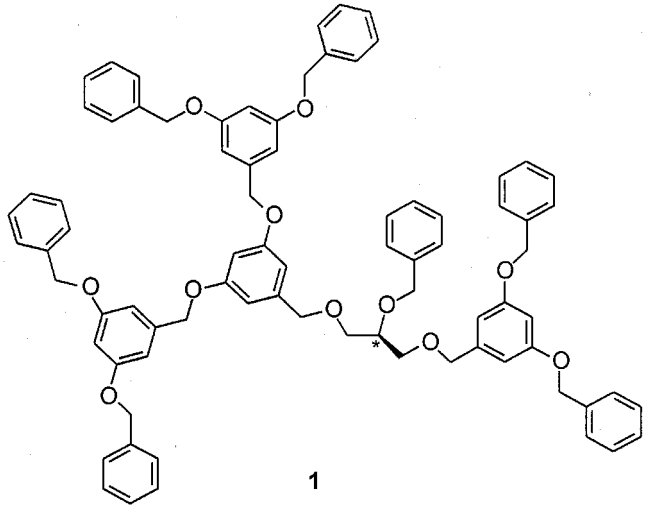

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Figure 1. Cryptochiral dendrimer **1** synthesised by Meijer et. al

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Here, we investigate the influences of the incorporation of planar-chiral [2.2]paracyclophanes, cycloenantiomerically chiral [2]rotaxanes and topologically chiral [2]catenanes as dendritic cores into Frechet-, and Chow-type dendrimers on the chiroptical properties. In contrast to already characterised planar-chiral [2.2]paracyclophanes with different substituents at one of their arene units,[8] cycloenantiomerically chiral [2]rotaxanes[9] and topologically chiral [2]catenanes,[9] the new dendro[2.2]phanes **2**, dendro[2]rotaxanes **3,** and dendro[2]catenanes **4** with a sterically demanding periphery which increases with the generation of the dendrons, and, in addition, provides more and more chromophores which might lead to dendritic effects such as cryptochirality (Figure 2).

The structural differences of **2**, **3**, and **4** opened up the question of how pronounced are the changes in both the enantiomeric resolution constants and the chiroptical properties with the variation of the generation of the dendritic molecule.

Results and Discussion

Synthesis of the Dendro[2.2]phanes 2

The planar-chiral dendro[2.2]paracyclophanes **2a−e** were prepared by potassium carbonate-mediated substitution of the Frechet-type dendritic bromides **6a−d** and the Chow-type dendritic bromide **6e** with a racemic mixture of the 4-

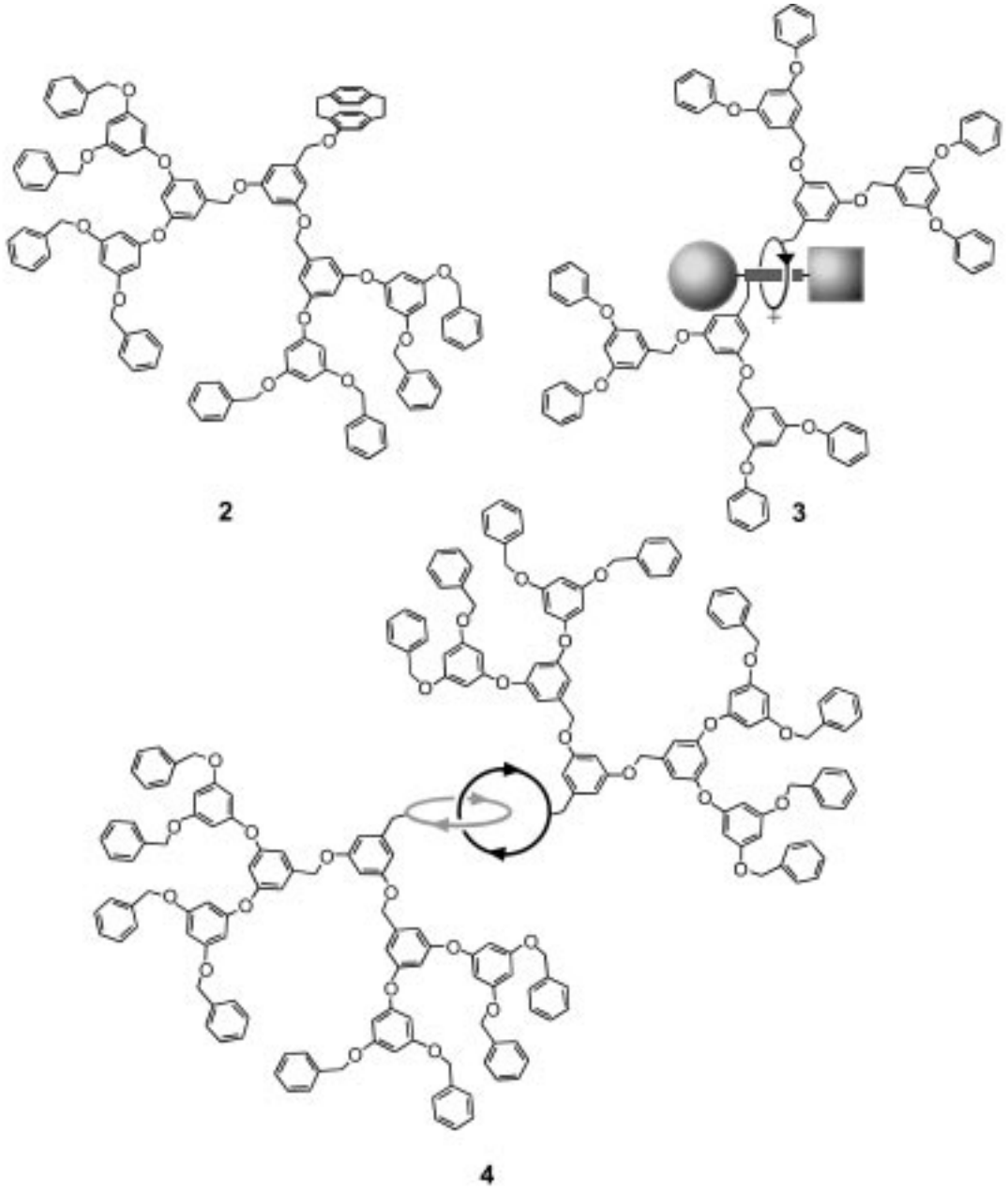
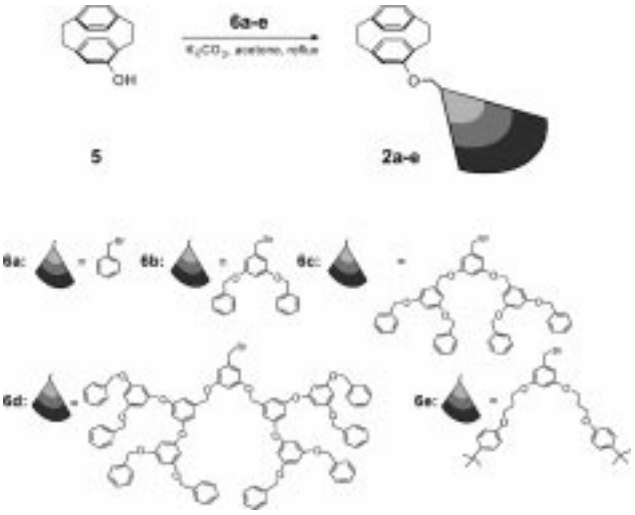


Figure 2. Dendrophane **2**, dendro[2]rotaxane **3**, and dendro[2]catenane **4**

hydroxy[2.2]paracyclophane **5** in refluxing acetone (Scheme 1). Yields of **2a−e** of up to 90% were obtained (Table 1). The larger sterical requirements of the dendrons seem to have no significant effect on the substitution reaction.



Scheme 1. Synthesis of the dendrophanes **2a−e**

Table 1. Yields of the dendro[2.2]phanes **2a−e**

Dendrophane	Yield [%]
2a	84
2b	90
2c	63
2d	70
2e	87

Synthesis of the Dendro[2]rotaxanes 3

The dendro[2]rotaxanes **3a−c,** with the cycloenantiomeric [2]rotaxane **7** as the core, were prepared by a chemoselective substitution of the Frechet-type dendritic bromides **6a−c** by the sulfonamide groups in both the axle and the wheel of racemic **7** in the presence of potassium carbonate in DMF at room temperature (Scheme 2).

The yields turned out to be remarkably high (54−92%) in most cases. Substitution with the sterically more demanding second generation dendryl unit **6c** yielded **3c** in 54% yield. Although this yield is somewhat lower than the others, the extension of the dendryl residues did not have a significant effect (see Table 2). Side products were identified as the monosubstituted [2]rotaxanes.[10]

Synthesis of the Dendro[2]catenanes 4

The dendro[2]catenanes **4b−d,** with the topologically chiral [2]catenane **8** as the core, were prepared by chemoselective substitution of the Frechet-type dendritic bromides **6b−d** with the sulfonamide groups in both macrocycles of racemic **8** in the presence of potassium carbonate in DMF at room temperature (Scheme 3).

Similar to the yields of the dendro[2]rotaxanes **3**, the yields of **4b−d** turned out to be high (73−81%) in most cases. Substitution with the sterically more demanding third generation dendryl unit **6d** yielded **4d** in 81% yield. Again, the extension of the dendryls did not have a significant effect (Table 3). In this case the side products were identified as the monosubstituted- and trisubstituted [2]catenanes.[10]

Enantioseparation and Chiroptical Properties of 2a−e, 3a−c and 4b−d

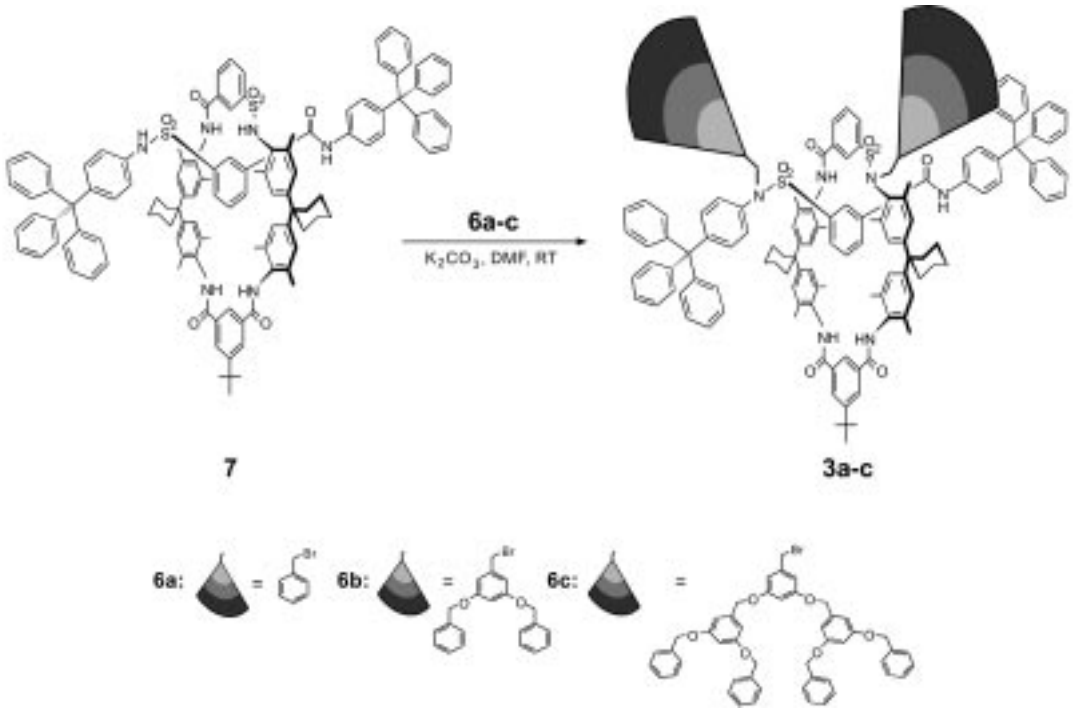
The baseline separation of the racemic mixtures of **2a−e** into their cycloenantiomers was possible by HPLC on a ''Chiralpak AD'' column with *n*-hexane/2-propanol.[11] The separation factors α of **2a−e** increase with increasing generation of the dendrimer and were found to range between 1.30−1.97 (Table 4).

The enantioresolution of **3a,b** was also possible with baseline separation by HPLC on a ''Chiralcel OD'' column with *n*-hexane/ethanol (Table 4). The separation factors α are 2.40 (**3a**) and 4.92 (**3b**). The enantioresolution of **3c** could not be accomplished, either on ''Chiralcel OD'' or on ''Chiralpak AD''.[11]

A baseline separation of the racemic mixture of **4b−d** could be achieved by HPLC on a chemically bonded ''Chiralpak AD'' column with *n*-hexane/chloroform/2-propanol (60:40:1). The separation factors are somewhat lower than with the other dendromolecules **2**, **3** and range between α = 1.36−2.07 (Table 4).

The Cotton effects obtained for each pair of enantiomers of **2a−c,e** are mirror images over the entire spectra in all cases. The CD spectra of the dendro[2.2]paracyclophanes **2a−c,e** in the range of 200−350 nm reach six distinct extrema in the aromatic region (Figure 3, Table 4). It was not possible to obtain CD spectra for **2d** because of its low solubility in all solvents tested. In marked contrast to our expectation of cryptochiral effects, the location of the extrema in all the CD spectra are near to identical for all the dendrimers, but they differ in the intensity of their Cotton effects. A comparison of **2a−c,e** at the extremum at 310 nm shows the intensity of the molar CD to increase linearly with higher generation, whereas the intensities of the absorption in the corresponding UV spectra are almost at the same level.[12] The increased chirality of the dendrimers of higher generation such as **2c** and **2e** cannot be due to the increased number of chromophoric groups incorporated in the dendrimer, because they are not chiral themselves.

The circular dichrograms of the dendro[2]rotaxanes **3a,b** show remarkably high molar CDs up to 236 $M^{-1}cm^{-1}$ which reach three distinct extrema in the aromatic region, whereas the enantiomers of the unsubstituted [2]rotaxane have only two extrema (Figure 3, Table 5). The location of the extrema in the CD spectra of the cycloenantiomers of **3a** differ from those of **3b**. The intensities of the first extremum at 216 nm (**3a**) and 181 nm (**3b**) differ by at least a factor of two whereas the other extrema remain at the same level. Obviously, the chiroptical properties of the cycloenantiomerically chiral [2]rotaxane **8** are not significantly influenced by the generation number of the dendritic sub-



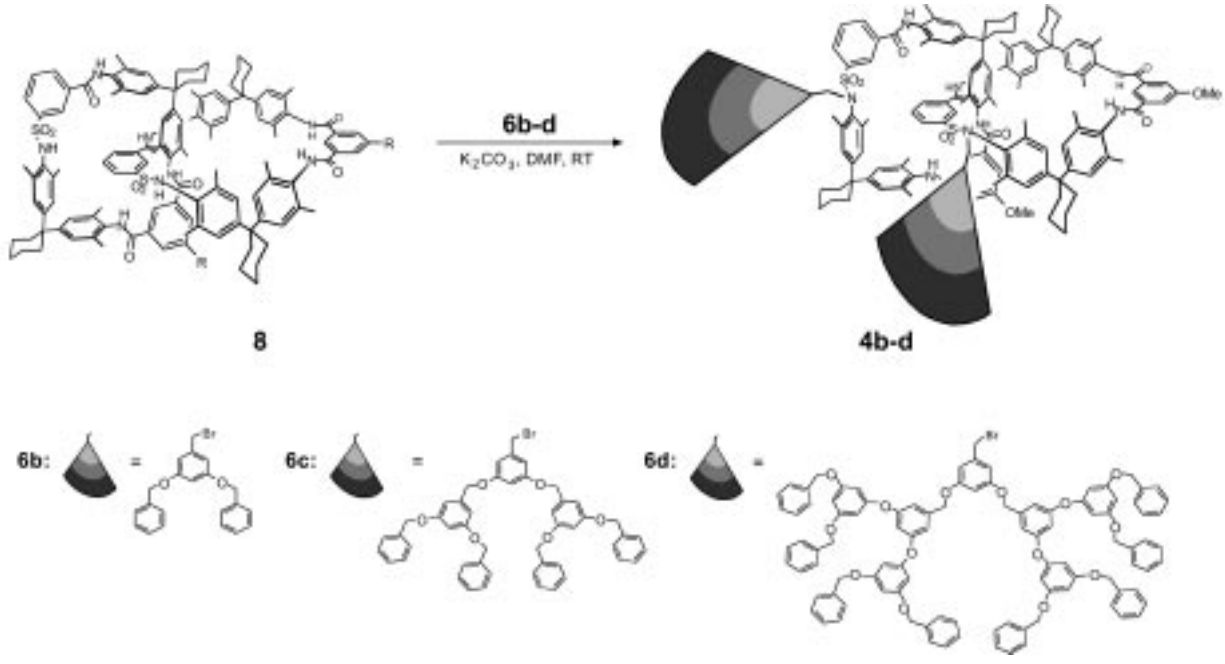
Scheme 2. Synthesis of the dendro[2]rotaxanes **3a−c**

Table 2. Yields of the Dendro[2]rotaxanes **3a−c**.

Rotaxane	Yield [%]
3a	64
3b	92
3c	54

Table 3. Yields of the Dendro[2]catenanes **4b−d**

Catenane	Yield [%]
4b	73
4c	79
4d	81



Scheme 3. Synthesis of the dendro[2]catenanes **4b−d**

Table 4. Separation factors α of **2a−e, 3a,b, 4b−d**

	α	Eluent[a]		α	Eluent[b]		α	Eluent[c]
2a	1.30	99:1[d]	**3a**	2.40	80:20			
2b	1.85	95:5	**3b**	4.92	75:25	**4b**	1.46	60:40:1
2c	1.31	75:25				**4c**	1.36	60:40:1
2d	1.89	96:4				**4e**	2.07	60:40:1
2e	1.97	95:5						

[a] (*n*-Hexane/2-propanol). − [b] (*n*-Hexane/ethanol). − [c] (*n*-Hexane/chloroform/2-propanol). − [d] The enantioseparation was undertaken at 0 °C.

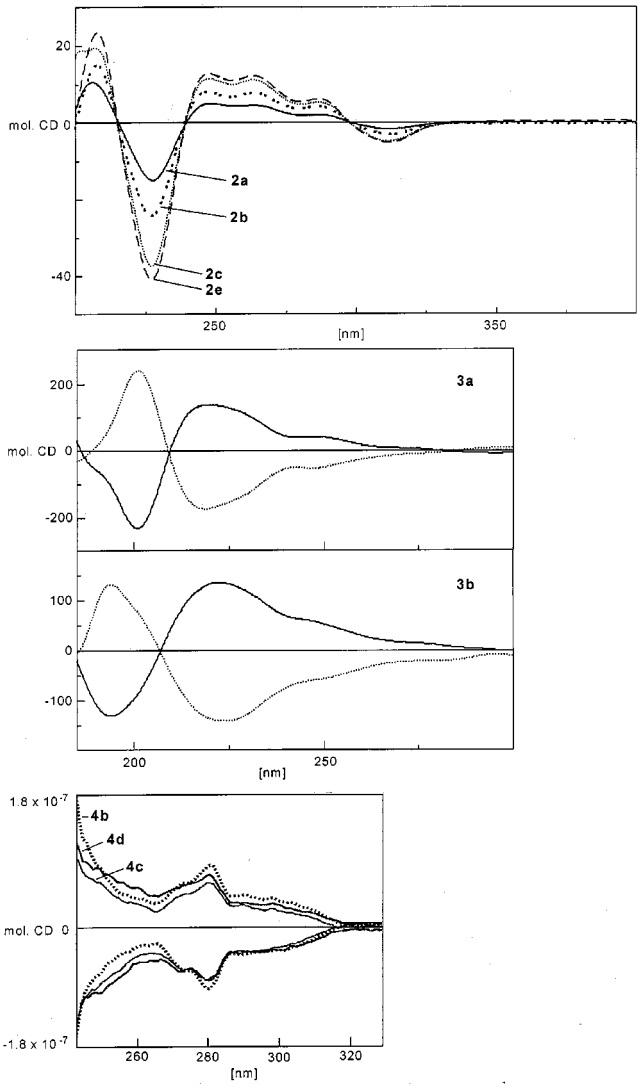


Figure 3. CD spectra of the dendrophanes **2a−c**,**e**, dendro[2]rotaxanes **3a**,**b** and dendro[2]catenanes **4b−d**

stituents in the CD spectra. The intensities of both dendro[2]rotaxanes **3a,b** are much higher than those of **8**.[9g] Again, we could not detect the expected decrease in the optical rotation of enantiomerically pure **3a,b** (Table 6).

The low solubility of **4b−d** in all the solvents tested restricted the measurement of CD spectra to THF. Therefore, we could just detect the very weak Cotton effects at wavelengths higher than 260 nm (Figure 3). A comparison of the

Table 5. Location [nm] and intensity [$M^{-1}cm^{-1}$] of the CD bands of **2a−c,e**

	208 nm	227 nm	247 nm	263 nm	285 nm	310 nm
2a	+11	−15	+5	+4	+2	−2
2b	+15	−24	+8	+7	+4	−3
2c	+19	−37	+11	+11	+5	−5
2e	+23	−43	+13	+12	+6	−5

Table 6. Location [nm] and intensity [$M^{-1}cm^{-1}$] of the CD bands of **7** and **3a,b**

	Extrema wavelength (intensity) [nm ($M^{-1}cm^{-1}$)]		
	1st	2nd	3rd
7	203/(114)	235/(34)	−
3a	216/(236)	224/(137)	263/(42)
3b	181/(139)	238/(135)	265/(61)

molar CD at the extremum at 283 nm of each dendro[2]catenane **4b−d** does not reveal any significant effect of the number of generations on the chiroptical properties of **4b−d**.

The pure enantiomers of the new chiral dendrimers with planar-chiral, cycloenantiomerically or topologically chiral cores presented here exhibit new dendritic effects − an increase in chirality with higher generations of dendritic molecules − in some cases. It has been shown that the chiroptical properties of dendrimers are dependent not only on their chiral core but also on the generation of the dendritic substituents. In the case of the dendro[2]rotaxanes and dendro[2]catenanes we interpret the changes in intensity, as well as the slight shift of the CD bands as the dendrimer generation increases, to be due to conformational changes in the structure of the chiral core. As generation size increases, the wheel of the rotaxane in **3** changes its position on its axle and the two macrocycles of the catenane in **4** change their position relative to each other. In the case of the dendrophanes **2** it is difficult to explain the results by a conformational change of the chiral core. Remarkably, the CD spectra of **2** only differ in their intensity and not in the wavelength of their absorption extrema. This suggests that a single chiral subunit can impart conformational orders in a more distant part of the molecule. These results contribute to the understanding of planar-chirality and cycloenantiomerism incorporated into the core of chiral dendrimers.

Experimental Section

General Remarks: All solvents were distilled prior to use and all other chemicals were of the best commercial quality available and used as received. The 4-hydroxy[2.2]paracyclophane **5**,[13] [2]rotaxane **7**[14] and [2]catenane **8**[15] were prepared as reported previously. Elemental analysis: Analytical facilities of the Kekule-Institut für Organische Chemie und Biochemie of the University of Bonn. FAB-MS: Concept 1H Kratos Analytical Ltd. Manchester, Great Britain, Matrix: *m*-nitrobenzoyl alcohol. MALDI-TOF: MALDI-TofSpecE, Micromass, Manchester, Great Britain, Matrix: 9-nitro-

anthracene or 2,5-dihydroxybenzoic acid. ^{1}H, ^{13}C NMR: AM 400 MHz, or DRX 500 MHz, Bruker, Analytische Meßtechnik GmbH, Karlsruhe, Germany. CD-Spectrometer: JASCO, J-720 Spectrometer, Labor- und Datentechnik GmbH, Groß-Umstadt, Germany.

General Procedure for the Synthesis of Dendritic [2.2]Paracyclophanes 2a−e: A mixture of 4-hydroxy[2.2]paracyclophane **5** (200 mg, 0.89 mmol), the appropriate dendritic benzyl bromide **6** (0.50 mmol), dried potassium carbonate (215 mg, 1.50 mmol) and 18-crown-6 (20 mg, 0.07 mmol) in 100 mL dry acetone was heated at reflux and stirred under argon for 48 h. After cooling, the mixture was filtered and the solid was washed twice with CH_2Cl_2 (100 mL each). The solvent was then removed from the combined organic layers under reduced pressure. The residue was submitted to column chromatographic purification on silica gel (SiO_2, 63−100 μm).

4-Benzyloxy[2.2]paracyclophane (2a): Colourless solid, m.p. 139 °C, R_f = 0.50 (dichloromethane/*n*-hexane 1:2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61−2.68 (m, 1 H, CH_2), 2.99−3.17 (m, 6 H, CH_2), 3.51−3.57 (m, 1 H, CH_2), 4.78 (d, ^2J = 11.5 Hz, 1 H, OCH_2), 5.02 (d, ^2J = 11.5 Hz, 1 H, OCH_2), 5.78 (s, 1 H, ArH), 6.31 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 1 H, ArH), 6.41 (dd, ^4J = 1.6, ^3J = 7.6 Hz, 1 H, ArH), 6.47 (d, ^3J = 7.6 Hz, 2 H, ArH), 6.54 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 1 H, ArH), 6.81 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 1 H, ArH), 7.38−7.55 (m, 5 H, PhH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.7, 34.1, 35.3, 35.4 (CH_2), 68.7 (OCH_2), 117.7, 124.7, 127.2, 127.8, 128.4, 128.6 (CH), 128.8 (Cq), 131.4, 133.1, 133.6, 135.0 (CH), 137.5, 138.7, 140.1, 142.0, 156.7 (Cq). − GC MS: *m/z* (%) = 314 (100) [M^+], 223 (89) [$M^+ - C_7H_7$], 91 [$C_7H_7^+$], 77 (5) [$C_6H_5^+$], 51 (4) [$C_4H_3^+$], t_R = 11.5 min. − $C_{23}H_{22}O$ (314.43): calcd. C 87.85, H 7.05, O 5.09; found C 87.86, H 7.05, O 5.09.

4-[3′,5′-Bis(benzyloxy)benzyloxy][2.2]paracyclophane (2b): Colourless solid, R_f = 0.90 (dichloromethane/*n*-hexane 3:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.58−2.65 (m, 1 H, CH_2), 2.97−3.11 (m, 6 H, CH_2), 3.20−3.51 (m, 1 H, CH_2), 4.70 (d, ^2J = 11.7 Hz, 1 H, OCH_2), 4.93 (d, ^2J = 11.7 Hz, 1 H, OCH_2), 5.10 (s, 4 H, OCH_2), 5.73 (s, 1 H, ArH), 6.29 (dd, ^4J = 1.2 Hz, ^3J = 7.4 Hz, 1 H, ArH), 6.37 (dd, ^4J = 1.2 Hz, ^3J = 7.7 Hz, 1 H, ArH), 6.44 (d, ^3J = 7.4 Hz, 2 H, ArH), 6.52 (dd, ^4J = 1.5 Hz, ^3J = 7.7 Hz, 1 H, ArH), 6.63 (t, ^4J = 2.1 Hz, 1 H, ArH), 6.75 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 1 H, ArH), 6.79 (d, ^4J = 2.1 Hz, 2 H, ArH), 7.31−7.47 (m, 10 H, ArH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.7, 34.1, 35.3, 35.4 (CH_2), 68.6, 70.2 (OCH_2), 101.4, 106.2, 117.7, 124.7, 127.6, 128.1, 128.3 (CH), 128.4, 128.5 (Cq), 128.7, 131.4, 133.0, 133.6, 135.0 (CH), 136.9, 138.7, 139.9, 140.1, 142.0, 156.6, 160.2 (Cq). − $C_{37}H_{34}O_3$ (526.67): calcd. C 84.37, H 6.51, O 9.11; found C 84.38, H 6.51, O 9.11.

4-[3′,5′-Bis[3′′,5′′-bis(benzyloxy)benzyloxy]benzyloxy][2.2]-paracyclophane (2c): Colourless solid, R_f = 0.54 (dichloromethane/*n*-hexane 3:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.58−2.64 (m, 1 H, CH_2), 3.00−3.10 (m, 6 H, CH_2), 3.44−3.51 (m, 1 H, CH_2), 4.70 (d, ^2J = 11.7 Hz, 1 H, OCH_2), 4.93 (d, ^2J = 11.7 Hz, 1 H, OCH_2), 5.05 (s, 12 H, OCH_2), 5.72 (s, 1 H, ArH), 6.28 (dd, ^4J = 1.4 Hz, ^3J = 7.8 Hz, 1 H, ArH), 6.38 (dd, ^4J = 1.9 Hz, ^3J = 8.0 Hz, 1 H, ArH), 6.42 (d, ^3J = 7.6 Hz, 2 H, ArH), 6.52 (dd, ^4J = 1.9 Hz, ^3J = 7.6 Hz, 1 H, ArH), 6.59 (d, ^4J = 1.6, 2 H, ArH), 6.71 (m, ^4J = 1.8 Hz, 6 H, ArH), 6.76 (d, ^4J = 1.8, 2 H, ArH), 7.30−7.41 (m, 20 H, PhH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.7, 34.1, 35.2, 35.3 (CH_2), 68.6, 70.0, 70.1 (OCH_2), 101.4, 101.6, 106.2, 106.3, 117.7, 124.7, 127.6, 127.8, 128.0, 128.4, 128.6, 131.4, 133.0, 133.6, 134.9, 136.8, 138.7, 139.3, 139.9, 140.1, 141.9, 156.6, 160.0, 160.2. − MALDI TOF MS: *m/z* (%) = 974.2 [M + Na]$^+$, 990.2 [M + K]$^+$. − $C_{65}H_{58}O_7$ (951.16).

4-[3′,5′-Bis[3′′,5′′-bis[3′′′,5′′′-bis(benzyloxy)benzyloxy]benzyloxy]-benzyloxy][2.2]paracyclophane (2d): Colourless solid, R_f = 0.68 (dichloromethane/*n*-hexane 7:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54−2.62 (m, 1 H, CH_2), 2.97−3.04 (m, 6 H, CH_2), 3.42−3.49 (m, 1 H, CH_2), 4.67 (d, ^2J = 11.7 Hz, 1 H, OCH_2), 4.90 (d, ^2J = 11.7 Hz, 1 H, OCH_2), 4.95 (s, 12 H, OCH_2), 5.00 (s, 16 H, OCH_2), 5.69 (s, 1 H, ArH), 6.26 (dd, ^4J = 1.4 Hz, ^3J = 7.8 Hz, 1 H, ArH), 6.34 (dd, ^4J = 1.9 Hz, ^3J = 8.0 Hz, 1 H, ArH), 6.39 (d, ^3J = 7.6 Hz, 2 H, ArH), 6.49 (dd, ^4J = 1.9 Hz, ^3J = 7.6 Hz, 1 H, ArH), 6.54−6.71 (m, 20 H, ArH), 6.75 (d, ^4J = 1.8, 2 H, ArH), 7.28−7.41(m, 40 H, PhH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.8, 34.3, 35.3, 35.4 (CH_2), 68.8, 70.1, 70.2 (OCH_2), 101.5, 101.7, 106.3, 106.5, 117.8, 124.8, 127.6, 127.8, 128.1, 128.5, 128.7, 131.5, 133.1, 133.6, 135.0, 136.9, 138.8, 139.3, 139.4, 140.1, 160.1, 160.2, 160.3. − MALDI TOF MS: *m/z* (%) = 1823.4 [M + Na]$^+$, 1839.2 [M + K]$^+$. − $C_{121}H_{106}O_{15}$ (1800.16).

4-[3′,5′-Bis[3′′-(4′′′-*tert*-butylphenyloxy)propane-1′-yloxy]-benzyloxy][2.2]paracyclophane (2e): Colourless solid, R_f = 0.80 (dichloromethane/*n*-hexane 3:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 [s, 18 H, ($C(CH_3)_3$)], 2.31 (m, 4 H, $CH_2CH_2CH_2$), 2.65−2.72 (m, 1 H, CH_2), 3.03−3.18 (m, 6 H, CH_2), 3.56−3.62 (m, 1 H, CH_2), 4.22 (m, 8 H, CH_2O), 4.74 (d, ^2J = 11.7 Hz, 1 H, OCH_2Ar), 4.98 (d, ^2J = 11.7 Hz, 1 H, OCH_2Ar), 5.79 (s, 1 H, ArH), 6.33 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 1 H, ArH), 6.43 (dd, ^4J = 1.6, ^3J = 7.6 Hz, 1 H, ArH), 6.49 (d, ^3J = 7.6 Hz, 2 H, ArH), 6.52 (t, ^4J = 2.0 Hz, 1 H, ArH), 6.58 (dd, ^4J = 1.6 Hz, ^4J = 7.6 Hz, 1 H, ArH), 6.75 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.84 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 1 H, ArH), 6.93 (d, ^3J = 8.9 Hz, 4 H, ArH), 7.38 (d, ^3J = 8.9 Hz, 4 H, ArH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.4, 31.6 (CH_2), 31.8 (CH_3), 34.1 [$C(CH_3)_3$], 34.2, 35.3, 35.4 (CH_2), 64.4, 64.7, 68.7 (OCH_2), 100.6, 105.8, 114.0, 117.8, 124.7, 126.3 (CH), 127.9 (Cq), 128.5, 131.5, 133.1, 133.6, 135.0 (CH), 138.8, 139.9, 140.2, 141.9, 143.5, 156.7, 160.3 (Cq). − MALDI TOF MS: *m/z* (%) = 727.3 [M + H]$^+$, 749.3 [M + Na]$^+$, 765.4 [M + K]$^+$. − $C_{49}H_{58}O_5$ (726.99).

General Procedure for the Synthesis of the Dendro[2]rotaxanes 3a−c: [2]Rotaxane **7** (100 mg, 0.05 mmol) and the appropriate dendritic benzyl bromide **6a−c** (0.05 mmol) were each dissolved in dry DMF (50 mL). At room temperature 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 3 days. After the addition of trichloromethane (100 mL) the solution was extracted three times with water (70 mL each). 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).

[2][*N*′,7′-(benzyl){*N*-[4-(triphenylmethyl)phenyl]-3-{[4-(triphenylmethyl)phenyl]amino}sulfonyl}benzamide]-[29′-*tert*-butyl-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro{cyclohexane-1,2′-[7,15,25,33]tetraaza[8]thiaheptacyclo [32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1′′-cyclohexane]-8′,14′,32′-trione}rotaxane (3a): Colourless solid, m.p. 219 °C, R_f = 0.62 (dichloromethane/ethyl acetate 30:1). − ^{1}H NMR (400 MHz, [D_7]DMF): δ = 1.11 (s, 6 H, CH_3), 1.29 (s, 9 H, CCH_3), 1.58 (s, 6 H, CH_3), 1.67 (br, 8 H, cyh), 2.00 (s, 4 H, cyh), 2.11 (s, 6 H, CH_3), 2.20 (s, 6 H, CH_3), 2.32 (s, 4 H, cyh), 2.53 (s, 4 H, cyh), 4.28−4.80 (m, 4 H, NCH_2), 6.42 (d, ^3J = 6.1 Hz, 2 H, benzyl), 6.52 (s, 1 H, sb), 6.89−7.50 (signal group, 55 H, aryl, sb, stop), 7.95 (dd, ^3J =

7.8 Hz, ^3J = 7.8 Hz, 1 H, sb), 8.04 (d, ^3J = 6.1 Hz, 2 H, aryl), 8.13 (s, 1 H, *t*bi), 8.19 (s, 1 H, sb), 8.23 (s, 1 H, *t*bi), 8.36 (s, 1 H, *t*bi), 8.52 (d, ^3J = 7.8 Hz, 1 H, sb), 8.61 (d, ^3J = 7.8 Hz, 1 H, sb), 8.99 (s, 1 H, NH), 9.20 (s, 1 H, NH), 9.32 (s, 1 H, NH), 10.43 (s, 1 H, NH). − ^{13}C NMR (100.6 MHz, [D$_7$]DMF): δ = 18.0, 18.1, 18.4, 18.9 (CH_3), 22.7, 22.9, 22.9, 26.0, 26.2, 33.6, 34.7, 35.7, 37.4 (CH_2), 44.8, 44.9 (Cq), 53.5, 53.9 (NCH_2), 64.5, 64.6 (Cq), 122.5, 123.4, 125.5, 125.8, 126.0, 126.2, 126.3, 127.0, 127.3, 127.5, 127.7, 127.8, 127.9, 128.0, 128.3, 129.8, 129.9, 130.0, 130.2, 130.3, 130.7, 130.9, 131.1, 131.2, 131.3 (CH), 131.3, 131.5, 131.9, 132.7, 133.7, 133.9, 134.2, 134.7, 134.9, 135.0, 135.2, 136.0, 136.6, 139.8, 142.5, 144.5, 146.0, 146.3, 146.6, 147.3, 148.4, 149.8, 153.1 (Cq), 163.8, 163.9, 164.4, 166.7 (CON). − FAB MS: *m/z* (%) = 2015.0 [M + H]$^+$. − $C_{134}H_{128}N_6O_8S_2$ (2014.66).

[2][*N*′,7′-(3,5-bis(benzyloxy)benzyl){*N*-[4-(triphenylmethyl)phenyl]-3-{[4-(triphenylmethyl)phenyl]amino}sulfonyl}benzamide]-[29′-*tert*-butyl-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro-{cyclohexane-1,2′-[7,15,25,33]tetraaza[8]thiaheptacyclo [32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1.^{9,13}.1^{27,31}]hexatetraconta-[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene20′,1′′-cyclohexane]-8′,14′,32′-trione}rotaxane (3b): Colourless solid, m.p. 169 °C, R_f = 0.57 (dichloromethane/ethyl acetate 30:1). − ^{1}H NMR (400 MHz, [D$_7$]DMF): δ = 1.09 (s, 6 H, CH_3), 1.27 (s, 9 H, CCH_3), 1.54 (br, 8 H, cyh), 1.62 (s, 6 H, CH_3), 2.18 (br, 16 H, cyh, CH_3), 2.31 (s, 4 H, cyh), 2.52 (s, 4 H, cyh), 4.89 (d, ^2J = 11.7 Hz, 2 H, NCH_2), 4.94 (d, ^2J = 11.7 Hz, 2 H, NCH_2), 5.09 (s, 4 H, OCH_2), 6.28 (s, 3 H, aryl), 6.43 (s, 4 H, OCH_2), 6.61 (s, 2 H, aryl), 6.68 (s, 2 H, aryl), 6.79−7.18 (signal group, 16 H, aryl, sb), 7.18−7.60 (signal group, 52 aryl, sb, stop), 7.95 (dd, ^3J = 7.7 Hz, ^3J = 7.8 Hz, 1 H, sb), 8.09 (s, 1 H, *t*bi), 8.17 (s, 1 H, *t*bi), 8.19 (s, 1 H, sb), 8.04 (d, ^3J = 6.1 Hz, 1 H, benzyl), 8.31 (s, 1 H, *t*bi), 8.53 (d, ^3J = 7.7 Hz, 1 H, sb), 8.62 (d, ^3J = 6.1 Hz, 1 H, benzyl), 9.01 (s, 1 H, NH), 9.20 (s, 1 H, NH), 9.39 (s, 1 H, NH), 10.42 (s, 1 H, NH). − ^{13}C NMR (100.6 MHz, [D$_7$]DMF): δ = 18.0, 18.7, 19.1, 19.7 (CH_3), 22.1, 22.3, 22.3, 25.3, 25.6, 33.2, 34.1 (CH_2), 29.9 (Cq), 44.2, 44.4 (Cq), 53.0, 53.2 (NCH_2), 63.9, 64.0 (Cq), 69.0, 69.1 (OCH_2), 100.4, 101.2, 104.7, 106.3, 108.7, 121.9, 123.0, 124.9, 125.6, 125.7, 126.4, 126.5, 127.0, 127.1, 127.2, 127.3, 127.4, 127.8, 127.9, 129.3, 129.4, 129.7, 130.1 (CH), 130.4, 130.6, 130.8, 130.9, 131.3, 132.1, 133.3, 133.4, 133.6, 134.0, 134.5, 134.7, 136.0, 136.5, 136.6, 136.7, 137.9, 139.3, 142.0, 144.1, 145.3, 145.7, 146.0, 146.8, 147.8, 149.5, 152.5, 158.9, 159.4 (Cq), 163.2, 163.4, 163.7, 166.1 (CON). − FAB-MS: *m/z* (%) = 2439.2 [M]$^+$. − $C_{162}H_{152}N_6O_{12}S_2$ (2439.15).

[2][*N*′,7′-(3,5-bis[3′,5′-bis(benzyloxy)benzyloxy]benzyl){*N*-[4-(triphenylmethyl)phenyl]-3-{[4-(triphenylmethyl)phenyl]amino}-sulfonyl}benzamide]-[29′-*tert*-butyl-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro{cyclohexane-1,2′-[7,15,25,33]tetraaza[8]thiaheptacyclo [32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1′′-cyclohexane]-8′,14′,32′-trione}-rotaxane (3c): Colourless solid, m.p. 78−80 °C, R_f = 0.39 (dichloromethane/cyclohexane/ethyl acetate 20:10:1). − ^{1}H NMR (400 MHz, [D$_7$]DMF): δ = 1.24 (s, 9 H, CCH_3), 1.41 (s, 12 H, CH_3), 1.54 (s, 6 H, CH_3), 1.62 (br, 8 H, cyh), 2.12 (br, 8 H, cyh), 2.23 (s, 6 H, CH_3), 2.52 (s, 4 H, cyh), 4.85 (d, ^2J = 12.1 Hz, 2 H, NCH_2), 4.91 (d, ^2J = 12.1 Hz, 2 H, NCH_2), 5.09 (s, 8 H, OCH_2), 5.12 (s, 8 H, OCH_2), 5.17 (s, 8 H, OCH_2), 6.27 (s, 2 H, benzyl), 6.46 (s, 2 H, benzyl), 6.61 (d, ^3J = 7.7 Hz, 1 H, sb), 6.68 (s, 2 H, benzyl), 6.75 (s, 8 H, benzyl), 6.81 (s, 4 H, benzyl), 6.61 (d, ^3J = 8.6 Hz, 2 H, anil), 7.09 (s, 4 H, aryl), 7.11 (s, 4 H, aryl), 7.18−7.60 (signal group, 79 H, anil, benzyl, sb, stop), 7.95 (dd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, 1 H, sb), 8.09 (s, 1 H, sb), 8.17 (s, 1 H, *t*bi), 8.19 (s, 1 H, sb), 8.04 (d, ^3J = 7.7 Hz, 1 H, sb), 8.28 (s, 1 H, *t*bi), 8.53 (d, ^3J = 7.7 Hz, 1 H, sb), 8.64 (s, 1 H, *t*bi), 9.00 (s, 1 H, NH), 9.22 (s, 1 H, NH), 9.36 (s, 1 H, NH), 10.42 (s, 1 H, NH). − ^{13}C NMR (100.6 MHz, [D$_7$]DMF): δ = 18.8, 19.1, (CH_3), 23.3, 23.4, 23.6, 26.6, 26.9, 27.3 (CH_2), 31.2 (CH_3), 45.5, 45.7 (Cq), 54.3, 54.7 (NCH_2), 65.3, 65.4 (Cq), 70.2, 70.3, 70.4, 70.5 (OCH_2), 101.6, 101.9, 102.5, 107.3, 107.6, 110.0, 126.3, 126.9, 127.0, 128.0, 128.3, 128.4, 128.5, 128.6, 129.2, 131.4, 131.7, 132.0, 132.1 (CH), 134.6, 134.7, 135.3, 135.7, 137.4, 137.9, 138.0, 138.1, 139.3, 140.3, 140.4, 140.6, 143.3, 145.4, 146.8, 147.1, 147.3, 137.9, 139.3, 142.0, 144.1, 145.3, 145.7, 146.0, 146.8, 147.8, 148.1, 149.1, 150.8, 153.8, 160.1, 160.7, 160.8, 160.9 (Cq), 164.5, 164.8, 164.9, 167.9 (CON). − FAB-MS: *m/z* (%) = 3311.6 [M + Na]$^+$. − $C_{218}H_{200}N_6O_{20}S_2$ (3288.15).

General Procedure for the Synthesis of Dendritic Catenanes 4b−d: Catenane **8** (100 mg, 0.05 mmol) and dried potassium carbonate (14 mg, 0.10 mmol) were dissolved in dry DMF (50 mL). After 30 minutes the appropriate dendritic benzyl bromide **6** (0.50 mmol) was added at room temperature. Stirring was continued for another 3 days. The mixture was filtered and the solvent was removed in vacuo. The crude product was then purified by column chromatography (SiO_2, 63−100 μm).

[2][29′-Methoxy-{33-*N*-(3,5-bis(benzyloxy)benzyl)}-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′-octa-methyldispiro{cyclohexane-1,2′-[7,15,25,33]tetraaza[8]thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1.^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20′,1′′-cyclohexane}-8′,14′,32′-trione]-[{29′-methoxy-{33-*N*-(3,5-bis(benzyloxy)benzyl)}-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro-{cyclohexane-1,2′-[7,15,25,33]tetraaza[8]thiaheptacyclo-[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}. 1.^{9,13}.1^{27,31}]hexatetraconta-[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1′′-cyclohexane}-8′,14′,32′-trione]catenane (4b): Colourless solid, R_f = 0.56 (chloroform/acetone 20:1). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.26 (s, 3 H, CH_3), 0.51 (s, 3 H, CH_3), 0.65 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 1.60 (s, 6 H, CH_3), 1.88 (s, 6 H, CH_3), 2.00 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.32 (s, 2 H, NCH_2), 2.47 (s, 2 H, NCH_2), 1.05−1.85 (m, 22 H, CH_2), 2.03−2.49 (m, 18 H, CH_2), 3.72 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 4.79 (s, 4 H, CH_2O), 4.86 (s, 4 H, CH_2O), 5.86 (s, 2 H, Ar-H), 6.20 (s, 2 H, Ar-H), 6.35 (s, 2 H, Ar-H), 6.42−6.83 (m, 18 H, Ar-H), 6.94−7.15 (m, 14 H, Ar-H), 7.20−7.47 (m, 10 H, Ar-H), 7.64 (t, 2 H, Ar-H), 7.72 (s, 2 H, Ar-H), 7.91 (s, 2 H, Ar-H), 7.99 (s, 2 H, Ar-H), 8.47 (s, 1 H, amide-H), 8.90 (s, 1 H, amide-H), 9.20 (s, 1 H, amide-H)). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.1, 14.1, 14.2, 14.6, 14.9, 16.7, 17.7, 17.8, 17.9, 18.1, 18.2, 18.4, 18.8, 18.9, 19.4, 19.5, 19.7, 20.0, 22.6, 22.9, 23.0, 23.1, 23.8, 24.5, 29.0, 30.4, 34.1, 35.5, 37.0, 38.8, 44.3, 44.7, 45.3, 53.6, 55.7, 55.9, 109.2, 123.1, 127.6, 127.7, 128.1, 128.2, 128.9, 129.9, 130.7, 131.0, 131.2, 131.3, 131.5, 131.6, 133.0, 133.3, 133.5, 133.7, 134.1, 134.5, 135.5, 135.7, 135.8, 135.9, 136.0, 136.5, 136.6, 136.9, 137.1, 138.3, 141.8, 142.0, 143.3, 150.7, 159.5, 159.8, 160.8, 160.9, 162.4, 163.1, 164.1, 164.5, 164.6. − MALDI TOF MS: *m/z* (%) = 2547.6 [M]$^+$. − $C_{162}H_{168}N_8O_{16}S_2$ (2547.24).

[2][29′-Methoxy-{33-*N*-(3,5-bis[3′,5′-bis(benzyloxy)benzyloxy]-benzyl}-8,8-dioxo[5′,17′,23′,35′,38′,40′,43′,45′-octamethyl-dispiro{cyclohexane-1,2′[7,15,25,33]tetraaza[8]thiaheptacyclo-[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}. 1.^{9,13}.1^{27,31}]hexatetraconta-[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20′,1′′cyclohexane}-8′,14′,32′-trione]-[{29′-methoxy-{33-*N*-

(3,5-bis[3′,5′-bis(benzyloxy)benzyloxy]benzyl}-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′octamethyldispiro{cyclohexane-1,2′-[7,15,25,33]tetraaza[8]thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1′′-cyclohexane}-8′,14′,32′-trione]catenane (4c): Colourless solid, R_f = 0.62 (chloroform/acetone 20:1). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.25 (s, 3 H, CH_3), 0.73 (s, 3 H, CH_3), 0.78 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.79 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.08 (s, 6 H, CH_3), 2.31 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 1.15–2.44 (m, 40 H, CH_2), 2.38 (s, 2 H, NCH_2), 2.52 (s, 2 H, NCH_2), 3.75 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 4.78 (s, 8 H, CH_2O), 5.00 (s, 8 H, CH_2O), 5.05 (s, 8 H, CH_2O), 6.22 (s, 2 H, Ar-H), 6.37 (s, 2 H, Ar-H), 6.45–6.71 (m, 10 H, Ar-H), 6.82–7.15 (m, 12 H, Ar-H), 7.20–7.58 (m, 60 H, Ar-H), 7.61 (s, 2 H, Ar-H), 7.76 (s, 2 H, Ar-H), 7.87 (s, 1 H, Ar-H), 7.91–8.08 (m, 6 H, Ar-H), 8.55 (s, 1 H, amide-H), 9.04 (s, 1 H, amide-H), 9.08 (s, 1 H, amide-H), 9.34 (s, 1 H, amide-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 16.7, 17.8, 17.9, 18.2, 18.4, 18.8, 19.0, 19.5, 19.8, 20.0, 21.3, 22.9, 23.0, 23.1, 29.0, 30.4, 31.1, 44.4, 44.7, 44.8, 45.3, 53.5, 55.7, 55.9, 101.5, 106.5, 106.6, 127.6, 127.7, 127.8, 128.1, 128.2, 128.7, 129.8, 130.9, 131.4, 131.7, 132.5, 133.3, 133.7, 134.1, 135.5, 135.6, 135.7, 136.6, 136.8, 136.9, 137.1, 139.0, 139.3, 143.3, 159.5, 159.7, 160.2, 160.3, 160.9, 162.3, 163.0, 164.5, 164.6, 170.3. – FAB-MS: *m/z* (%) = 3396.7 $[M]^+$. – $C_{218}H_{216}N_8O_{24}S_2$ (3396.22).

[2][29′-Methoxy-{33-*N*-(3,5-Bis[3′,5′-bis[3′′,5′′-bis(benzyloxy)-benzyloxy]benzyloxy]benzyloxy)}-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′-octa-methyldispiro{cyclohexane-1,2′-[7,15,25,33]-tetraaza[8]thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1′′cyclohexane}-8′,14′,32′-trione]-[{29′-methoxy{33-*N*-(3,5-bis[3′,5′-bis[3′′,5′′-bis(benzyloxy)benzyloxy]benzyloxy]benzyloxy)}-8,8-dioxo-[5′,17′,23′,35′,38′,40′,43′,45′octa-methyldispiro{cyclohexane-1,2′-[7,15,25,33]tetraaza[8]thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1′′-cyclohexane}-8′,14′,32′-trione]catenane (4d): Colourless solid, R_f = 0.74 (chloroform/acetone 20:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.26 (s, 3 H, CH_3), 0.75 (s, 3 H, CH_3), 0.78 (s, 3 H, CH_3), 1.25 (s, 6 H, CH_3), 1.31 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.56 (s, 6 H, CH_3), 1.66 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.30 (s, 2 H, NCH_2), 2.52 (s, 2 H, NCH_2), 1.10–1.92 (m, 24 H, CH_2), 1.96–2.45 (m, 16 H, CH_2), 3.74 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 4.75 (m, 8 H, CH_2O), 4.83–5.00 (m, 48 H, CH_2O), 6.23 (s, 2 H, Ar-H), 6.39 (s, 2 H, Ar-H), 6.44 (s, 2 H, Ar-H), 6.48–6.76 (m, 54 H, Ar-H), 6.80 (s, 2 H, Ar-H), 6.95 (s, 2 H, Ar-H), 7.01 (s, 2 H, Ar-H), 7.05 (s, 2 H, Ar-H), 7.10 (s, 2 H, Ar-H), 7.20–7.48 (m, 68 H, Ar-H), 7.64–8.03 (m, 14 H, Ar-H), 8.55 (s, 1 H, amide-H), 9.04 (s, 1 H, amide-H), 9.06 (s, 1 H, amide-H), 9.33 (s, 1 H, amide-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.0, 18.1, 18.5, 18.6, 18.7, 19.1, 19.5, 19.7, 19.9, 20.5, 22.7, 22.8, 23.0, 23.6, 26.1, 26.3, 28.8, 29.1, 30.8, 31.6, 35.4, 37.2, 38.6, 44.2, 44.5, 44.6, 45.1, 53.3, 53.6, 55.5, 55.7, 101.4, 101.5, 106.3, 106.4, 106.5, 126.8, 126.9, 127.1, 127.4, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 128.4, 128.7, 128.8, 129.6, 130.6, 130.7, 131.0, 131.2, 131.5, 132.0, 133.3, 133.5, 133.8, 133.9, 134.3, 134.5, 134.6, 135.3, 135.4, 135.5, 135.6, 135.7, 135.9, 136.4, 136.5, 136.6, 136.7, 137.0, 138.0, 138.9, 139.0, 139.1, 139.2, 139.5, 141.4, 142.4, 143.1, 145.2, 145.3, 146.4, 146.6, 147.8, 150.7, 151.1, 159.2, 159.4, 160.7, 160.8, 162.0, 162.8, 163.6, 164.3, 164.4. – MALDI TOF MS: *m/z* (%) = 5094.4 $[M]^+$. – $C_{330}H_{312}N_8O_{40}S_2$ (5094.17).

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