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Dendrimers with inherently axially chiral units

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We have designed and successfully synthesised dendrimers with axially chiral units in the interior structure. Starting from chiral 2,2′-dimethoxy-1,1′-binaphthalene building blocks **2** and **4** and from the four-directional initiator cores **7** and **8** the dendritic homochiral and heterochiral oligomers **9–16** were prepared. Using the $[\phi]_D$ and $\Delta\varepsilon$ values of monomers **2** and **4**, we calculated $[\phi]_D$ and $\Delta\varepsilon$ values for dendrons **11**, **13**, and dendrimers **9**, **10**, **15** and **16**. Although the observed molar optical rotation $[\phi]_D$ of the dendrimers agrees relatively well with the calculated values, the CD measurements of all the dendrimers in THF and CH_2Cl_2, except that of heterochiral dendrimer **16** in THF, were significantly different from the calculated values. The intensive hypochromism of the dendrimers (between 37–59% in THF) and the agreement between the calculated and observed $\Delta\varepsilon$ values of the dendrons (between 14 and 6% in THF) led to the assumption that the hypochromic effect is caused by intramolecular interactions. From the NMR measurements it was proved that in the homochiral dendrimer **15**, the N–H groups of the amides can form intramolecular hydrogen bonds that in $CHCl_3$, with the help of the axially chiral moieties, cause a different conformation of the molecule than in the diastereomeric dendrimer **16**.

Dendrimers, cascade molecules that are synthesised in a stepwise fashion, are characterised by a highly-branched structure that consists of a well-defined number of generations and end groups. The first report on chiral dendrimers appeared in 1979, when Denkewalter described[1] a divergent procedure for the synthesis of L-lysine based dendrimers. Since then, many publications on the issue of chirality and dendrimers have appeared and this topic has been reviewed by Newkome[2] and others.[3,4] The application of asymmetric dihydroxylation to the rapid construction of chiral dendrimers has been reported,[5] and the constitution, configuration and optical activity of chiral dendrimers have been systematically studied.[6] Dendrimers based on saccharides,[7] polyfunctional amino acids,[8] as well as non-natural chiral building blocks[9] have been recently reported. To the best of our knowledge, there are only three papers in the literature dealing with chiral dendrimers based on chiral 1,1′-binaphthalenes.[10,11] In those works the relationships between the dendrimer's chiroptical properties and the torsion angle of the chiral 1,1′-binaphthalene cores were studied. There have been many reports dealing with the application of axially chiral 1,1′-binaphthalene oligomers in the formation of chiral clathrates or in catalytic asymmetric synthesis.[12] Recently in the literature, successful achievements in the application of chiral dendrimers to asymmetric synthesis have been reported.[13] Here we present the application of 3- or 3,3′-substituted inherently axially chiral 2,2′-dimethoxy-1,1′-binaphthalenes as building blocks for the synthesis of highly functionalised dendrimers.

Results and discussion

Synthesis of axially chiral building blocks and the nonchiral four-directional core

The starting materials for the chiral linkers and terminal units are two derivatives of methyl 2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate **1** and **3**, which are synthetically available in both enantiomerically pure forms and whose syntheses have been described previously.[14] Each enantiomer of acid **1** was treated with oxalyl chloride. The resulting chlorides were linked, using quinoline,[15] to 5-aminoisophthalic acid. Dicarboxylates (*R*)-**2** and (*S*)-**2** were obtained in yields of 82 and 81.5%, respectively, in one step. They were used for the construction of dendrimers with chiral linking units (Scheme 1). The reaction of ester (*S*)-**3** with ethylenediamine yields amide **4** in 94% yield. The hydrolysis of (*S*)-**3** with potassium hydroxide has been previously described[14] and affords acid **5** in almost quantitative yield. Both **2** and **5** were used as chiral surface units. The synthesis of tetracyano derivative **6** and its application in the preparation of a four-directional initiator core has been already described[16] by Newkome. Tetraamine **7** was prepared by the reduction of the cyano groups in **6** with a borane–THF complex in 72% yield.

Synthesis of dendrimers having axially chiral 2,2′-dimethoxy-1,1′-binaphthalene units

The convergent synthetic approach was used in the preparation of all of the dendritic oligomers. Scheme 2 shows the preparation of two different dendrimers that have four (*S*)-2,2′-dimethoxy-1,1′-binaphthalene units linked to the initiator core. Amine (*S*)-**4** was attached to carbonyl chloride, formed from acid **8**,[16] to give the dendrimer **9** in 51% yield after chromatography. Similarly, acid (*S*)-**5** was treated with oxalyl chloride to afford (*S*)-2,2′-dimethoxy-1,1′-binaphthalene-3-carbonyl chloride, which was reacted with **7** in the presence of 4-dimethylaminopyridine (DMAP) to give the homochiral dendrimer **10** in 55% yield. In comparison with **9**, this strategy resulted in the formation of a dendrimer that has a shorter chain connecting the initiator core and the 1,1′-binaphthalene moieties.

Following the convergent approach, (*S*)-**4**, (*S*)-**2** and (*R*)-**2** were used for the preparation of homochiral and heterochiral monodendrons and dendrimers. (*S*)-**2** was treated with oxalyl chloride and the resulting dichloride was reacted with amine (*S*)-**4** in the presence of DMAP in CH_2Cl_2 to yield the

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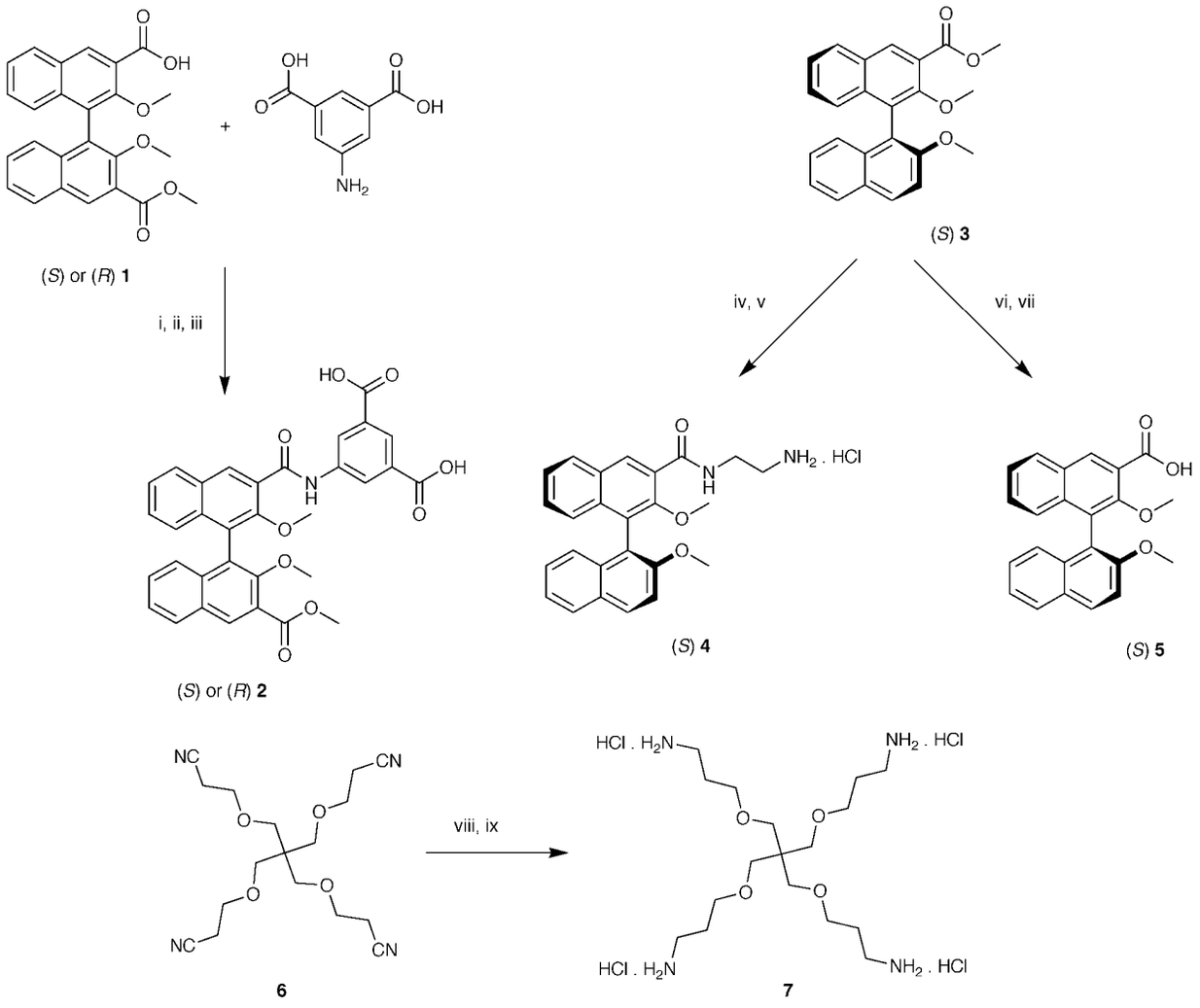


Scheme 1 *Reagents and conditions*: i, ClCOCOCl, CH_2Cl_2; ii, quinoline, THF; iii, HCl; iv, $NH_2CH_2CH_2NH_2$; v, HCl, MeOH; vi, KOH, MeOH; vii, HCl; viii, BH_3·THF, THF; ix, HCl, MeOH.

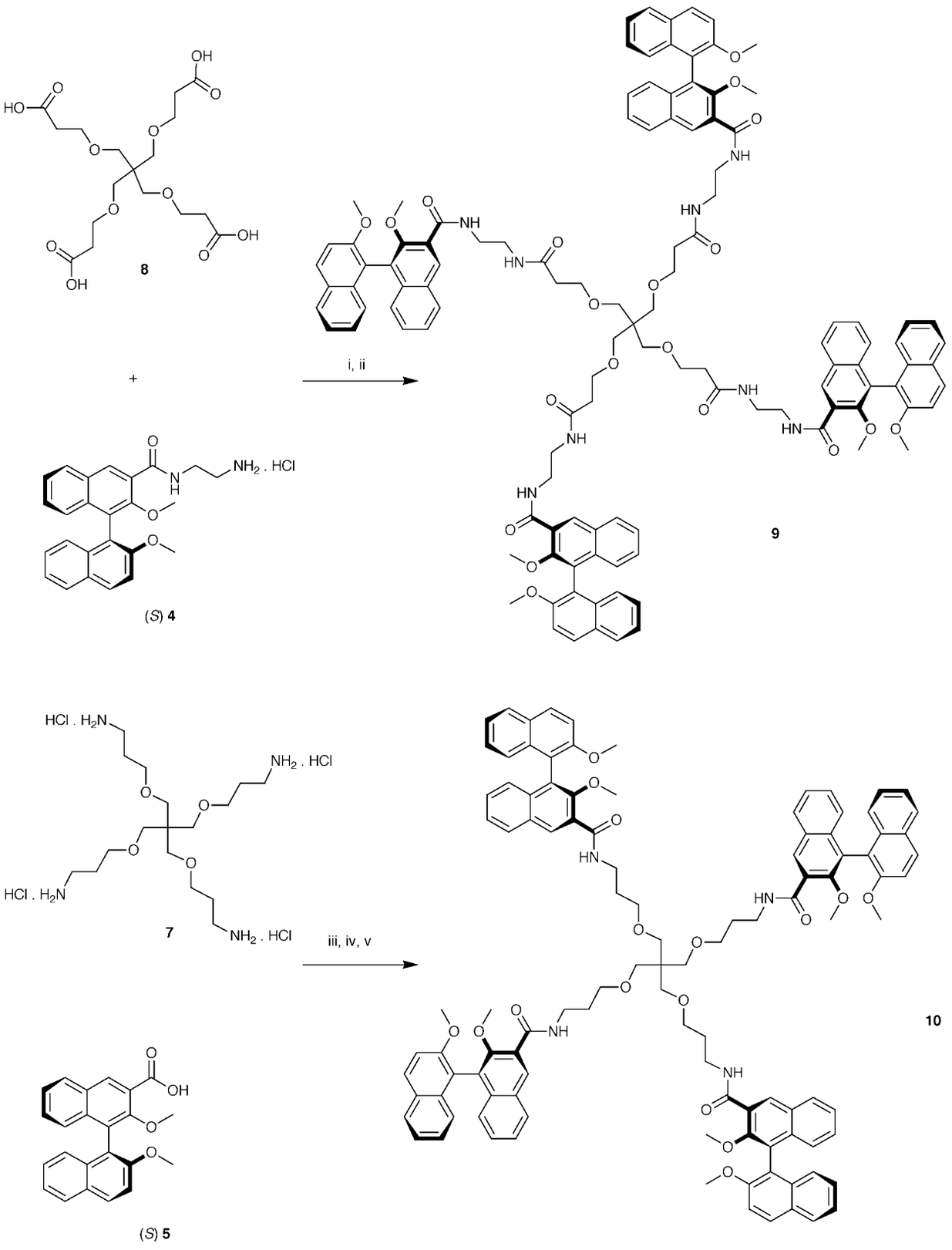
homochiral monodendron **11** in 75% yield after chromatography. Similarly, the heterochiral monodendron **13** was obtained in 62% yield from acid (*R*)-**2** and amine (*S*)-**4**. The methoxycarbonyl groups of oligomers **11** and **13** were converted into amides *via* reaction with ethylenediamine (see Scheme 3). The resulting monodendrons **12** and **14** were successfully attached to the initiator core **8**, which was activated by 1,1′-carbonyldiimidazole. In this way we prepared two 1.5-generation diastereomeric dendrimers, **15** and **16** (see Scheme 4). After repeated chromatography, homochiral dendrimer **15** was isolated in 19% yield. Dendrimer **16** was isolated from the reaction mixture by flash chromatography in 27% yield. The heterochiral layer-block[17] dendrimer **16** has eight (*S*)-2,2′-dimethoxy-1,1′-binaphthalene units on the surface and four (*R*)-2,2′-dimethoxy-1,1′-binaphthalene units in the interior of the molecule.

NMR studies of the conformational behaviour of dendrimers

The oligomeric 1,1′-binaphthyl structures **9–16** posses relatively flexible nonchiral aliphatic chains that link the chiral aromatic moieties. The conformation of the aromatic part is determined by the torsion angle θ between the two naphthalene subunits of the binaphthalenic moieties and, in the case of compounds **2** and **11–16** also by the conformation of the amide bonds connecting the isophthalic and the binaphthalenic units. Flexibility, internal steric interactions, possible hydrogen bonds between amide and methoxy groups, hydrophobic/hydrophilic interactions caused by the different characters of the core (the core is water soluble and the biaryl unit is relatively non-polar) and interior or exterior of the dendrimer determine the conformational arrangement in the dendrimer skeleton.

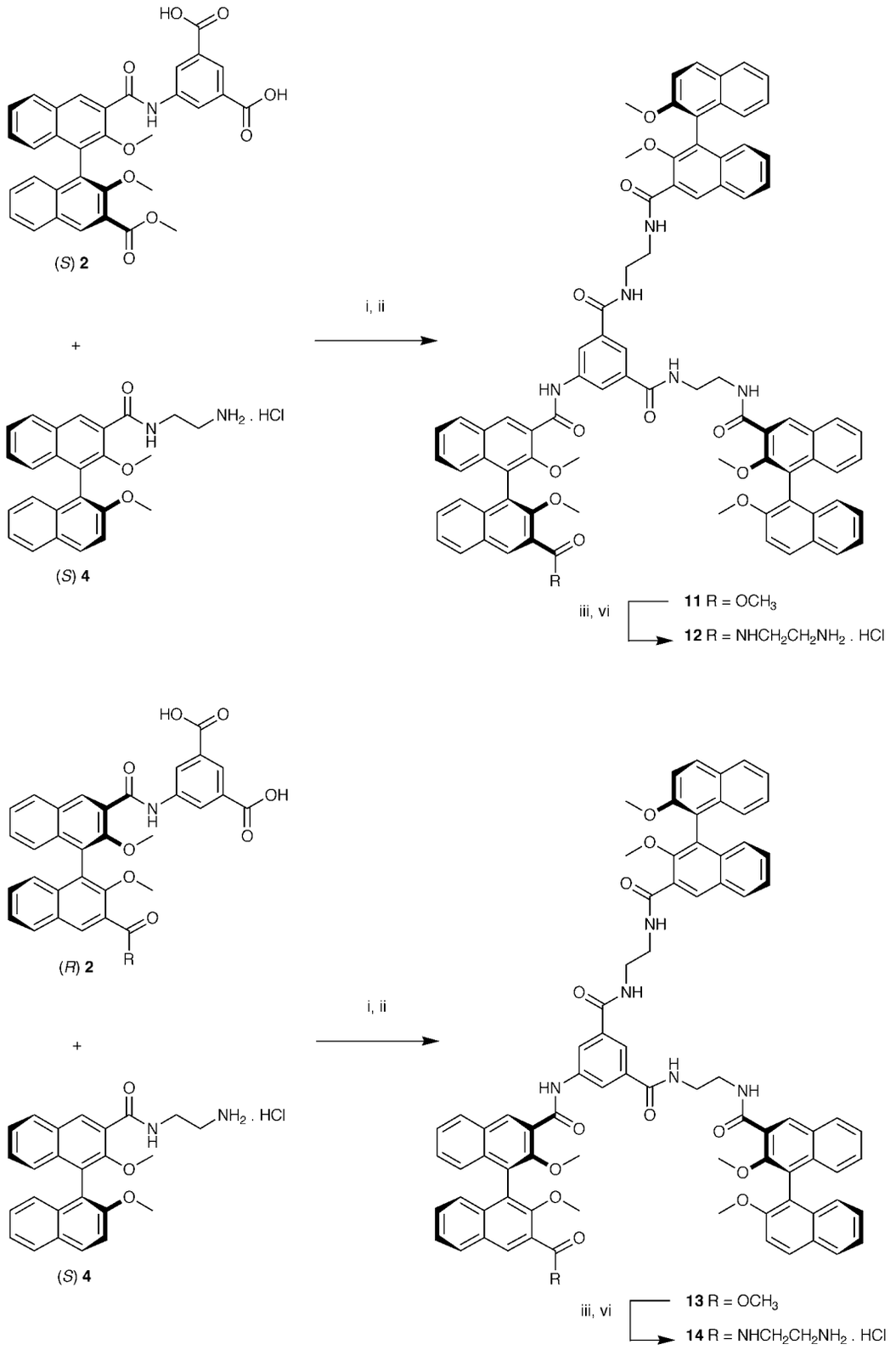
Compounds **9** and **10** have relatively simple ^{1}H NMR spectra that could be fully assigned (see Experimental section). The different lengths of the aliphatic chains that connect the core and the biaryl units lead to different splitting patterns for the methylene signals in the ^{1}H NMR spectra of **9** and **10**. The longer chain in **9** probably leads to greater conformational flexibility that results in methylene group NMR signals that are broad singlets in $CDCl_3$. Cooling of **9** in chloroform from 300 to 220 K resulted only in the broadening of NMR signals and the signals of amide protons *24* and *27* (for numbering see Fig. 1) shifted to lower field by approximately 0.4 ppm. The nonamidic NMR signals showed shifts of less than 0.05 ppm. Similar results were obtained when the solvent was replaced by 20% methanol-d_4 in $CDCl_3$. A strong change in solvent polarity was necessary to significantly alter the NMR spectra. The methylene protons measured in DMSO-d_6 are sharp signals with the expected multiplicity.

The ^{1}H NMR spectrum of **10** is rather different. The methylene groups of the aliphatic chain can be divided into two classes. The first one appears to exhibit greater conformational rigidity at room temperature. The protons 25_a, 25_b, 28_a and 28_b are, as a result of the chiral environment, non-equivalent and show ^{1}H NMR signals with expected splitting patterns. Low-temperature NMR measurements showed only the expected



Scheme 2 *Reagents and conditions*: i, $SOCl_2$; ii, DMAP, CH_2Cl_2; iii, ClCOCOCl, CH_2Cl_2; iv, DOWEX 1X2; v, DMAP, CH_2Cl_2.

signal broadening (Fig. 2). The methylenes *26* and *27* appear as a quintet and triplet respectively. At room temperature no anisotropy effect was observed. The geminal protons of methylenes *26* and *27* are equivalent. However, when we decreased the temperature to 260 K, the signal of methylene *26* stayed equivalent (see quintet in NMR), and methylene protons 27_a and 27_b, probably as a result of their greater conformational rigidity, lost their equivalence. The former A_2X_2 spin system triplet changed to a broad ABX_2 mutiplet. As shown in Fig. 2, at various temperatures the differences between the chemical shifts of the aliphatic protons are less than 0.05 ppm. This implies that they are almost independent of temperature, which further supports our assumption that intramolecular dynamic processes are occurring. A similar



Scheme 3 *Reagents and conditions*: i, ClCOCOCl, CH_2Cl_2; ii, DMAP, CH_2Cl_2; iii, $NH_2CH_2CH_2NH_2$, iv, HCl, MeOH.

temperature dependence could also be seen in temperature-dependent circular dichroism studies. The apparent deviations in the CD spectra are observable when the temperature decreased to under 10 °C (Fig. 3). Replacement of $CDCl_3$ with solvents of higher polarity has relatively little influence on the multiplicity of the aliphatic signals. In comparison to **9**, hydrogen bonding seems to be less important for the internal organisation of **10**.

Only very small differences are observable in the high resolution 600 MHz NMR spectra of diastereomers **11** and **13** in $CDCl_3$ (Fig. 4 and 5). When the dendritic skeleton of compound **13** was covalently bond to the four-directional initiator core to give the heterochiral oligomer **16**, the NMR spectrum in $CDCl_3$ showed broadened signals but was otherwise similar to that of compound **13**, indicating that all four dendritic wedges in the molecule are equivalent. When we compare this spectrum with the spectrum of diastereomer **15**, however, the multiplicity of signals is substantially changed.

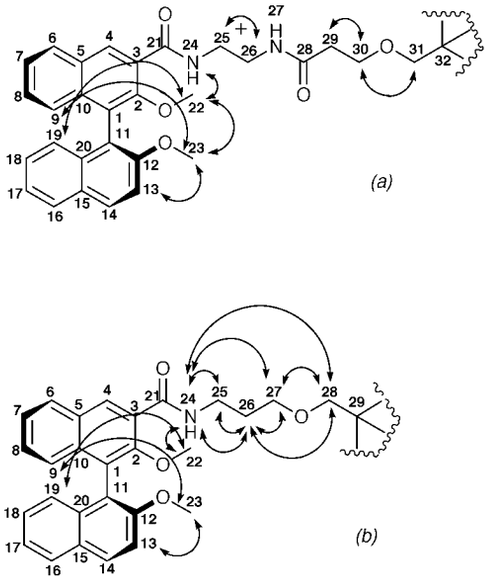


Fig. 1 Numbering and schematically represented negative or positive NOEs obtained from the ROESY spectra of compounds **9** (*a*) and **10** (*b*).

This can be seen in Fig. 6, which compares the detailed spectra of some aromatic signals. Several signals that were singlets in **16** are multiplets in **15**. Multiplets, corresponding to the aryl protons *4*, *14* and *42*, show that the homochiral dendrimer **15**

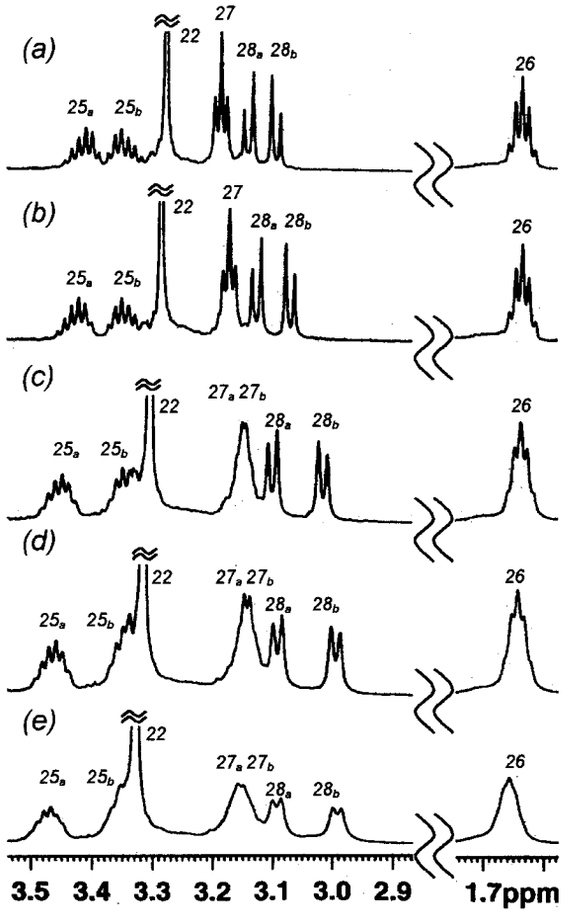


Fig. 2 The ^{1}H NMR spectra, at 600.13 MHz, of the aliphatic protons of compound **10** in $CDCl_3$ at various temperatures (*a*) 320, (*b*) 300, (*c*) 260, (*d*) 240 and (*e*) 220 K. Equivalent methylene protons are labelled in spectra with letters without an index.

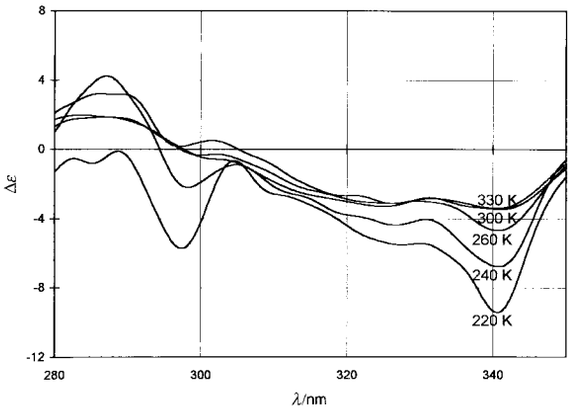


Fig. 3 CD spectra of dendrimer **10** in CH_2Cl_2 at various temperatures.

can slowly interconvert and has several conformations. The replacement of $CDCl_3$ with DMSO-d_6 caused the sharpening of all NMR signals and the spectra of dendrimers **15** and **16** became almost identical. ^{1}H NMR spectra are concentration-independent in the range of 10^{-2} to 10^{-4} M and additional GPC analysis performed in chloroform did not confirm the formation of molecular aggregates. We can assume that the different conformation behaviours of **16** and **15** are caused only by the formation of intramolecular hydrogen bonds, which are affected by the chirality of the biaryl units in molecules.

The one dimensional ^{1}H NMR spectra were complemented by ^{13}C NMR spectra and by nuclear Overhauser effect measurements. The ^{13}C NMR spectra of dendrimers **9**, **10** and **16** indicated that all of the dendritic wedges were equivalent. In the case of homochiral dendrimer **15**, however, all of the ^{13}C NMR signals were broadened and it was not possible to detect some carbonyl signals, indicating some asymmetry in the molecule. Some characteristic ^{13}C NMR signals for compound **9–16** are listed in Table 1. In the NOESY spectra of compounds **15** and **16** and the ROESY spectra of compounds **9**, **10**, **11** and **13** we were able to see cross peaks from through-space interactions between the each of the binaphthyl methoxy groups and the protons in position 8 of the neighbouring naphthalene. This, in conjunction with CPK modelling, indicated that the biaryl torsion angles, θ, in each of the compounds are likely to be greater then 90° in solution. This conclusion is in agreement with the published X-ray data of 2,2′-dimethoxy-1,1′-binaphthalene.[18] In the NOESY and ROESY spectra taken in $CDCl_3$, evidence for through-space interactions between the protons of the amide groups directly linked to the naphthalene moieties and protons of the neighbouring methoxy groups was seen. At the same time,

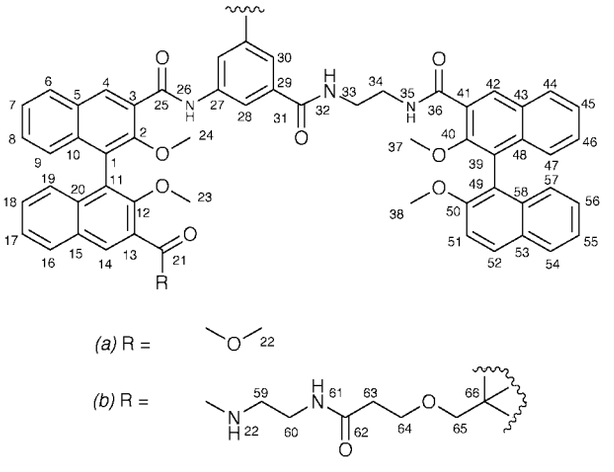


Fig. 4 Numbering of compounds (*a*) **11**, **13** and (*b*) **15**, **16**.

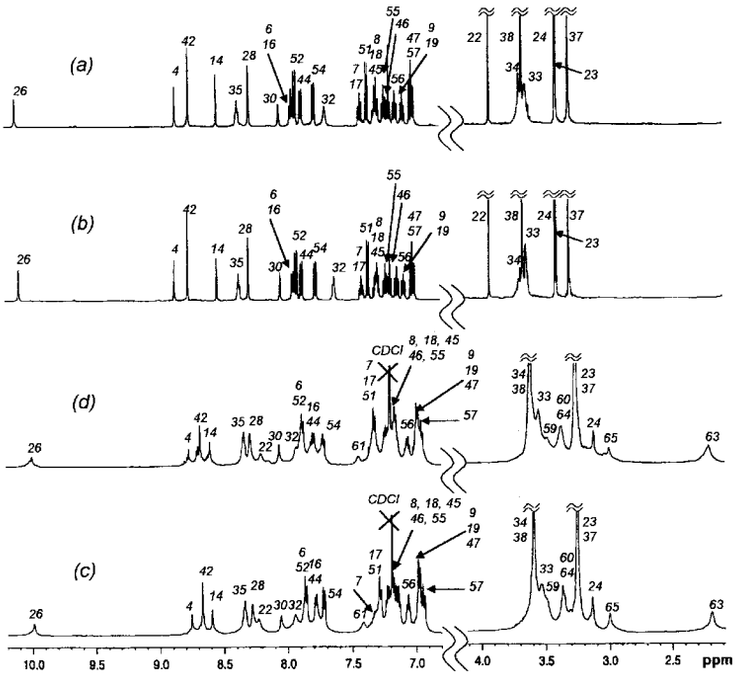


Fig. 5 The ^{1}H NMR spectra, at 600.13 MHz, of monodendrons **11**, **13** and dendrimers **15**, **16** in $CDCl_3$.

no cross peaks between the amide hydrogens and aromatic protons in position 4 of the naphthalene moiety were found. This indicates the presence of relatively stable intramolecular hydrogen bonds between the amide protons and methoxy oxygens. However, in the more polar DMSO-d_6 the intramolecular hydrogen bonds in the dendritic molecules are broken and the through-space interactions between the amide hydrogens and the aromatic protons in the 4,4′ positions of the biaryls are observable. In the case of dendrimer **10**, unexpected intramolecular through-space interactions between the initiator core and the aromatic moiety were seen in the ROESY spectra, as shown in Fig. 1.

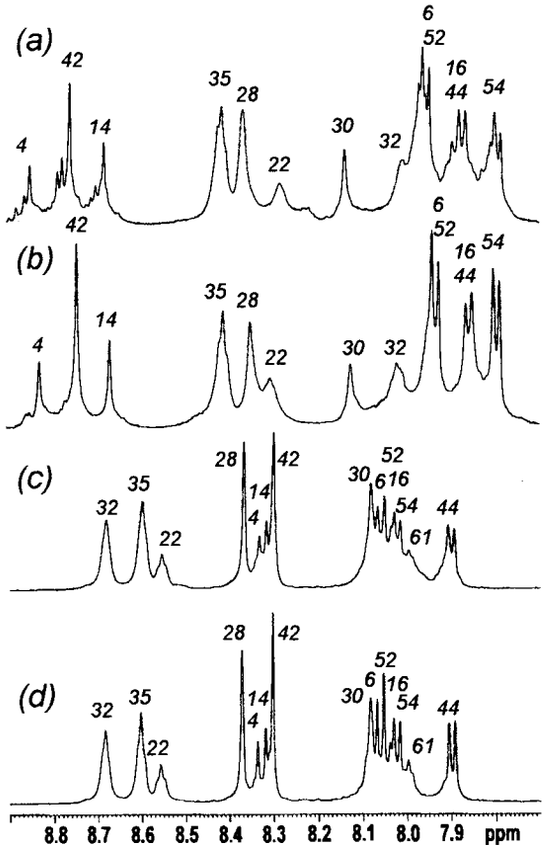


Fig. 6 The compared ^{1}H NMR spectra, at 600.13 MHz and 300 K, of selected aromatic protons of compound **15** in (*a*) $CDCl_3$ and (*c*) DMSO-d_6, and **16** in (*b*) $CDCl_3$ and (*d*) DMSO-d_6.

The chiroptical properties of oligomers with axially chiral building blocks

The chiral character of the biaryl units that were incorporated into the dendrimers also allowed us to study their chiroptical properties. For the construction of the dendritic structures, the two axially chiral units **2** and **4** were used. Table 2 compares the isotropic and anisotropic properties of the (*S*) building blocks. The two compounds showed substantially different specific rotations. While amide **4**'s negative specific rotation is relatively independent of the solvent and concentration, the specific rotation of **2** is variably dependent upon the solvent used. For example in THF, which is a better electron lone pair donor solvent than CH_2Cl_2 or $CHCl_3$, (*S*)-**2** exhibits a small negative optical rotation. In CH_2Cl_2 and $CHCl_3$ (*S*)-**2** shows positive optical rotation.[19] The chiroptical properties of **2** could be also influenced by the relative orientation of the aminoisophthalic and binaphthalene moieties in the molecule. The CD spectra measured in CH_2Cl_2 and THF confirm this fact. Amide (*S*)-**4** exhibits a similar couplet of Cotton effects (CE) in both solvents, having a positive maximum at approximately wavelength 235 nm and a negative one at 251 nm. In the region of wavelength 250 nm, (*S*)-**2** has a positive maximum at 250 nm in CH_2Cl_2. That has relatively intense shoulder which is not seen for **4**. This probably results from the superposition of a weak negative maximum corresponding to the naphthalene chromophore and a strong positive CE from the acylaminoisophthaloyl moiety of (*S*)-**2**. In THF, the CD curve has an intense sharp positive CE maximum at 246 nm, a broad positive CE maximum at 269 nm and a weak negative maximum at 256 nm.[20]

Table 3 lists the UV absorptions of the biaryl oligomers. As shown, the oligomers with three and four biaryl units **9**, **10**, **11** and **13** have very similar UV spectra. Dendrimers **15** and **16**, however, have slightly different UV spectra from the oligomers. The UV study also reveals that in the wavelength range of 240–

Table 1 The ^{13}C NMR data of monodendrons and dendrimers for selected aromatic and carbonyl carbons in $CDCl_3$

Sample	*(Ar) C-O-Me*	*-CO-NH-*
9	153.28 (2), 154.84 (12)	166.67 (21), 172.18 (28)
10	153.39 (2), 155.04 (12)	165.82 (21)
11	153.02 (2), 153.20 (40), 154.47 (12), 154.86 (50)	163.63 (25), 166.55 (31), 167.48 (36)
12	152.94, 153.04, 153.33, 154.69	163.66, 165.73, 166.64, 167.21
13	153.02 (2), 153.21 (40), 154.48 (12), 154.86 (50)	163.54 (25), 166.51 (31), 167.47 (36)
15	153.11, 153.24, 153.47, 154.81	163.63, br 166.73, 167.19, 172.41
16	153.11, 153.25, 153.51, 154.82	163.57, 166.74, 166.92, 167.23, 172.66

Table 2 The chiroptical and UV properties of monomers **2** and **4**

Sample	Solvent	$[\alpha]_D$[a]	c[c]	ε_{max}[d] (λ_{max})[e]	$\Delta\varepsilon_{max}$[e] (λ_{max})[e]
2	CH_2Cl_2	+72.7 (0.22)[b]	2	9.1 (242)	+27.0 (250)
				3.1 (280)	−6.0 (288)
				0.5 (340)	+2.5 (307)
2	THF	−4.7 (1.00)[b]	2	10.4 (236)	+22.0 (246)
				1.1 (284)	−1.4 (256)
				0.5 (331)	+3.0 (269)
					−4.2 (288)
4	CH_2Cl_2	−72.2 (0.18)[b]	6	5.7 (241)	+105.8 (234)
				1.2 (284)	−56.6 (251)
				0.5 (338)	+4.4 (287)
					−1.4 (342)
4	THF	−71.8 (1.00)[b]	2	9.5 (233)	+66.3 (236)
				0.8 (295)	−34.6 (251)
				0.6 (338)	−6.5 (297)
					−6.2 (322)
					−5.9 (338)

[a]Specific rotation in 10^{-1} deg cm^2 g^{-1}. [b]Concentration in g per 100 ml of solvent. [c]Concentration in 10^{-5} M. [d]ε_{max} in 10^4 dm^3 mol^{-1} cm^{-1}. [e]λ_{max} in nm. [f]$\Delta\varepsilon_{max}$ in dm^3 mol^{-1} cm^{-1}.

260 nm, the extinction coefficients, ε, of the bands are very similar. This means that the magnitudes of the extinction coefficients are not linearly related to the number of biaryl units in the molecule.

Table 4 summarises the specific and molar optical rotations of the dendrimers **9**, **10**, **15** and **16**. It was discovered that the magnitude of the molar optical rotation $[\phi]_D$ increases with the generation number in the molecule. As a matter of fact, the molar optical rotation is linearly related to the number of monomer building blocks. By adding the $[\phi]_D$ values of the individual monomer units, the theoretical $[\phi]_D$ values of the oligomers were computed. The comparison between the measured and computed $[\phi]_D$ values demonstrates the validity of this approach. Compound **10**, which should have the less flexible chain (see above), showed the greatest difference between theoretical and observed $[\phi]_D$ values (24%) of the molecules tested. We can conclude that in our case the overall molar optical rotation of the biaryl containing oligomers does not depend much on the conformational behaviour of the molecule. This fact is in agreement with the results of investigations of other groups that used different chiral building blocks.[6,17]

The circular dichroism (CD) measurements of the dendrimers and monodendrons **9**, **10**, **11**, **13**, **15** and **16** were carried out in CH_2Cl_2 and THF. Although these solvents are not completely transparent in the wavelength ranges used, the dendrimers were insoluble in the more convenient solvents (methanol, acetonitrile, hexane). The data obtained from the spectra were compared with values for $\Delta\varepsilon$ predicted by superimposing the CD curves of the monomer units (*S*)-**2**, (*R*)-**2** and (*S*)-**4**. An example is given in Fig. 7 where the spectra of compounds **11** and **13**, measured in THF, are compared with the computed ones. In our work we focused on the band of the CD signals at around 252 nm, which corresponds to an allowed π–π^* transition of the aromatic chromophores. In this region, the transmission of the solvent is greater than 85%. From Fig. 7 it can be observed that for monodendrons **11** and **13**, the wavelengths and intensities of the negative CEs are in agreement with the computed data. The differences between the calculated and measured values of $\Delta\varepsilon$ are +14 and +6% for **11** and **13**, respectively. In CH_2Cl_2 the absolute value of the difference increases only slightly. In contrast to the ε values in UV spectra, the $\Delta\varepsilon$ values of oligomers **11** and **13** are linearly related to the number of chiral units. The calculated λ_{max} was in good agreement with that observed. This result is consistent with the above discussed NMR measurements. We can assume that the 2,2′-dimethoxy-1,1′-binaphthalene aromatic chromophores behave relatively independently of each other in a dendritic molecule. In sharp contrast to the monodendrons **11**, **13**, the tested dendrimers **9**, **10** and **15** exhibit a large hypochromic effect at 252 nm (Table 5). Heterochiral dendrimer **16** did not, however, show a pronounced hypochromic effect in THF. Concentration dependence measurements, which were performed in the range of 10^{-4} to 10^{-6} M, proved that this hypochromism cannot be explained by a

Table 3 The UV data of monodendrons **11** and **13**, and dendrimers **9**, **10**, **15** and **16** observed in CH_2Cl_2 and THF

Solvent	**9**	**10**	**11**	**13**	**15**	**16**
CH_2Cl_2	248[a]	246[a]	246[a]	248[a]	256[a]	258[a]
	(5.02)[b]	(5.01)[b]	(5.14)[b]	(5.04)[b]	(5.05)[b]	(5.05)[b]
	284[a]	284[a]	284[a]	284[a]	294[a]	296[a]
	(4.65)[b]	(4.51)[b]	(4.67)[b]	(4.69)[b]	(5.07)[b]	(5.07)[b]
	338[a]	338[a]	338[a]	338[a]	338[a]	336[a]
	(4.34)[b]	(4.17)[b]	(4.17)[b]	(4.08)[b]	(4.75)[b]	(4.77)[b]
THF	243[a]	242[a]	246[a]	245[a]	251[a]	250[a]
	(5.05)[b]	(5.17)[b]	(5.02)[b]	(5.15)[b]	(5.46)[b]	(5.46)[b]
	283[a]	284[a]	284[a]	283[a]	283[a]	283[a]
	(4.48)[b]	(4.51)[b]	(4.61)[b]	(4.65)[b]	(5.20)[b]	(5.20)[b]
	294[a]	294[a]	327[a]	326[a]	324[a]	324[a]
	(4.45)[b]	(4.47)[b]	(4.17)[b]	(4.15)[b]	(4.74)[b]	(4.74)[b]
	318[a]	318[a]	338[a]	338[a]	338[a]	338[a]
	(4.04)[b]	(4.08)[b]	(4.20)[b]	(4.18)[b]	(4.75)[b]	(4.75)[b]
	338[a]	338[a]				
	(4.23)[b]	(4.23)[b]				

[a]λ_{max} in nm. [b]Log ε_{max} in dm^3 mol^{-1} cm^{-1}.

Table 4 Observed and computed molar optical rotations $[\phi]_D$ of dendrimers in $CDCl_3$

Sample	FW	c^a	$[\alpha]_D{}^b$	Units	Measured $[\phi]_D{}^c$	Calculated $[\phi]_D{}^c$	Difference $[\Delta\phi_r]^d$
9	1953	0.32	−55.5	4	−1083.92	−1269.36	15
10	1726	1.01	−55.8	4	−963.11	−1269.36	24
15	5842	0.20	−22.2	12	−1296.92	−1585.00	18
16	5842	0.21	−51.6	12	−3014.47	−3492.00	14

[a]Concentration in g per 100 ml of solvent. [b]Specific rotation in 10^{-1} deg cm^2 g^{-1}. [c]Molar rotation in 10 deg cm^2 mol^{-1}. [d]Percentage difference between the calculated and the measured molar rotations.

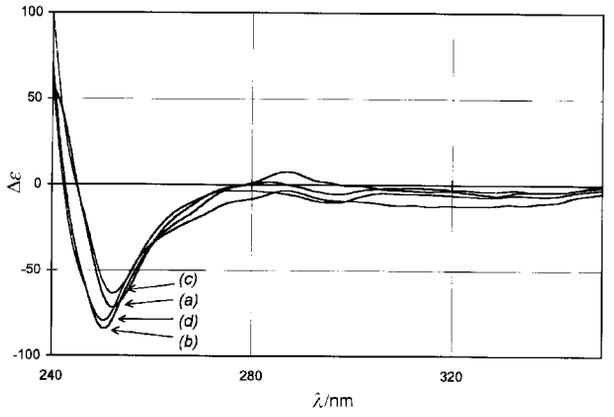


Fig. 7 CD spectra of diastereomeric monodendrons (*a*) **11** and (*b*) **13** in THF, and spectra of (*c*) **11** and (*d*) **13** in THF calculated from the CD of monomer units.

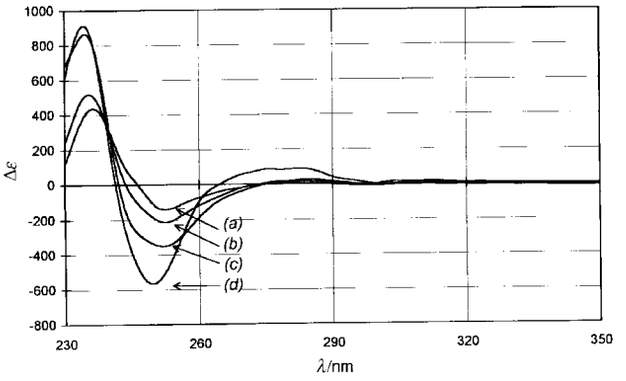


Fig. 8 CD spectra of homochiral dendrimer **15** in different solvents: (*a*) (1.71×10^{-5} M) in THF; (*b*) (1.26×10^{-5} M) in CH_2Cl_2; (*c*) calculated spectrum in CH_2Cl_2; (*d*) (1.26×10^{-5} M) in CH_2Cl_2–2% CF_3COOH.

concentration effect only because $\Delta\varepsilon$ did not change by more than 10% for any of the monomers under these conditions. A similar effect has been observed for dendrimers having a 1,1′-binaphthalenyl core. The hypochromism in their CD spectra and $[\phi]_D$ values increase as a function of dendrimer generation.[11] This effect was explained by the change in torsion angle between the naphthyl units.[11,21] However, in our studied dendrimers the hypochromic effect in the CD spectra is not accompanied by increasing $[\phi]_D$ values. These results prompted us to conclude that, rather than invoking changes in torsion angles between the naphthyl units, the hypochromism could be explained by differences in the conformations about the bonds linking the biaryl groups to the amides in compounds **2**, **4**, **11** and**13** *versus* dendrimers **9**, **10**, **15** and **16**. This proposed effect of amide groups on the intensity could also explain the hyperchromism observed in CD spectra when CH_2Cl_2 solutions of the dendrons and dendrimers containing an acylaminoisophthalic moiety were acidified with 2% trifluoroacetic acid (TFA) (Fig. 8). Usually, increasing the polarity of the solvent causes a hypochromic effect in CD spectra. In this case the change from the less polar aprotic to the acidic protic solvent led to the protonation of the molecules and hence conformational changes at the isophthalic and the naphthalenic moieties. The hyperchromism of the band at 252 nm is accompanied by a blue shift of around 2 nm and by the formation of two overlapping bands at 276 and 282 nm. The CD spectra taken in THF, which is a proton acceptor, did not show any changes after the addition of TFA.

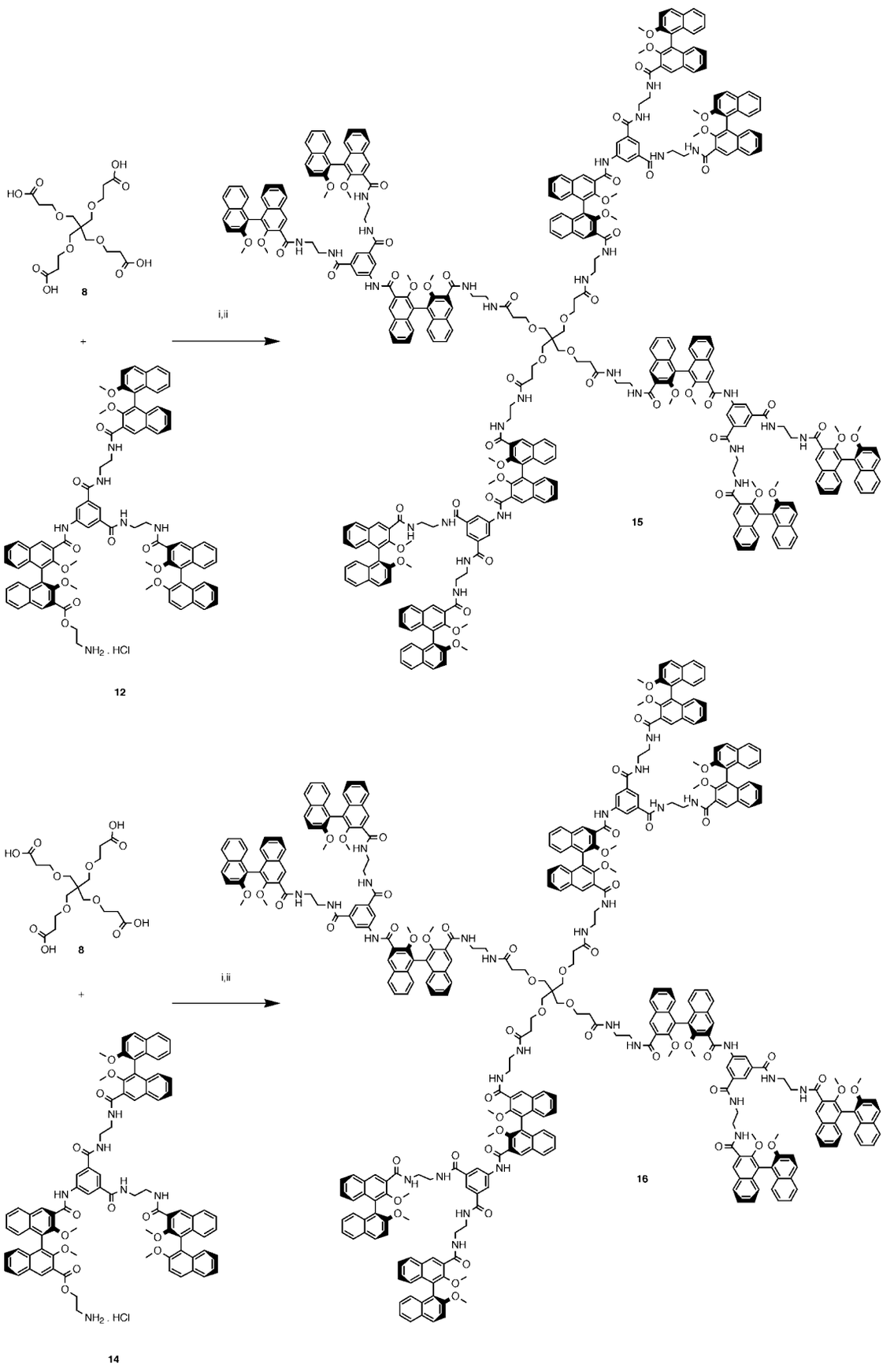
Conclusion

We have successfully designed new monodisperse dendrimeric compounds formed from chiral 2,2′-dimethoxy-1,1′-binaphthalene building blocks. This very versatile axially chiral building block can now be incorporated in dendrimer structures as core, branching and connecting as well as surface units. 1,1′-Binaphthalene-2,2′-diol and its derivatives are known to serve as catalysts for a plethora of asymmetric reactions.[22] Consequently, a broad range of dendritic catalysts for enantioselective reactions is now easily accessible. The feasibility of such an approach has been recently proved.[23] From the point of view of new materials the incorporation of chiral units able to complex transition metals could lead to the synthesis of supermolecules with novel properties.[24] Finally, dendritic molecular devices with the capability of biomolecular

Table 5 The observed and calculated CD data of aromatic π–π* transition bands

Sample	Solvent	c^a	Measured CD $\Delta\varepsilon_{max}{}^b$ (λ_{max})^c	Calculated CD $\Delta\varepsilon_{max}{}^b$ (λ_{max})^c	Difference[d]
9	CH_2Cl_2	2.5	−100.0 (252)	−226.4 (251)	−56
9	THF	2.0	−57.3 (252)	−138.5 (251)	−59
10	CH_2Cl_2	2.5	−120.6 (252)	−226.4 (251)	−47
10	THF	2.5	−87.7 (251)	−138.5 (251)	−37
11	CH_2Cl_2	10.9	−81.2 (253)	−87.8 (252)	−8
11	THF	1.3	−71.1 (252)	−62.2 (252)	+14
13	CH_2Cl_2	10.4	−113.8 (251)	−139.5 (251)	−18
13	THF	3.5	−84.1 (251)	−79.3 (251)	+6
15	CH_2Cl_2	1.3	−213.9 (252)	−351.3 (252)	−39
15	THF	1.4	−143.5 (252)	−248.8 (252)	−42
16	CH_2Cl_2	2.5	−340.7 (251)	−558.0 (251)	−61
16	THF	1.4	−262.7 (252)	−317.2 (251)	−17

[a]Concentration in 10^{-5} mol dm^{-3}. [b]$\Delta\varepsilon_{max}$ in dm^3 mol^{-1} cm^{-1}. [c]λ_{max} in nm. [d]Percentage difference between the maxima of the calculated and measured bands.



Scheme 4 *Reagents and conditions*: i, CDI, CH_2Cl_2; ii, DMAP, CH_2Cl_2.

recognition could be constructed based on axially chiral synthons.[25] The conformational flexibility of the compounds was probed by measuring their chiroptical properties. The CD spectra of the dendrimers in THF and CH_2Cl_2 solutions showed a nonlinear dependence of the intensity of the aromatic π–π^* transition bands on the number of chiral units. This

nonlinearity was not observed for the monodendrons however. This effect, which is mainly observable for homochiral dendrimers, is probably influenced by the conformational flexibility and internal organisation of the chains inside the molecules. The flexibility can be controlled by the length of the chain connecting the initiator core and the aromatic moiety as shown in the examples of dendrimers **9** and **10**. The amide bonds and unshared electron pairs of the heteroatoms in all of the dendrimers form strong intramolecular hydrogen bonds in nonpolar solvents which, with the help of the axially chiral moieties, led to different types of conformational behaviour in the chains of the diastereomeric dendrimers **15** and **16**.

Acknowledgements

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Experimental

Melting points were measured on a Boetius apparatus (VEB Kombinat NAGEMA) and are not corrected. Optical rotations were recorded on a JASCO Digital Polarimeter DIP370, CD spectra on a JASCO J-715 spectropolarimeter, UV spectra on a Varian DMS 200 spectrometer, IR spectra on a Nicolet 750 FT IR spectrometer and NMR spectra on a Varian Gemini 300HC spectrometer (300.075 and 75.461 MHz) and a Bruker Avance 600 (600.13 and 150.902749 MHz). Chemical shifts (δ/ppm) are given relative to tetramethylsilane as internal standard. Solvents used are indicated in brackets. ^{1}H–^{1}H COSY spectra were also taken for each molecule. When necessary, TOCSY, NOESY or ROESY 2D spectra were also taken. In order to prevent spin diffusion processes in the NOE measurements, the mixing times were kept shorter than 80 ms. The Attached Proton Test (APT) was used to identify the carbon substitution pattern for each of the ^{13}C NMR signals. For complete assignments of ^{13}C NMR spectra HMBC and HSQC 2D NMR methods were used. Electron impact mass spectra (EI-MS) were recorded with a JEOL DX 303/DA 5000 or HP 5971 mass spectrometer, having an inlet from a gas chromatograph HP 598 equipped with a DB-5 column. Fast atom bombardment mass spectra (FAB-MS) were recorded with a ZAB-EQ (VG Analytical) mass spectrometer, using fast atoms of Xe. The matrices used are indicated in brackets. Chemical ionisation mass spectra (CI-MS) were recorded with a Finnigan MAT 95 mass spectrometer, using methane. Gel permeation chromatography (GPC) was accomplished on Jordi-Gel DVB 500 and 1000 A columns, using a liquid chromatograph Ecom (pump LCP 4000 and UV detector LCD 2563). The eluents used are indicated in brackets. High performance liquid chromatography (HPLC) was performed on the Ecom chromatograph (pump LCP 4000, gradient programmer GP4, UV detector LCD 2040 and LCD 2082), using columns with stationary phases LiChrospher 100 RP-18, LiChrospher® Si 100 and Chiralpak OP+. Measurements on the Chiralpak OP+ column were always performed with methanol as the eluent.

General procedure for the preparation of aromatic acid chlorides

Oxalyl chloride (5 equiv. for every carboxy group) and several drops of dry dimethylformamide (DMF) were added dropwise to 0.5 M solutions of the carboxylic acids in CH_2Cl_2. Excess oxalyl chloride and CH_2Cl_2 were, after 5 h of stirring, removed *in vacuo* and the residue was dried at 40 °C under 2.5 kPa for 1 h. Crude chloride was immediately used in the next reaction.

(*S*)-5-(2,2′-Dimethoxy-3′-methoxycarbonyl-1,1′-binaphthyl-3-ylcarboxamido)isophthalic acid (*S*)-2

Acid (*S*)-**1** (6 mmol) was converted to its acid chloride as described above. A suspension of 5-aminoisophthalic acid (2.17 g, 12 mmol) and quinoline (2.12 mL, 18 mmol) in dry THF (80 mL) was cooled to 0 °C. To this stirred suspension was added dropwise a solution of the acid chloride in dry THF (20 mL). After 1 h the mixture was allowed to warm to room temperature (rt) and stirred for 15 h. Then the solvent was removed *in vacuo*, the residue was mixed with a solution of 10% HCl (100 mL) and the mixture was extracted with diethyl ether (3×100 mL). The combined organic layers were subsequently extracted with water (100 mL), dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was refluxed at 100 °C in a mixture of toluene–acetone (60 mL, 5:1) for 1 h. The mixture was allowed to cool to rt and filtered. The white crystals were washed with toluene and dried at 70 °C for 24 h. According to NMR analysis, no further purification of the product was necessary; yield 81.5%. For elemental analysis, the acid was recrystallised from methanol; mp 268–270 °C; $[\alpha]_D^{25} = -4.7$ ($c = 1.0$ in THF); $[\alpha]_D^{22} = +39.9$ ($c = 0.19$ in $CHCl_3$); $[\alpha]_D^{22} = +72.7$ ($c = 0.22$ in CH_2Cl_2); ^{1}H NMR (300 MHz, acetone-d_6, 23.5 °C, TMS): $\delta = 3.53$ (s, 3H; OCH_3), 3.62 (s, 3H; OCH_3), 4.01 (s, 3H; $COOCH_3$), 7.18–7.22 (m, 2H; ArH), 7.44–7.61 (m, 4H; ArH), 7.51 (m, 2H; ArH), 8.52 (s, 1H; ArH), 8.63 (s, 1H; ArH), 8.73 (s, 1H; ArH), 8.85 (s, 2H; ArH); ^{13}C NMR, APT (75.461 MHz, acetone-d_6, 23.5 °C, TMS): δ (CH_3 and CH) = 53.34, 62.93, 63.06, 126.59, 126.93, 127.25, 127.34, 127.43, 129.77, 130.14, 130.73, 130.76, 133.59, 134.56, δ (CH_2 and C) = 127.16, 130.09, 131.19, 131.68, 133.26, 136.76, 137.05, 141.39, 154.74, 155.91, 166.27, 167.44, 167.86; IR (KBr): $\nu = 1728$ cm^{-1} (C=O); Mass spectrum (FAB, glycerol–thioglycerol): *m/z* (%), 580.2 (45) [$M^+ + H$] (for $M = C_{33}H_{25}NO_9$ calc. 580.2), 399.2 (100) [$M^+ - C_8H_6NO_4$]; $C_{33}H_{25}NO_9 \cdot H_2O$: calc. C 66.33, H 4.55, N 2.34; found C 66.44, H 4.69, N 2.36%.

(*R*)-5-(2,2′-Dimethoxy-3′-methoxycarbonyl-1,1′-binaphthyl-3-ylcarboxamido)isophthalic acid (*R*)-2

This compound was prepared from an optically pure enantiomer in the same way as (*S*)-**2**; yield 82%; mp 267–270 °C (methanol); $[\alpha]_D^{25} = +4.7$ ($c = 1.0$ in THF); ^{1}H NMR and IR data of (*R*)-**2** are identical with the data referring to (*S*)-**2**; $C_{33}H_{25}NO_9 \cdot H_2O$: calc. C 66.33, H 4.55, N 2.34; found C 66.31, H 4.56, N 2.51%.

(*S*)-2-(2,2′-Dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethylammonium chloride (*S*)-4

The compound (*S*)-**3** (3.6 g, 9.66 mmol) was dissolved in freshly distilled, dry ethylenediamine (15 mL) at 20 °C, stirred for 24 h, and extracted with water (100 mL) and $CHCl_3$ (3×100 mL). The combined organic layers were washed with water (100 mL), dried ($MgSO_4$) and the solvent was removed *in vacuo*. Drying for 24 h at 60 °C under 250 Pa gave rise to amorphous, pale yellow (*S*)-2-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethylamine; yield 88%. The amine was dissolved in ethanol (200 mL). To this solution was added a 10% solution of HCl in methanol (5 mL). The solvent was removed *in vacuo*. The resulting salt did not crystallise, and was therefore precipitated from diethyl ether and, after filtration, dried for several days at 80 °C under 200 Pa; yield 94%; mp 151–155 °C ($CHCl_3$); $[\alpha]_D^{20} = -71.8$ ($c = 1.00$ in THF); $[\alpha]_D^{22} = -68.4$ ($c = 0.04$ in $CHCl_3$); $[\alpha]_D^{22} = -72.2$ ($c = 0.18$ in CH_2Cl_2); spectral data for (*S*)-2-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethylammonium chloride (*S*)-**4**: ^{1}H NMR (300 MHz, DMSO-d_6, 23.5 °C, TMS): $\delta = 3.02$ (t,

^3J(H,H) = 5.6 Hz, 2H; CH_2–amine), 3.38 (s, 3H; OCH_3), 3.58 (q, ^3J(H,H) = 6.0 Hz, 2H; CH_2–amide), 3.77 (s, 3H; OCH_3), 6.90–6.98 (m, 2H; ArH), 7.24–7.37 (m, 3H; ArH), 7.48 (t, ^3J(H,H) = 7.7 Hz, 1H; ArH), 7.67 (d, ^3J(H,H) = 9.0 Hz, 1H; ArH), 7.96–8.16 (m, 3H; ArH), 8.41 (s, 1H; ArH), 8.68 (t, ^3J(H,H) = 5.5 Hz, 1H; CONH); ^{13}C NMR, APT (75.461 MHz, DMSO-d_6, 23.5 °C, TMS): δ (CH_3 and CH) = 55.98, 60.97, 113.69, 123.41, 124.28, 124.68, 125.36, 126.55, 127.64, 128.05, 130.00, 130.18, δ (CH_2 and C) = 37.08, around 39.5 (in place of signal DMSO), 117.36, 125.50, 128.50, 129.08, 129.49, 133.21, 134.16, 152.80, 154.56, 166.66; $C_{25}H_{25}N_2O_3Cl{\cdot}1.5H_2O$: calc. C 64.72, H 6.08, N 6.04, Cl 7.64; found C 64.67, H 6.06, N 5.80, Cl 7.45%.

Tetrakis(5-amino-2-oxapentyl)methane hydrochloride 7

To a solution of tetrakis[(cyanoethoxy)methyl]methane **6** (700 mg, 2 mmol) in dry tetrahydrofuran (THF) (10 mL), stirred at 0 °C under N_2, a solution of borane–tetrahydrofuran complex (1.0 M solution, 20 mL, 20 mmol) was added dropwise. After three weeks of standing, more borane–tetrahydrofuran complex (10 mL, 10 mmol) was added. After two months the reaction was quenched by careful dropwise addition of a solution of HCl (10 mL, 15%) in dry methanol to the stirred and ice-cooled reaction mixture. The precipitate was decanted, separated and washed with a sufficient amount of THF. The product was dried at 110 °C under 200 Pa for several days to yield 71.5% of a glassy solid; ^{1}H NMR (300 MHz, D_2O, 23.5 °C, TMS): δ = 1.97 (quintet, ^3J(H,H) = 6.6 Hz, 8H; CH_2), 3.12 (t, ^3J(H,H) = 7.1 Hz, 8H; CH_2N), 3.50 (s, 8H; CCH_2O), 3.62 (t, ^3J(H,H) = 5.6 Hz, 8H; CH_2O); ^{13}C NMR, APT (75.461 MHz, D_2O, 23.5 °C, TMS): δ (CH_2 and C) = 29.94, 40.98, 47.91, 72.23, 73.61; IR ($CHCl_3$): ν = 3410 cm^{-1} (N–H); Mass spectrum (FAB, glycerol–thioglycerol): *m/z* (%), 435.4 (30) [$M^+ - 2\times$HCl], 365.3 (100) [$M^+ + H - 4\times$HCl].

(*S*,*S*,*S*,*S*)-Tetrakis({*N*-[2-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethyl]aminocarbonylethoxy}methyl)methane 9

A mixture of **8** (22 mg, 51.8 μmol), freshly distilled thionyl chloride (750 μL, 10.36 mmol) and dry CH_2Cl_2 (2 mL) was stirred at rt for 18 h. The solvent and excess thionyl chloride were removed *in vacuo* and the crude product was dried at 70 °C under 250 Pa. The resulting tetrakis[(carboxyethoxy)-methyl]methane tetrachloride was dissolved in dry CH_2Cl_2 (2 mL) and added dropwise to a solution of (*S*)-**4** (100 mg, 228 μmol) and DMAP (72.4 mg, 593 μmol) in dry CH_2Cl_2 (2 mL) cooled to 0 °C. After 3 h the reaction mixture was allowed to warm to rt and stirred for 16 h until GPC analysis indicated no changes in composition. The mixture was added to a 10% solution of HCl, extracted with CH_2Cl_2 (3 × 15 mL) and the combined organic layers were extracted with water (2 × 15 mL). The organic residue was dried ($MgSO_4$) and the solvent removed *in vacuo*. The product was subjected to silica gel chromatography (Kieselgel 60PF_{254}, $CHCl_3$–methanol 95:5) and dried at 50 °C under 250 Pa; yield 51 mg, 51%; $[\alpha]_D^{20} = -55.5$ (c = 0.32 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, 26.8 °C, TMS): δ = 2.31 (br s, 8H; 29), 3.15 (br s, 8H; 31), 3.30 (br s, 12H; 22), 3.38 (br s, 8H; 26), 3.49 (br s, 16H; 25 and 30), 3.67 (br s, 12H; 23), 6.97 (d, ^3J(H,H) = 8.4 Hz, 4H; 19), 7.01 (d, ^3J(H,H) = 8.5 Hz, 4H; 9), 7.13 (t, ^3J(H,H) = 7.5 Hz, 4H; 18), 7.18 (t, ^3J(H,H) = 7.6 Hz, 4H; 8), 7.23 (t, ^3J(H,H) = 7.4 Hz, 4H; 17), 7.29 (t, ^3J(H,H) = 7.2 Hz, 4H; 7), 7.35–7.39 (m, 8H; 13 and 27), 7.78 (d, ^3J(H,H) = 8.1 Hz, 4H; 16), 7.85 (d, ^3J(H,H) = 7.6 Hz, 4H; 6), 7.93 (d, ^3J(H,H) = 9.1 Hz, 4H; 14), 8.25 (br s, 4H; 24), 8.63 (s, 4H; 4); ^{13}C NMR, (150.9 MHz, $CDCl_3$, 26.8 °C, TMS): δ = 36.75 (29), 39.58 (25), 39.92 (26), 45.23 (32), 56.47 (23), 61.52 (22), 67.43 (30), 69.20 (31), 113.41 (13), 118.19 (11), 123.76 (17), 124.84 (19), 125.35 (9), 125.45 (3), 125.58 (7), 126.34 (1), 126.86 (18), 128.04 (8 and 16), 129.01 (15), 129.32 (6), 130.19 (14), 130.25 (5), 132.85 (4), 133.79 (20), 135.47 (10), 153.28 (2), 154.84 (12), 166.67 (21), 172.18 (28); IR ($CHCl_3$): ν = 1649.9 cm^{-1} (C=O), ν = 3369.1 cm^{-1} (N–H); Mass spectrum (FAB, dithiothreitol–dithioerythritol): *m/z* (%), 1954.2 (100) [$M^+ + H$] (for $M = C_{117}H_{116}N_8O_{20}$ calc. 1953.8).

(*S*,*S*,*S*,*S*)-Tetrakis{[3-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)propoxy]methyl}methane 10

The hydrochloride of amine **7** was converted in water to free tetraamine in almost quantitative yield by anion exchange (DOWEX 1X2, 200–400 mesh) in a hydroxide cycle. Acid (*S*)-**5** (579 μmol) was converted to its acid chloride as described above then was dissolved in dry CH_2Cl_2 (5 mL) and added dropwise to a mixture of freshly prepared tetraamine (44 mg, 121 μmol), 4-dimethylaminopyridine (DMAP) (71 mg, 579 μmol) in CH_2Cl_2 (3 mL). The mixture was cooled to −5 °C and after 3 h allowed to warm to rt. Three days later GPC confirmed no further changes in composition. The reaction solution was subjected to silica gel chromatography (Kieselgel 60 H, $CHCl_3$–methanol 20:1). Then it was dried at 50 °C under 2.5 kPa for 3 h to yield amorphous colourless dendrimer **10**; yield 55.5%; $[\alpha]_D^{20} = -55.8$ (c = 1.01 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, 26.8 °C, TMS): δ = 1.64 (quintet, ^3J(H,H) = 6.5 Hz, 8H; 26), 3.07 (d, ^2J(H,H) = 9.0 Hz, 4H; 28_a), 3.13 (d, ^2J(H,H) = 9.0 Hz, 4H; 28_b), 3.18 (t, ^3J(H,H) = 6.0 Hz, 8H; 27), 3.29 (s, 12H; 22), 3.36 (sextet, $^{2,3}J$(H,H) = 6.5 Hz, 4H; 25_a), 3.43 (sextet, $^{2,3}J$(H,H) = 6.5 Hz, 4H; 25_b), 3.64 (s, 12H; 23), 6.96 (d, ^3J(H,H) = 8.5 Hz, 4H; 19), 6.99 (d, ^3J(H,H) = 8.5 Hz, 4H; 9), 7.10 (dt, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.0 Hz, 4H; 18), 7.18 (dt, ^3J(H,H) = 6.2 Hz, ^4J(H,H) = 1.0 Hz, 4H; 8), 7.20 (dt, ^3J(H,H) = 6.3 Hz, ^4J(H,H) = 0.9 Hz, 4H; 17), 7.30 (dt, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 0.7 Hz, 4H; 7), 7.34 (d, ^3J(H,H) = 9.1 Hz, 4H; 13), 7.75 (d, ^3J(H,H) = 8.2 Hz, 4H; 16), 7.84 (d, ^3J(H,H) = 8.2 Hz, 4H; 6), 7.89 (t partially covered by the signals of 14, ^3J(H,H) = 5.6 Hz, 4H; 24), 7.90 (d, ^3J(H,H) = 9.1 Hz, 4H; 14), 8.63 (s, 4H; 4); ^{13}C NMR, (150.9 MHz, $CDCl_3$, 26.8 °C, TMS): δ = 29.83 (26), 37.78 (25), 45.38 (29), 56.61 (23), 61.66 (22), 69.43 (27), 69.76 (28), 113.62 (13), 118.62 (11), 123.95 (17), 125.13 (19), 125.54 (9), 125.68 (7), 126.35 (3), 126.52 (1), 127.03 (18), 128.01 (8), 128.21 (16), 129.22 (15), 129.49 (6), 130.28 (14), 130.60 (5), 133.07 (4), 134.09 (20), 135.50 (10), 153.39 (2), 155.04 (12), 165.82 (21); IR ($CHCl_3$): ν = 1648.6 cm^{-1} (C=O), ν = 3390.3 cm^{-1} (N–H); Mass spectrum (FAB, dithiothreitol–dithioerythritol): *m/z* (%): 1726.0 (100) [$M^+ + H$] (for $M = C_{109}H_{104}N_4O_{16}$ calc. 1725.8); $C_{109}H_{104}N_4O_{16}{\cdot}H_2O$: calc. C 75.07, H 6.13, N 3.21; found C 74.93, H 6.35, N 3.04%.

(*S*,*S*,*S*)-5-(2,2′-Dimethoxy-3′-methoxycarbonyl-1,1′-binaphthyl-3-ylcarboxamido)-*N*,*N*-bis[2-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethyl]isophthalamide 11

Acid (*S*)-**2** (59 mmol) was converted to its acid chloride as described above and then was dissolved in dry CH_2Cl_2 (6 mL). The solution was added dropwise to a stirred mixture of (*S*)-**4** (520 mg, 1.3 mmol), DMAP (159 mg, 1.3 mmol) and dry CH_2Cl_2 (3.5 mL) cooled to −15 °C. After 2 h the mixture was allowed to warm to rt. After 6 h the solution was mixed with a 10% solution of HCl (50 mL), extracted with $CHCl_3$ (20 mL), water (25 mL) and a saturated solution of Na_2CO_3 (25 mL). The combined organic layers were dried ($MgSO_4$), the solvent removed *in vacuo* and the residue subjected to silica gel TLC (Kieselgel 60 H, $CHCl_3$–methanol 20:1) to yield amorphous **11**; yield: 65%); mp 190–191 °C ($CHCl_3$); $[\alpha]_D^{20} = -57.8$ (c = 1.0 in THF); ^{1}H NMR (600 MHz, $CDCl_3$, 26.8 °C, TMS): δ = 3.30 (s, 6H;37), 3.39 (s, 3H; 23), 3.40 (s, 3H; 24), 3.64 (br q, ^3J(H,H) = 3.0 Hz, 4H; 33), 3.66 (s, 6H; 38), 3.65–3.70 (m together with the singlet of signal 38, 4H; 34), 3.92

(s, 3H; 22), 6.99 (d, ^3J(H,H) = 9.6 Hz, 2H; 57), 7.01 (d, ^3J(H,H) = 9.6 Hz, 2H; 47), 7.07 (d, ^3J(H,H) = 7.8 Hz, 1H; 19), 7.08 (d, ^3J(H,H) = 8.4 Hz, 1H; 9), 7.13 (dt, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.2 Hz, 2H; 56), 7.18 (dt, ^3J(H,H) = 7.1 Hz, ^4J(H,H) = 1.2 Hz, 2H; 46), 7.22 (dt, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.2 Hz, 2H; 55), 7.26–7.31 (m, 4H; 8, 18 and 45), 7.35 (d, ^3J(H,H) = 9.0 Hz, 2H; 51), 7.39–7.42 (m, 2H; 7 and 17), 7.68 (br s, 2H; 32), 7.76 (d, ^3J(H,H) = 8.4 Hz, 2H; 54), 7.86 (d, ^3J(H,H) = 8.4 Hz, 2H; 44), 7.91 (d, ^3J(H,H) = 9.0 Hz, 2H; 52), 7.93 (d, ^3J(H,H) = 7.8 Hz, 1H; 16), 7.95 (d, ^3J(H,H) = 7.8 Hz, 1H; 6), 8.04 (s 1H; 30), 8.27 (s, 2H; 28), 8.37 (t, ^3J(H,H) = 5.4 Hz, 2H; 35), 8.53 (s, 1H; 14), 8.75 (s, 2H; 42), 8.85 (s, 1H; 4), 10.11 (s, 1H; 26); ^{13}C NMR, (150.9 MHz, $CDCl_3$, 26.8 °C, TMS): δ = 39.44 (34), 41.72 (33), 52.50 (22), 56.47 (38), 61.57 (37), 62.11 (23), 62.14 (24), 113.45 (51), 118.21 (49), 121.36 (30), 121.85 (28), 123.77 (55), 124.86 (57 and 13), 125.19 (41), 125.34 (47), 125.43 (3), 125.52 (19 or 9), 125.53 (9 or 19), 125.56 (45), 125.72 (1), 125.77 (11), 125.81 (17), 125.96 (7), 126.32 (39), 126.90 (56), 128.02 (54), 138.04 (46), 128.67 (8), 128.92 (18), 129.02 (53), 129.30 (16), 129.46 (44), 129.62 (15), 129.67 (6), 130.18 (52), 130.33 (5), 130.37 (43), 133.32 (42), 133.80 (58), 133.90 (14), 134.42 (4), 135.49 (29), 135.54 (48), 135.61 (20), 135.73 (10), 138.99 (27), 153.02 (2), 153.20 (40), 154.47 (12), 154.86 (50), 163.63 (25), 166.55 (31), 166.72 (21), 167.48 (36); IR ($CHCl_3$): ν = 1727 cm^{-1} (C=O ester), ν = 1652 cm^{-1} (C=O amide), ν = 3374 cm^{-1} (N–H); Mass spectrum (FAB, dithiothreitol–dithioerythritol): *m/z* (%), 1344.4 (100) [M$^+$] (for M = $C_{83}H_{69}O_{13}N_5$ calc. 1344.5); $C_{83}H_{69}O_{13}N_5 \cdot 0.5H_2O$: calc. C 73.65, H 5.21, N 5.17; found C 73.57, H 5.28, N 5.35%.

(*S*,*S*,*S*)-5-[2,2′-Dimethoxy-3′-(2-aminoethylaminocarbonyl)-1,1′-binaphthyl-3-ylcarboxamido]-*N*,*N*-bis[2-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethyl]isophthalamide hydrochloride 12

Homochiral dendron **11** (1.26 g, 937 μmol) was dissolved in freshly distilled ethylenediamine (10 mL) and stirred for 19 h at rt. The reaction mixture was added to cold (0 °C) water (50 mL) and extracted with $CHCl_3$ (150 mL). The organic layer was extracted with water (50 mL) and dried ($MgSO_4$), the solvent was removed *in vacuo* and the residue subjected to silica gel TLC (Kieselgel 60 H, $CHCl_3$–acetone–methanol 100:20:10). Subsequently the solvent was removed, the product dried at 50 °C under 250 Pa for 48 h to yield homochiral dendron [G-1]-$CONHCH_2CH_2NH_2$. The resulting amine was dissolved in $CHCl_3$. After adding a solution of 15% HCl (100 μL) in dry methanol, the solvent was removed *in vacuo* to yield hydrochloride **12**. This product was dried following the procedure for the pure amine; yield: 84%; mp 215–223 °C ($CHCl_3$); $[\alpha]_D^{20} = -23.0$ (c = 0.50 in THF); $[\alpha]_D^{20} = -16.6$ (c = 0.32 in THF); ^{1}H NMR for free amine (300 MHz, $CDCl_3$, 23.5 °C, TMS): δ = 3.05 (t, 2H; CH_2), 3.25–3.50 (m, 14H; CH_2 and OCH_3), 3.66–3.80 (m, 16H; CH_2, NH_2 and OCH_3), 7.02–7.48 (m, 21H; ArH), 7.81–8.04 (m, 9H; ArH), 8.17 (s, 1H; ArH), 8.30–8.52 (m, 4H; CONH and ArH), 8.65–8.95 (m, 4H; ArH), 10.10–10.25 (m, 1H; CONH); ^{13}C NMR, APT (75.461 MHz, $CDCl_3$, 23.5 °C, TMS): δ (CH_3 and CH) = 56.31, 61.42, 61.77, 61.96, 113.30, 121.60, 123.63, 124.69, 125.21, 125.44, 126.74, 127.90, 129.23, 130.06, 132.94, δ (CH_2 and C) = 39.29, 41.03, 41.29, 42.96, 118.02, 125.27, 125.30, 126.19, 126.47, 128.87, 130.17, 133.64, 134.97, 135.34, 135.42, 138.75, 152.94, 153.04, 153.33, 154.69, 163.66, 165.73, 166.64, 167.21; IR ($CHCl_3$): ν = 1652 cm^{-1} (C=O), ν = 3377 cm^{-1} (N–H); Mass spectrum (FAB, dithiothreitol–dithioerythritol): *m/z* (%): 1373.7 (100) [M$^+$ + H] (for M = $C_{84}H_{72}N_7O_{12}$ calc. 1371.5); $C_{84}H_{73}N_7O_{12}Cl \cdot 3H_2O$: calc. C 69.01, H 5.45, N 6.71; found C 68.96, H 5.59, N 6.46.

(*S*,*S*,*R*)-5-(2,2′-Dimethoxy-3′-methoxycarbonyl-1,1′-binaphthyl-3-ylcarboxamido)-*N*,*N*-bis[2-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethyl]isophthalamide 13

Following the procedure for **11**, (*R*)-**2** and (*S*)-**4** yielded the glassy heterochiral dendron **13**; yield: 62%; mp 190–191 °C ($CHCl_3$); $[\alpha]_D^{20} = -52.5$ (c = 1.0 in THF); NMR and IR data of this compound were almost identical with the data referring to **11**; Mass spectrum (FAB, dithiothreitol/dithioerythritol): *m/z* (%), 1344.4 (90) [M$^+$] (for M = $C_{83}H_{69}O_{13}N_5$ calc. 1344.5); $C_{83}H_{69}O_{13}N_5 \cdot 0.5H_2O$: calc. C 73.65, H 5.21, N 5.17; found C 73.62, H 5.28, N 5.23.

(S,S,R)-5-[2,2′-Dimethoxy-3′-(2-aminoethylaminocarbonyl)-1,1′-binaphthyl-3-ylcarboxamido]-N,N-Bis[2-(2,2′-dimethoxy-1,1′-binaphthyl-3-ylcarboxamido)ethyl]isophthalamide hydrochloride 14

Following the procedure for **12**, dendron **13** yielded amorphous **14**; yield: 80%; mp 207–210 °C ($CHCl_3$); $[\alpha]_D^{20} = -75.6$ (c = 0.5 in THF); The ^{1}H NMR (300 MHz, $CDCl_3$) and IR data of **14** were identical with the data referring to diastereomer **12**; Mass spectrum (FAB, dithiothreitol–dithioerythritol): *m/z* (%): 1372.3 (100) [M$^+$ + H] (for M = $C_{84}H_{72}N_7O_{12}$ calc. 1372.5); $C_{84}H_{73}N_7O_{12}Cl \cdot 5H_2O$: calc. C 67.35, H 5.58, N 6.54; found C 67.36, H 5.55, N 6.30%.

Homochiral dendrimer [G1,5] 15

A suspension of **3** (10 mg, 23.6 μmol) in a solution of 1,1′-carbonyldiimidazole (CDI) (15.3 mg, 94.3 μmol) in CH_2Cl_2 (1.5 mL) was stirred at rt under N_2 for 48 h. To this mixture was added a solution of DMAP (42 mg, 342 μmol) and dendron **12** (142 mg, 103.7 μmol) in dry CH_2Cl_2 (5 mL). The reaction was monitored by GPC. After 4 days the solvent was removed *in vacuo* and the residue was subjected three times to silica gel chromatography (Kieselgel 60 H, $CHCl_3$–methanol 20:1). The product was dissolved in a minimum amount of $CHCl_3$ then precipitated into methanol and dried at 60 °C under 250 Pa to yield amorphous white dendrimer G-1.5 **15**; yield 19%; mp 214–218 °C ($CHCl_3$–methanol); $[\alpha]_D^{20} = -22.2$ (c = 0.20 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, 26.8 °C, TMS): δ = 2.21 (br s, 8H; 63), 2.99–3.06 (m, 8H; 65), 3.12–3.18 (m, 12H; 24), 3.25–3.27 (m, 36H; 23 and 37), 3.37 (br s, 16H; 60 and 64), 3.48 (br s partially covered by the singlet of signal 33, 8H; 59), 3.55 (br s, 16H; 33), 3.60–3.63 (m, 40H; 38 and 34), 6.90 (d partially covered by the signals of 9, 19 and 47, ^3J(H,H) = 8.4 Hz, 8H; 57), 6.97–6.99 (m, 16H; 9, 19 and 47), 7.04–7.08 (m, 8H; 56), 7.14–7.26 (m, 32H; 8, 18, 45, 46, 55), 7.30–7.36 (m, 16H; 7, 17, 51), 7.44 (br s, 4H; 61), 7.71–7.82 (m, 20H; 16, 44, 54), 7.86–7.93 (m, 12H; 6 and 52), 7.94 (br s partially covered by the signals of 6 and 52, 8H; 32), 8.06 (s, 4H; 30), 8.16–8.20 (m, 4H; 22), 8.28 (br s, 8H; 28), 8.34 (br s 8H; 35), 8.60–8.64 (m, 4H; 14), 8.67–8.71 (m, 8H; 42), 8.76–8.80 (m, 4H; 4), 9.96–10.01 (m, 4H; 26); ^{13}C NMR (75.461 MHz, $CDCl_3$, 23.5 °C, TMS): δ = 36.59, br 39.40, 39.97, 40.94, br 45.30, 56.38, 61.52, 61.86, 62.02, 67.29, 68.94, 113.41, 118.13, 121.70, 123.69, 124.80, 125.30, 125.48, 125.86, 126.26, 126.81, 127.98, 128.48, 128.95, 129.33, 130.18, 133.05, 133.73, 135.05, 135.46, 138.91, 153.11, 153.24, 153.47, 154.81, 163.63, br 166.73, 167.19, br 172.41; IR ($CHCl_3$): ν = 1532.9 cm^{-1} (amide II), ν = 1650.0 cm^{-1} (amide I), ν = 3363.7 cm^{-1} (N–H); Mass spectrum (FAB, dithiothreitol–dithioerythritol): *m/z* (%): 5842.3 (100) [M$^+$] (for M = $C_{353}H_{312}N_{28}O_{56}$ calc. 5842.5).

Heterochiral dendrimer [G1,5] 16

Following the procedure for **15**, dendrimer **16** was obtained from acid **8** and dendron **14**. The product was purified by chromatography only once; yield: 27%; mp 210–213 °C ($CHCl_3$–methanol); $[\alpha]_D^{20} = -51.6$ (c = 0.21 in $CHCl_3$); ^{1}H

NMR (600 MHz, $CDCl_3$, 26.8 °C, TMS): $\delta = 2.10$ (br s, 8H; 63), 3.00 (br s, 8H; 65), 3.13 (s, 12H; 24), 3.24 (s, 24H; 37), 3.25 (s, 12H; 23), 3.35 (br s, 16H; 60 and 64), 3.50 (br s partially covered by the singlet of signal 33, 8H; 59), 3.53 (br s, 16H; 33), 3.59 (br s, 28H; 38 and 34), 6.94 (br d, $^3J(H,H) = 9.0$ Hz, 8H; 57), 6.97–6.99 (m, 16H; 9, 19 and 47), 7.06 (br t, $^3J(H,H) = 7.5$ Hz, 8H; 56), 7.13–7.24 (m, 32H; 8, 18, 45, 46, 55), 7.27–7.36 (m, 16H; 7, 17, 51), 7.42 (br s, 4H; 61), 7.72 (br d, $^3J(H,H) = 8.0$ Hz, 8H; 54), 7.76–7.79 (m, 12H; 16 and 44), 7.85–7.87 (m, 12H; 6 and 52), 7.94 (br s, 8H; 32), 8.05 (br s, 4H; 30), 8.23 (br s, 4H; 22), 8.28 (br s, 8H; 28), 8.34 (br s 8H; 35), 8.59 (s, 4H; 14), 8.67 (s, 8H; 42), 8.75 (s, 4H; 4), 9.99 (s, 4H; 26); ^{13}C NMR, APT (75.461 MHz, $CDCl_3$, 23.5 °C, TMS): δ (CH_3 and CH) = 56.40, 61.53, 61.90, 62.04, 113.42, 121.67, 123.74, 124.85, 125.32, 125.51, 126.84, 127.98, 128.49, 128.55, 129.34, 129.64, 130.14, 132.99, δ (CH_2 and C) = 36.51, 39.42, 39.60, 39.80, 41.19, 45.22, 67.26, 68.95, 118.21, 124.97, 125.58, 125.87, 126.27, 127.13, 128.98, 130.27, 133.78, 135.07, 135.46, 138.92, 153.11, 153.25, 153.51, 154.82, 163.57, 166.74, 166.92, 167.23, 172.66; IR ($CHCl_3$): $\nu = 1532.9$ cm^{-1} (amide II), $\nu = 1650.0$ cm^{-1} (amide I), $\nu = 3363.7$ cm^{-1}(N–H); Mass spectrum (FAB, dithiothreitol–dithioerythritol): *m/z* (%): 5843.9 (100) [$M^+ + H$] (for $M = C_{353}H_{312}N_{28}O_{56}$ calc. 5842.5).

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