Synthesis and Characterization of Axially Chiral Molecules Containing Dendritic Substituents

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Received November 10, 1997

Keywords: Chirality / Dendrimers / Chiral auxiliaries

Enantiomerically pure, axially chiral (*S*)-1,1′-bi-2-naphthol has been used as a core material to which Fréchet-type dendritic wedges of the zeroth up to the fourth generation were attached, yielding the first axially chiral dendrimers **1–5**. The chiroptical features of these compounds were studied and revealed an increasing molar optical activity for higher generations of dendrimers. This effect can be explained by a larger torsional angle between the naphthyl units, caused by steric repulsions between the dendritic wedges. However, the effect is marginal, indicating a high degree of flexibility present in the axially chiral dendrimers.

Introduction

The cooperative action of chiral entities in macromolecular systems has revealed a number of intriguing properties, demonstrating the effects of chirality both at the local and the mesoscopic level.[1] By combining the asymmetry of chirality with the high degree of symmetry present in dendrimers,[2] a new class of materials is produced: chiral dendrimers.[3] Since the first patents by Denkewalter et al.[4] and the pioneering papers of Tomalia and Newkome[2b][2c] the field of dendrimers has developed immensely, leading to a large variety of different nanosized chiral architectures.[3] A number of advanced applications that are foreseen for these dendrimers rely on the chirality of the system, e.g. biocompatibility, molecular recognition, and asymmetric catalysis, while chirality in dendrimers can also be used as a very effective tool for studying interactions within the overall structure of the dendrimer. A fascinating example of molecular recognition has been reported by the group of Seebach et al.[5] In addition, we have used chirality in dendrimers to study both the density in the shell of the dendritic box as well as the molecular recognition of guests encapsulated within the box.[6] In these and many other studies on chiral dendrimers,[7][8][9] it is noteworthy that the chirality is almost always introduced by using stereocenters. So far, only one example is known in which planar dissymmetry is reported;[10] however, no examples are known to us that rely on axial chirality.

In many studies Fréchet-type[2f][2g] dendritic wedges and polyether dendrimers are employed because of the high purity that can be obtained by using the convergent approach. Our recent studies of chiral objects[11] and the studies reported by Schlüter et al.[12] of dendritic cylinders revealed that dendrimers using the Fréchet wedges are rather flexible and that interactions between the different groups are only present at very high generations of dendrimers. In the experiments reported in this paper, we have used enantiomerically pure, axially chiral (*S*)-1,1′-bi-2-naphthol as a chiral core molecule. This compound is well known for the strong dependence of its optical activity on the torsional angle between the two naphthyl units, as was demonstrated for a series of modified bridged 1,1′-binaphthyl-2,2′-diethers.[13] We have attached the Fréchet wedges to the enantiomerically pure bisnaphthyl unit. The molar optical rotation of these dendrimers has been used to probe the effect of steric hindrance of the wedges of different generation on the torsional angle of the bisnaphthyl unit.

Results and Discussion

The synthesis of the axially chiral dendrimers (Scheme 1) was performed according to the strategy for the synthesis of the dendritic wedges introduced by Fréchet[2f][2g] using (*S*)-1,1′-bi-2-naphthol as the core molecule. The dendrimer of the zeroth generation was produced using DMF as the solvent with NaH as a base. For the remaining dendrimers (*S*)-(−)-1,1′-bi-2-naphthol in its enantiomerically pure form, as shown by HPLC using a Pirkle column, was reacted with the bromide of the Fréchet-type dendritic wedges using potassium carbonate as the base and acetone as the solvent, while 18-crown-6 was used as phase-transfer catalyst. Purification was accomplished by precipitation and/or column chromatography. HPLC analysis, using a chiral Pirkle column was used to check if racemization had occurred during the reaction. The use of this technique on the dendrimer-modified binaphthyls proved impossible due to the fact that no difference could be made between the two enantiomers, indicating the flexible nature of these compounds. Therefore, we focussed our attention on a model compound, 2,2′-dimethoxy-1,1′-binaphthalene; the syn-

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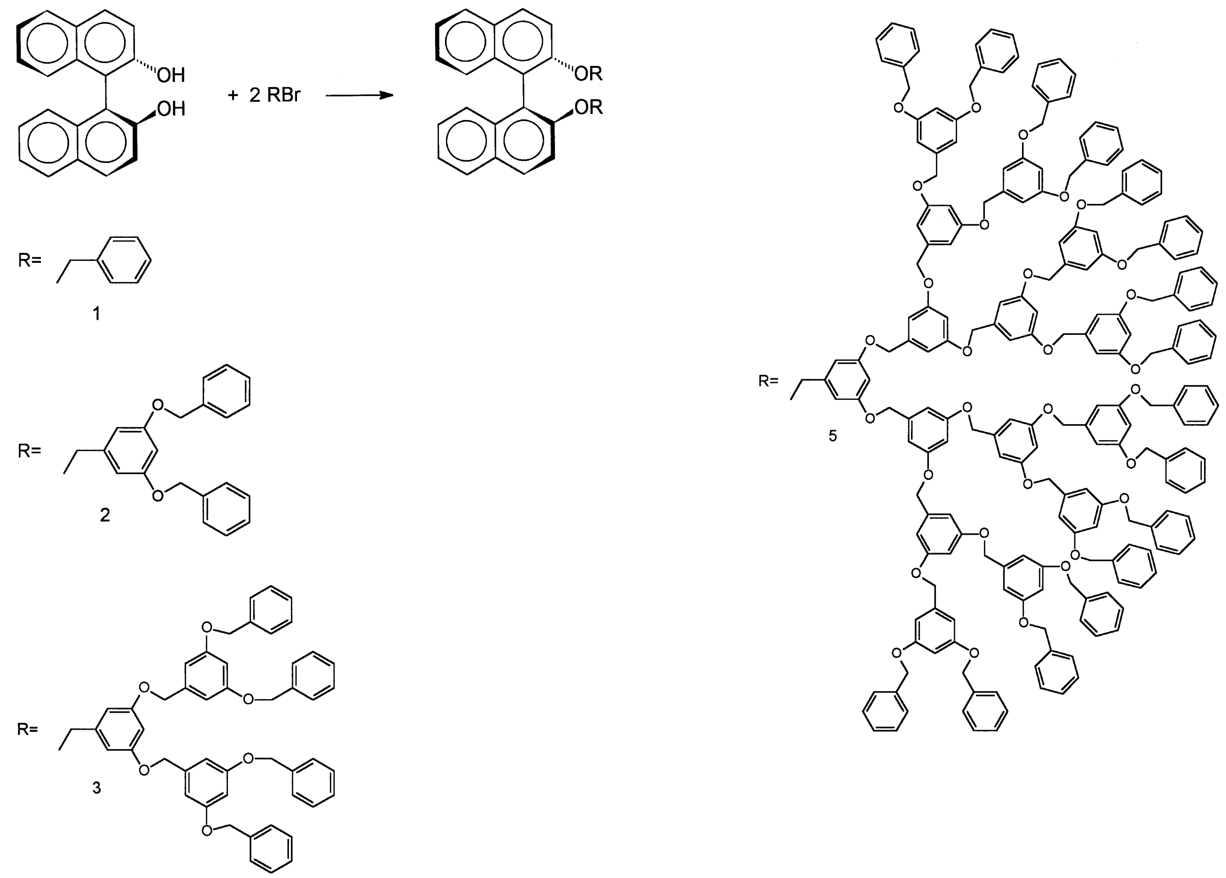
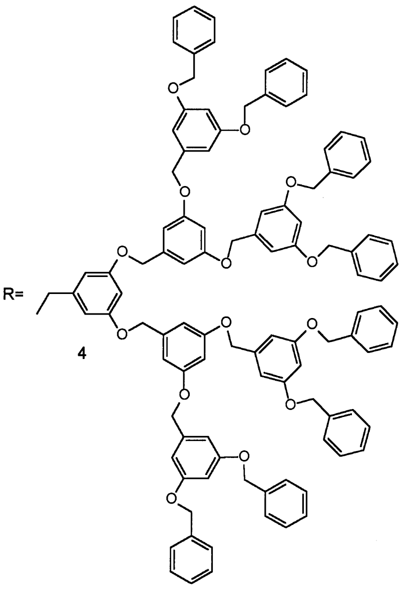
Scheme 1. The (*S*)-(−)-1,1′-bi-2-naphthol based dendrimers **1−5**





thetic procedure used for the alkylation, did not lead to any racemization.

All ^{1}H-, ^{13}C-NMR, FTIR, UV and LSIMS/MALDI-TOF-MS spectroscopic data are in full agreement for the compounds synthesized. Characterization using ^{13}C-NMR spectroscopy is based on an XHCORRD-correlation NMR experiment of 2,2′-dimethoxy-1,1′-binaphthalene, a compound well-documented in the literature.[13] In the characterization of the dendrimers using ^{13}C-NMR spectroscopy the signal for C-5 of the bisnaphthol unit is missing, which is probably due to an overlap with a signal from the phenyl end group of the dendritic wedge. Also, the LSIMS mass data (for compounds **1−4**) and the MALDI-TOF-MS data (for **5**) are in good agreement for the compounds obtained (Table 1). However, for **4** a signal is present that can be attributed to a dendritic wedge of the third generation in which carbon−carbon coupling has taken place. This is also well known from the literature.[2f][2g] ^{1}H-NMR spectroscopy was used to determine the amount of carbon−carbon coupling in this denditic wedge, although no significant signal from this compound could be detected.

Table 1. Mass data for the axially chiral dendrimers **1−5**

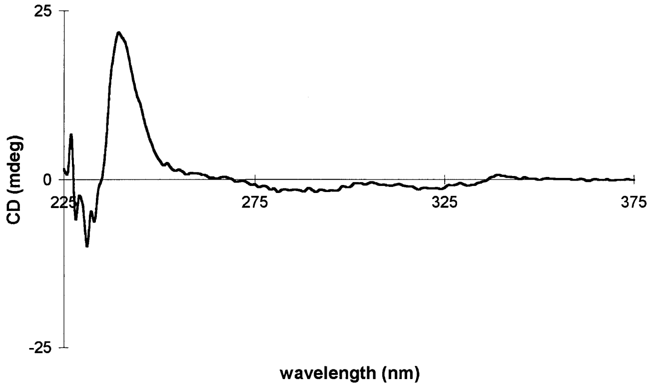
Compound	Calculated mass	Mass found
1	466.59	466 (M)
2	891.09	891(M)/913 (M + Na)
3	1740.07	1739 (M)
4	3438.03	3461 (M + Na)
5	6833.99	6874 (M + K)

For the chiroptical features of these compounds the molar optical rotation was determined for the dendrimers using CH_2Cl_2 as a solvent and the results are depicted in Table 2. (Negative values for the optical rotation were also observed when using acetone or toluene as a solvent). Roughly constant values for the molar rotation as measured at 589 nm were obtained for the dendrimers of the zeroth and first generation of approximately −200, whereas an increase was observed to −271, −424 and −650 for dendrimers of the second, third and fourth generation, respectively. For compounds **1−5** Optical Rotatory Dispersion (ORD) and Circular Dichroism (CD) studies were also performed. These studies confirmed the optical rotation data, but gave no additional information concerning the local chirality in the core or wedges. A typical CD spectrum for compound **2** is shown in Figure 1.

Table 2. The optical rotation for the bisnaphtol dendrimers **1−5**

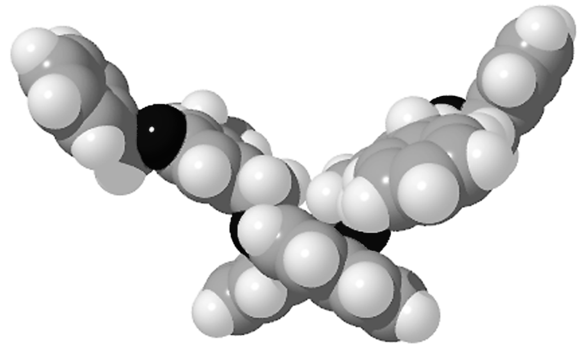
Generation	$[\alpha]_D^{20}$	Molecular weight (g/mol)	Molar rotation
1	−45.5	466.59	−212
2	−22.8	891.09	−203
3	−15.6	1740.07	−271
4	−12.3	3438.03	−424
5	−9.5	6833.99	−650

Figure 1. Circular dichroism (CD) spectrum of **2**



When comparing the molar optical rotations of **1−5** to the data for the aforementioned bridged enantiomerically pure (*S*)-1,1′-binaphthyl-2,2′-diethers,[13] the latter are shown to have positive values for the molar optical rotations ranging from +739 for the compound with a butane spacer up to +2324 for a methane spacer. This is in sharp contrast to the dendrimers which exhibit a negative value for the optical rotation. These results prompted us to conclude that for the bridged systems a high degree of conformational rigidity is present with a small torsional angle between the two naphthyl units, leading to a positive optical rotation. The dendrimers on the other hand, showed negative values for the optical rotation, indicating a torsional angle between the naphthyl units exceeding 90°, due to steric repulsions between the dendritic wedges. A molecular modelling picture of **2** is presented in Figure 2. By going to higher generations of dendrimers, the steric hindrance between the dendritic wedges leads to larger negative values for the molar optical rotation.

Figure 2. Molecular modelling presentation of **2**



In conclusion, we have observed an increasingly negative value for the molar optical rotation in going to higher generations of dendrimers. This can be attributed to steric repulsions between the dendritic wedges, causing a larger torsional angle between the two naphthyl units, which is reflected in a larger negative value for the optical rotation. However, the effects are not as dramatic compared to the sterically congested alkyl ether bridged systems,[13] indicating the conformational freedom of the dendritic wedges. In the near future we intend to focus our attention on sterically more congested analogs of these type of dendrimers.

P.M. van Lier is gratefully acknowledged for providing us with the enantiomerically pure (*S*)-(−)-2,2′-bi-naphthol. *Peter R. Ashton* and *Sergey A. Nepogodiev* from the University of Birmingham are acknowledged for the measurements of the mass spectra of the dendrimers. *Bert Groenendaal* at the University of Berkeley is acknowledged for the MALDI-TOF-MS measurement of compound **5** and for providing us with the [G-4]Br. Part of this investigation was supported by *The Netherlands Foundation for Chemical Research (SON)*, with financial aid from *The Netherlands Organization for Scientific Research (NWO)*. *DSM Research* is gratefully acknowledged for an unrestricted research grant.

Experimental Section

General: Solvents were of c.p. quality, except those used as reaction solvents which were of p.a. quality. − ^{1}H-NMR spectra: Bruker AM-400 (400.1 MHz); internal standard tetramethylsilane (TMS). − ^{13}C-NMR spectra: Bruker AM-400 (100.6 MHz); internal standard tetramethylsilane (TMS). − Column chromatography: Silica gel 60 (Merck: particle size 0.063−0.200 mm). − Thin layer chromatography (TLC): Foil plates, silica gel 60 F_{254} (Merck: layer thickness 0.2 mm). − IR spectra: Perkin Elmer 1600 series FT-IR (data in cm^{-1}). − ORD/CD measurements: Jasco 600 spectropolarimeter (using CH_2Cl_2 as a solvent, distilled from P_2O_5). − Optical rotations: Jasco DIP-370 digital polarimeter. − LSIMS spectra: VG ZabSpec mass spectrometer, using a *p*-nitrobenzyl alcohol matrix (University of Birmingham). − Microanalyses were performed on a Perkin Elmer 2400 series II machine. - MALDI-TOF-MS: Voyager DE spectrometer with an α-cyano-4-hydroxycinnamic acid matrix (University of Berkeley). − The following abbreviations are used in the peak assignment: Ar refers to aromatic rings derived from 3,5-dihydroxybenzyl alcohol or bromide at the reactive center. Ar′, Ar′′ and Ar′′′ refer to the aromatic rings derived from 3,5-dihydroxybenzyl alcohol, one, two and three generations from the reaction center, respectively. Ph refers to aromatic rings derived from benzyl alcohol. − The Fréchet-type dendritic wedges were synthesized as described in the literature.[2f][2g]

Binaphthalene Dendrimer (**1**): To a solution of (*S*)-1,1′-bi-2-naphthol (0.57 g, 2.0 mmol) in DMF (30 ml) was added pentane-washed sodium hydride (0.30 g, 13 mmol). After stirring at room temp. for 1 h, benzylbromide (0.70 g, 4.1 mmol) was added and the mixture was heated at 75°C for 4 d. Then water (2 ml) was added to the mixture and the solvent was evaporated in vacuo, yielding the crude product, which was purified by column chromatography (toluene). This furnished pure **1** (0.81 g, 1.74 mmol, 87%) as a yellowish glass-like substance. − TLC (toluene): R_f = 0.65. − $[\alpha]_D^{20}$ = −45.5 (*c* = 0.47, CH_2Cl_2). − ^1H NMR (400 MHz, $CDCl_3$): δ = 4.96 (s, 4 H, C*H*$_2$Ph), 6.91 (dd, *J* = 7.4 and 1.7 Hz, 2 H, PhH-*ortho*), 7.01−7.06 (m, 2 H, PhH-*meta*), 7.05 (d, *J* = 9.0 Hz, 2 H, H-8), 7.16 (ddd, *J* = 7.8, 6.4 and 1.1 Hz, 2 H, H-7), 7.21 (t, *J* = 7.8 Hz, 2 H, PhH-*para*), 7.26 (ddd, *J* = 8.0, 6.5 and 1.4 Hz, 2 H, H-6), 7.34 (d, *J* = 9.0 Hz, 2 H, H-3), 7.80 (d, *J* = 8.2 Hz, 2 H, H-5), 7.84 (d, *J* = 9.0 Hz, 2 H, H-4). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 71.0 (*C*H$_2$Ph), 115.9 (C-3), 120.6 (C-1), 123.6 (C-6), 125.5 (C-8), 126.3 (C-7), 126.6, 127.2, 128.0, (PhCH), 127.8 (C-5), 129.2 (C-4) 129.4 (C-4a), 134.1 (C-8a), 137.5 (PhC-*ipso*), 154.0 (C-2). − IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (=C−H), 2925 and 2866 (−CH$_2$−), 1621, 1590, 1506 (C=C), 1452 (CH$_2$), 1270 (arylalkyl ether). − Mass spectra for $C_{34}H_{26}O_2$ (calculated mass: 466.58), found: 466 [M]. − $C_{34}H_{26}O_2$: calcd. C 87.53, H 5.62; found C 87.56, H 5.74.

Binaphthalene Dendrimer (**2**): A mixture of (*S*)-(−)-1,1′-bi-2-naphthol (145 mg, 0.506 mmol), 3,5-bis(benzyloxy)benzyl bromide (397,4 mg, 1.037 mmol), 18-crown-6 (0.03 g, 0.1 mmol) and potassium carbonate (2.5 g, 18 mmol) in acetone (40 ml) was heated under reflux with vigorous stirring for 2 d. The reaction mixture was allowed to cool to room temp. and the salts were removed by filtration. The filtrate was concentrated in vacuo and the residue was precipitated with methanol twice. Removal of the last traces of solvent in vacuo yielded pure **2** (0.37 g, 0.42 mmol, 83%) as a slightly yellow foam. − $[\alpha]_D^{20}$ = −22.8 (*c* = 0.89, CH_2Cl_2). − ^1H NMR: (400 MHz, $CDCl_3$): δ = 4.60 (2*d, *J* = 11.6 Hz, 8 H, ArOC*H*$_2$Ph), 4.99 (s, 4 H, CH$_2$Ar), 6.20 (d, *J* = 2.1 Hz, 4 H, ArH-2,6), 6.35 (t, *J* = 2.1 Hz, 2 H, ArH-4), 7.21−7.37 (m, 26 H, PhH, H-6, H-7, H-8), 7.44 (d, *J* = 9.0 Hz, 2 H, H-3), 7.77 (d, *J* = 8.0 Hz, 2 H, H-5), 7.88 (d, J = 9.0 Hz, 2 H, H-4). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 69.7 (ArO*C*H$_2$Ph), 70.8 (*C*H$_2$Ar), 101.4 (ArC-4), 105.0 (ArC-2,6), 115.6 (C-3), 120.6 (C-1), 123.8 (C-6), 125.4 (C-8), 126.5 (C-7), 127.7, 127.9, 128.5 (PhCH), 129.3 (C-4a), 129.4 (C-4), 134.1 (C-8a), 136.8 (PhC-*ipso*), 139.9 (ArC-1), 153.9 (C-2), 159.7 (ArC-3,5). − IR (KBr): $\tilde{\nu}$ = 3031 cm^{-1} (=C−H), 2927 and 2868 (−CH$_2$−), 1595 and 1507 (C=C), 1452 (CH$_2$), 1264 (arylalkyl ether). − Mass spectra for $C_{62}H_{50}O_6$ (calculated mass: 891.07), found: 891 [M], 913 [M + Na]. − $C_{62}H_{50}O_6$: calcd. C 83.57, H 5.66; found C 83.76, H 5.72.

Binaphthalene Dendrimer (**3**): A mixture of (*S*)-(−)-1,1′-bi-2-naphtol (143.6 mg, 0.502 mmol), 3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyl bromide (0.82 g, 1.02 mmol), 18-crown-6 (0.03 g, 0.1 mmol) and potassium carbonate (2.5 g, 18 mmol) in acetone (50 ml) was heated under reflux with vigorous stirring for 2 d. The reaction mixture was allowed to cool to room temp. and the salts were removed by filtration. The filtrate was concentrated in vacuo and was precipitated with methanol. Removal of the last traces of solvent in vacuo furnished pure **3** (0.85 g, 0.489 mmol, 97%) as a slightly yellow foam. − $[\alpha]_D^{20}$ = −15.6 (*c* = 1.74, CH_2Cl_2).− ^1H NMR (400 MHz, $CDCl_3$): δ = 4.47 (s, 8 H, ArOC*H*$_2$Ar′), 4.93 (s, 20 H, C*H*$_2$Ar, Ar′OC*H*$_2$Ph), 6.14 (d, *J* = 2.1 Hz, 4 H, ArH-2,6), 6.28 (t, *J* = 2.1 Hz, 2 H, ArH-4), 6.54 (t, *J* = 2.2 Hz, 4 H, Ar′H-4), 6.57 (d, *J* = 2.2 Hz, 8 H, Ar′H-2,6), 7.15−7.38 (m, 48 H, PhH, H-3, H-6, H-7, H-8), 7.69 (dd, *J* = 8.5 and 1.5 Hz, 2 H, H-5), 7.79 (d, *J* = 9.0 Hz, 2 H, H-4). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 69.5 (ArO*C*H$_2$Ar′), 69.9 (Ar′O*C*H$_2$Ph), 70.6 (*C*H$_2$Ar), 101.2 (ArC-4), 101.4 (Ar′C-4), 105.0 (ArC-2,6), 106.5 (Ar′C-2,6), 115.5 (C-3), 120.5 (C-1), 123.7 (C-6), 125.3 (C-8), 126.4 (C-7), 127.4, 127.9, 128.5 (PhCH), 129.3 (2*, C-4a, C-4), 134.0 (C-8a), 136.7 (PhC-ipso), 139.1 (Ar′C-1), 139.8 (ArC-1), 153.7 (C-2), 159.5 (ArC-3,5), 160.0 (Ar′C-3,5). − IR (KBr): $\tilde{\nu}$ = 3061 and 3031 cm^{-1} (=C−H), 2927 and 2869 (−CH$_2$−), 1595 and 1497 (C=C), 1451 (CH$_2$). − Mass spectra for $C_{118}H_{98}O_{14}$ (calculated mass: 1740.06), found: 1739.4 [M]. − $C_{118}H_{98}O_{14}$: calcd. C 81.45, H 5.68; found C 81.59, H 5.73.

Binaphthalene Dendrimer (**4**): A mixture of (*S*)-(−)-1,1′-bi-2-naphthol (143.0 mg, 0.499 mmol), 3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}benzyl bromide (1.68 g, 1.01 mmol), 18-crown-6 (0.03 g, 0.1 mmol) and potassium carbonate (2.5 g, 18 mmol) in acetone (50 ml) was heated under reflux with vigorous stirring for 2 d. The reaction mixture was allowed to cool to room temp. and the salts were removed by filtration. Column filtration (DCM/toluene, 4:1) furnished pure **4** (1.35 g, 0.39 mmol, 79%) as a slightly yellow foam. − TLC (DCM/toluene, 4:1): R_f = 0.5. − $[\alpha]_D^{20}$ = −12.3 (*c* = 1.01, CH_2Cl_2). − ^1H NMR (400 MHz, $CDCl_3$): δ = 4.41 (s, 8 H, ArOC*H*$_2$Ar′), 4.84 (s, 16 H, Ar′OC*H*$_2$Ar″), 4.92 (s, 36 H, C*H*$_2$Ar, Ar″OC*H*$_2$Ph), 6.11 (d, *J* = 2.1 Hz, 4 H, ArH-2,6), 6.23 (t, *J* = 2.1 Hz, 2 H, ArH-4), 6.50−6.53 (m, 20 H, Ar′H-2,6, Ar′H-4, Ar″H-4), 6.63 (d, *J* = 2.1 Hz, 16 H, Ar″H-2,6), 7.16−7.32 (m, 86 H, PhH, H-6, H-7, H-8), 7.35 (d, *J* = 9.0 Hz, 2 H, H-3), 7.69 (d, *J* = 7.7 Hz, 2 H, H-5), 7.77 (d, *J* = 9.0 Hz, 2 H, H-4). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.6 (ArO*C*H$_2$Ar′), 69.8 (Ar′O*C*H$_2$Ar″), 70.0 (Ar″O*C*H$_2$Ph), 70.5 (CH$_2$Ar), 101.0 (ArC-4), 101.5 (Ar″C-4), 101.6 (Ar′C-4), 105.1 (ArC-2,6), 106.3 (Ar″C-2,6), 106.6 (Ar′C-2,6), 115.5 (C-3), 120.6 (C-1), 123.8 (C-6), 125.3 (C-8), 126.5 (C-7), 127.5, 127.9, 128.5 (PhCH), 129.3 (2*, C-4, C-4a), 134.1 (C-8a), 136.7 (PhC-*ipso*), 139.2 (Ar′C-1), 139.3 (Ar″C-1), 139.8 (ArC-1), 153.7 (C-2), 159.6 (ArC-3,5), 159.9 (Ar′C-3,5), 160.1 (Ar″C-3,5). − IR (KBr): $\tilde{\nu}$ = 3060 and 3030 cm^{-1} (=C−H), 2926 and 2869 (−CH$_2$−), 1595 and 1497 (C=C), 1451 (CH$_2$). − Mass spectra for $C_{230}H_{194}O_{30}$ (calculated mass: 3438.04), found: 3461 [M + Na], 4187 [M + (G − 2) + Na]. − $C_{230}H_{194}O_{30}$: calcd. C 80.35, H 5.69; found C 80.52, H 5.73.

Binaphthalene Dendrimer (**5**): A mixture of (*S*)-(−)-1,1′-bi-2-naphthol (4.303 mg, 15.0 μmol), 3,5-bis(3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}benzyloxy)benzyl bromide (103.5 mg, 30.9 μmol), 18-crown-6 (2.6 mg, 10 μmol) and potassium carbonate (180 mg, 1.3 mmol) in acetone (5 ml) was heated under reflux with vigorous stirring for 2 d. The reaction mixture was allowed to cool to room temp. and the salts were removed by filtration. Column chromatography (DCM/toluene, 5:1) furnished pure **5** (56.8 mg, 8.3 μmol, 55%) as a slightly yellow foam. − TLC (DCM/toluene, 5:1): R_f = 0.6. − $[\alpha]_D^{20}$ = −9.5 (*c* = 0.57, CH_2Cl_2). − ^1H NMR (400 MHz, $CDCl_3$): δ = 4.35 (s, 8 H, ArOC*H*$_2$Ar′), 4.76 (s, 16 H, Ar′OC*H*$_2$Ar″), 4.78 (s, 32 H, (Ar″OC*H*$_2$Ar‴), 4.86 (s, 68 H, CH$_2$Ar, Ar‴OC*H*$_2$Ph), 6.08 (d, *J* = 2.1 Hz, 4 H, ArH-2,6), 6.20 (t, *J* = 2.1 Hz, 2 H, ArH-4), 6.46-6.48 (m, 28 H, Ar′H-4, Ar″H-4, Ar‴H-4), 6.50 (d, *J* = 2.1 Hz, 8 H, Ar′H-2,6), 6.57−6.59 (m, 48 H, Ar″H-2,6, Ar‴H-2,6), 7.05−7.35 (m, 166 H, PhH, H-6, H-7, H-8), 7.37 (d, *J* = 9.0 Hz, 2 H, H-3), 7.67 (d, *J* = 7.7 Hz, 2 H, H-5), 7.74 (d, *J* = 9.0 Hz, 2 H, H-4). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 69.5 (ArO*C*H$_2$Ar′), 69.8 (Ar′O*C*H$_2$Ar″), 69.8 and 69.9 (Ar″O*C*H$_2$Ar‴ and Ar‴O*C*H$_2$Ph), 70.3 (CH$_2$Ar), 100.9 (ArC-4), 101.5 (Ar′C-4, Ar″C-4, Ar‴C-4), 105.1 (ArC-2,6), 106.3 (Ar″C-2,6, Ar‴C-2,6), 106.5 (Ar′C-2,6), 115.4 (C-3), 120.4 (C-1), 123.7 (C-6), 125.3 (C-8), 126.4 (C-7), 127.5, 127.9, 128.5 (PhCH), 129.3 (2*, C-4, C-4a), 134.1 (C-8a), 136.7 (PhC-*ipso*), 139.1, 139.3 (Ar′C-1, Ar″C-1, Ar‴C-1), 139.8 (ArC-1), 153.6 (C-

2), 159.5 (ArC-3,5), 159.8 (Ar′C-3,5), 159.9 (Ar″C-3,5), 160.0 (Ar‴C-3,5). − IR (KBr): $\tilde{\nu}$ = 3062 and 3030 cm^{-1} (=C−H), 2919 and 2870 (−CH$_2$−), 1594 and 1497 (C=C), 1449 (CH$_2$). − Mass spectra for $C_{454}H_{386}O_{62}$ (calculated mass: 6833.99), found: 6873.7 [M + K]. − $C_{454}H_{386}O_{62}$: calcd. C 79.79, H 5.69; found C 79.61, H 5.80.

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