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Chiroptical properties of dendrimers with stereogenic end groups

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Abstract: The synthesis of dendrimers with stereogenic end groups **3*S*-[G_n]** and **3*R*-[G_n]** (**n**=1–4, 7), obtained from the condensation of (*S*)-(−)-α-methylbenzylamine, or (*R*)-(+)-α-methylbenzylamine with aldehyde terminated dendrimers is described up to the seventh generation (up to 384 stereogenic groups). The chemiospecific reduction of the imine bonds thus created affords two new series of stereogenic dendrimers **4*S*-[G_n]** and **4*R*-[G_n]** (**n**=1–4). Then, the reaction with Ph_2PCH_2OH gives a series of stereogenic phosphino terminated dendrimers **5*S*-[G_n]** and **5*R*-[G_n]** (**n**=1–4). Studies of the chiroptical properties of all these non-hindered stereogenic dendrimers indicate that each terminal group behaves independently and that the specific rotation depends only on the number of stereogenic groups grafted on the dendrimer, whatever the generation is. © 1997 Published by Elsevier Science Ltd

Introduction

The nanoscopic size of dendrimers,[1] their definite structure, and above all the possibility to follow the evolution of properties as a function of the number of generations, render dendrimers highly attractive for the study of chiroptical properties of macromolecules, both from a fundamental point of view and in the perspective of asymmetric catalysis.[2] Several ways of synthesis of stereogenic dendrimers have been described in the past few years, most of them being derived from the natural "chiral pool" materials;[3] generally, the chiroptical properties of these dendrimers have not been reported. Some recent papers deal with racemic dendrimers[4] or with very small stereogenic dendrimers (core or first generation).[2a–c,5] However, few reports concern studies of stereogenic dendrimers with more than two layers. Seebach *et al.* have shown that the specific activity of a dendrimer with a stereogenic core and achiral branches decreases from generation one to generation three, as could be anticipated.[6] The behaviour is less clear for "fully" stereogenic dendrimers, where both the core and the building units of the branches are chiral: Seebach *et al.* observed a reversal of the sense of rotation on going from the first to the second generation, or from the second to the third, which might be due to conformationally stereogenic substructures in the stereogenic branches,[6a,7] whereas Sharpless *et al.* observed that the molar specific rotation is approximately proportional to the number of stereogenic units up to the fourth generation.[8] Recently, McGrath *et al.* have reported a convergent synthesis of fully stereogenic dendrons and observed in several cases only small change in molar rotation per stereogenic unit on going from zeroth to second generation.[9]

The behaviour of dendrimers with stereogenic substituents only on the surface is also rather puzzling: Newkome *et al.* reported that the molecular ellipticity (θ) increases proportionate to the number of stereogenic groups up to generation two,[10] whereas Meijer *et al.* showed that all the amino acid terminated dendrimers they studied undergo a decrease to almost zero of their specific rotation on going from the first to the fifth generation.[11] This behaviour is presumably due to the rigidity of the surface shell, the dense packing being enhanced by hydrogen bonding, which leads to a number of conformations that are frozen.[11a] The dense packing for this series of dendrimers has been proved by the encapsulation of various hosts,[12] and some of these hosts display an interesting induced specific activity.[13] On the other hand, the use of modified amino acids with less N–H bonds give

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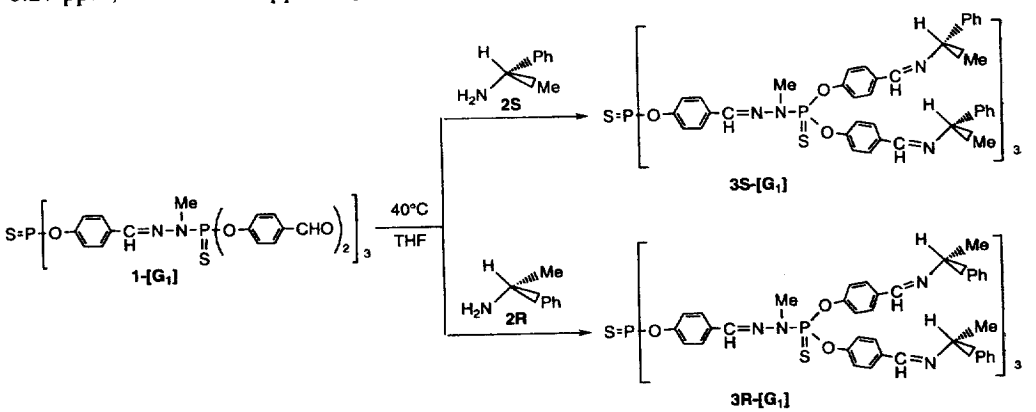
dendrimers whose specific rotation remains constant for all generations.[11a,b] Vögtle also reported a nearly constant specific activity with increasing generations for dendrimers bearing planar stereogenic paracyclophane.[14]

It appears from all these results that the chiroptical properties of sterically non-hindered dendrimers with stereogenic end groups have never been studied up to high generations. We have already reported a method of synthesis of dendrimers which does not undergo the dense packing phenomenon at least up to the eleventh generation[15] due to the use of long building units (nine bonds). We have also demonstrated that these dendrimers display a versatile reactivity,[15b,c,16] which make them very suitable candidates to study the variation of chiroptical properties as a function of generations.

Results and discussion

Syntheses

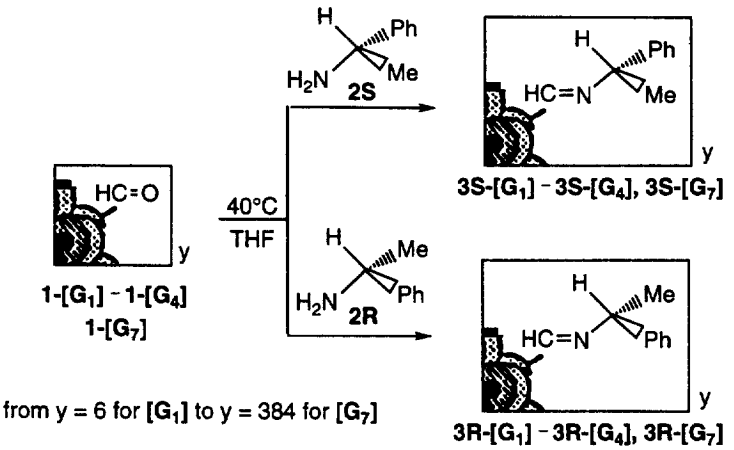
The family of dendrimers we have already described bears either -$P(S)Cl_2$ or -CHO functions as end groups, depending on the step of the construction considered.[15] We choose to use dendrimers with aldehyde end groups to perform reactions with methylbenzylamine (both separated enantiomers). The condensation was first carried out with the first generation of the dendrimer **1-[G_1]** (6 aldehyde end groups) and 6 equivalents of (*S*)-(−)-α-methylbenzylamine **2*S***, or (*R*)-(+)-α-methylbenzylamine **2*R***, heating for 24h at 40°C in THF (Scheme 1). The formation of dendrimers **3*S*-[G_1]** (or **3*R*-[G_1]**) induces a slight deshielding of the signal corresponding to the three phosphorus of the first generation P_1 (δ ^{31}P=60.0 ppm for **1-[G_1]**; δ ^{31}P=61.7 ppm for **3*S*-[G_1]** or **3*R*-[G_1]**). The condensation is also unambiguously characterised by the total disappearance of the signals of the aldehyde groups and the appearance of signals corresponding to the imine groups in ^{1}H and ^{13}C NMR, and IR spectra (δ ^{1}H=8.27 ppm; δ ^{13}C=158.0 ppm; $\nu_{C=N}$=1644 cm^{-1}).



Scheme 1.

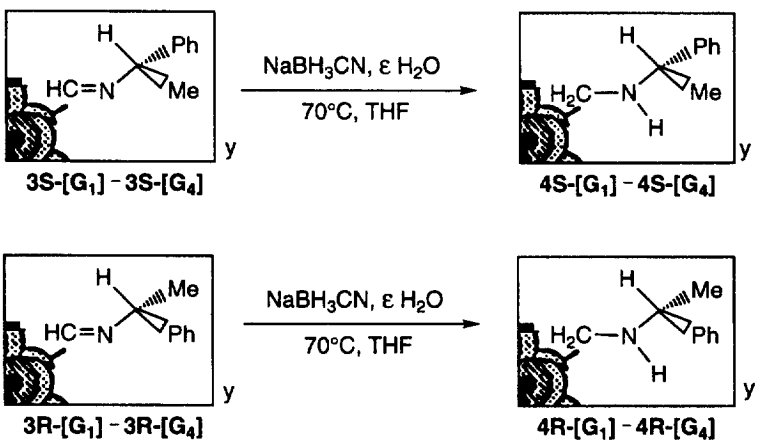
Analogous condensation reactions have been carried out starting from the second, the third, the fourth and even the seventh generation of the dendrimer **1-[G_n]** (12, 24, 48, and 384 aldehyde end groups, respectively) (Scheme 2). In all cases, the condensation occurs quantitatively and affords dendrimers **3*S*-[G_n]** or **3*R*-[G_n]** (**n**=2, 3, 4, 7) in very good yield after work up. All these compounds are characterised by NMR, IR and elemental analyses as were **3*S*-[G_1]** and **3*R*-[G_1]**.

Both series of stereogenic dendrimers with imine end groups **3*S*-[G_n]** and **3*R*-[G_n]** (**n**=1–4) are precursors of two new series of stereogenic dendrimers **4*S*-[G_n]** and **4*R*-[G_n]**, obtained by reduction of the imine bonds. To perform this reaction, we choose a mild reducer, $NaBH_3CN$ with a catalytic amount of water in THF, in order to reduce only the imine bonds and not the hydrazone functions of the skeleton of the dendrimer. The reduction of all the imine groups occurs after heating for five days at 70°C (Scheme 3). In all cases, the reduction induces in ^{31}P NMR a slight deshielding of the signal



Scheme 2.

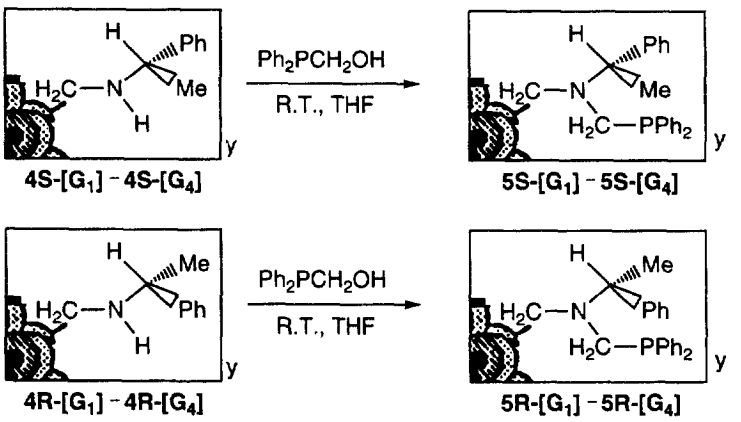
corresponding to the phosphorus of the external layer. The formation of dendrimers **4*S*-[G$_1$]–4*S*-[G$_4$]** and **4*R*-[G$_1$]–4*R*-[G$_4$]** is characterised in ^{1}H NMR by the disappearance of the signal of the imine functions and the appearance of signals corresponding to the CH_2-NH groups (δ=1.56–1.96 ppm, NH; δ=3.50–3.54 ppm, CH_2). Furthermore, the chemiospecificity of the reduction is demonstrated by ^{13}C NMR, which displays not only a singlet for the CH_2-NH groups (δ=50.8–51.0 ppm) but also a doublet for the CH=N-N groups (δ=137.7–138.5 ppm, J_{CP}=11.8–14.5 Hz), which proves the absence of reduction of the hydrazone bonds.



Scheme 3.

The presence of N–H bonds incited us to try to graft phosphines on the stereogenic dendrimers **4*S*-[G$_1$]–4*S*-[G$_4$]** and **4*R*-[G$_1$]–4*R*-[G$_4$]**, using the procedure we already described for achiral dendrimers.[16b,d] The reaction of Ph_2PCH_2OH[17] with **4*S*-[G$_1$]–4*S*-[G$_4$]** or **4*R*-[G$_1$]–4*R*-[G$_4$]** occurs at room temperature in THF and affords in good yield the corresponding stereogenic phosphino terminated dendrimers **5*S*-[G$_1$]–5*S*-[G$_4$]** and **5*R*-[G$_1$]–5*R*-[G$_4$]** as powders very sensitive to oxidation (Scheme 4, Figure 1). The characterisation of these compounds by ^{31}P NMR shows in particular the presence of a singlet at δ=−26.8 ppm corresponding to the $Ph_2PCH_2NR^*$ groups, whereas ^{13}C NMR

displays the presence of two types of CH_2 groups (δ=52.5–52.7, s, C_6H_4-CH_2-N; δ=54.0–54.3, d, $^1J_{CP}$=7.5–9.1 Hz, CH_2-P).



Scheme 4.

Study of chiroptical properties

The five series of dendrimers with stereogenic end groups **3*S*-[G$_1$]–3*S*-[G$_4$]**, **3*S*-[G$_7$]**, **3*R*-[G$_1$]–3*R*-[G$_4$]**, **3*R*-[G$_7$]**, **4*S*-[G$_1$]–4*S*-[G$_4$]**, **4*R*-[G$_1$]–4*R*-[G$_4$]**, and **5*S*-[G$_1$]**, **5*S*-[G$_4$]** appeared to be very suitable for the study of chiroptical properties of dendrimers, versus the number of generation. Studies were first conducted with the stereogenic imine terminated dendrimers **3*R*-[G$_n$]** and **3*S*-[G$_n$]** up to the seventh generation in THF. The sign of the specific rotation changes on going from the methylbenzylamine to the imine **3-[G$_1$]**; ([α]$_D$=−39 for **2*S***, [α]$_D$=+79.0 for **3*S*-[G$_1$]**; [α]$_D$=+38 for **2*R***, [α]$_D$=−79.2 for **3*R*-[G$_1$]**). The same phenomenon occurs for all the other generations. We also observed that the specific rotation slightly decreases when the number of generations increases ([α]$_D$=+79.0 for **3*S*-[G$_1$]**; [α]$_D$=+59.3 for **3*S*-[G$_7$]**) (Figure 2a), whereas the molar specific rotation increases exponentially with the number of generations (Figure 2b). In order to get the deepest insight into the significance of these observations, we calculated the contribution of each stereogenic unit to the molar specific rotation of the dendrimer. Figure 2c shows that the value of the molar rotation divided by the number of stereogenic units is a constant for all generations, at least up to generation seven. On the other hand, the slight decrease of the specific rotation is easily explained by the fact that the contribution of the stereogenic groups to the molecular weight of the stereogenic dendrimer (calculated as[3×2^n×(M.W. of **2**−H$_2$)]/[M.W. of **3-[G$_n$]**] %) slightly decreases from 35.00% for **3-[G$_1$]** to 27.46% for **3-[G$_7$]**. Indeed, the plot of the absolute value of the mean specific rotation (calculated as {([α]$_D$ of **3*S*-[G$_n$]**)−([α]$_D$ of **3*R*-[G$_n$]**)}/2) versus this theoretical decrease is linear (Figure 2d). We can conclude from these experimental data and calculations that the specific rotation of these series of dendrimers depends only on the number of stereogenic units, without any alteration which could be induced by the dendritic structure. In other words, each terminal group of the dendrimer behaves like an isolated molecule, whatever the generation is.

In order to determine if this behaviour reflects a general trend for non-hindered dendrimers, we determined also the specific rotation of the reduced stereogenic dendrimers **4*S*-[G$_1$]–4*S*-[G$_4$]** and **4*R*-[G$_1$]–4*R*-[G$_4$]**. Here again, we observed a change of the sign of the specific rotation on going from the imine to the amine (for example: [α]$_D$=−79.2 for **3*R*-[G$_1$]**; [α]$_D$=+24 for **4*R*-[G$_1$]**). The specific rotation slightly decreases with the generation (Figure 3a), whereas the molar rotation increases exponentially ([α]$_{mol}$=−54.3 for **4*S*-[G$_1$]**; [α]$_{mol}$=−427.4 for **4*S*-[G$_4$]**) (Figure 3b). These values indicate that the contribution of each stereogenic unit to the molar specific rotation remains a constant

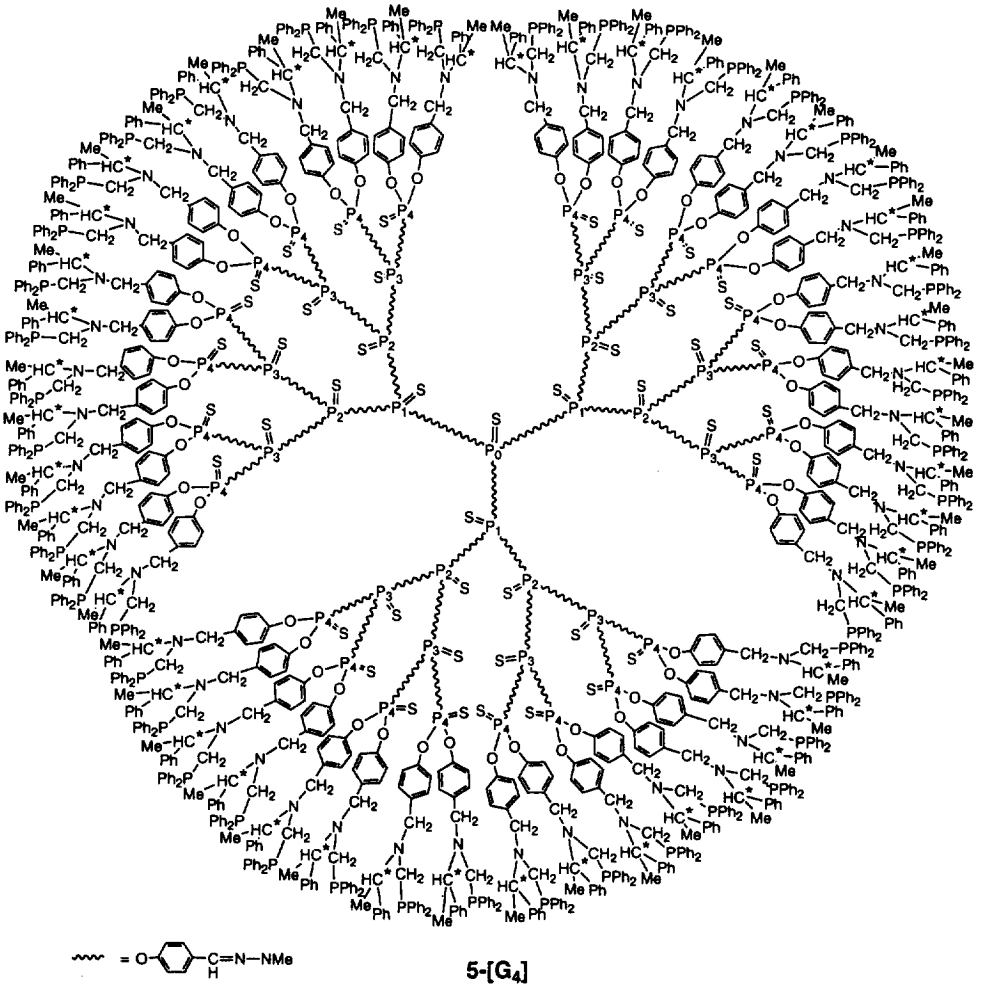


Figure 1. Dendrimer **5-[G$_4$]**.

for all the generations (Figure 3c). The slight decrease of the specific rotation can be explained as previously for dendrimers **3-[G$_n$]** by a lower percentage of contribution of the stereogenic moieties to the molecular weight of the stereogenic dendrimer for high generations (Figure 3d). This means that the conclusions drawn for dendrimers **3-[G$_n$]** are perfectly suitable for the series of dendrimers **4*S*-[G$_n$]** and **4*R*-[G$_n$]** (**n**=1–4).

Furthermore, the specific rotation of the phosphine terminated dendrimers **5*S*-[G$_n$]** (**n**=1, 4) also follows the rules determined for the series **3-[G$_n$]** and **4-[G$_n$]** ($[\alpha]_D$=+22.4, $[\alpha]_{mol}$=+72.4 for **5*S*-[G$_1$]**; $[\alpha]_D$=+17.8, $[\alpha]_{mol}$=+534.5 for **5*S*-[G$_4$]**). These compounds and the corresponding *R* isomers will be interesting to test in asymmetric catalysis.

Conclusion

We have demonstrated for the first time, and for five series of stereogenic dendrimers, that the value of the molar specific rotation of non-hindered dendrimers with stereogenic end groups depends only and linearly on the number of stereogenic groups, whereas the value of the specific rotation depends linearly on the percentage in weight of contribution of the stereogenic groups to the molecular weight

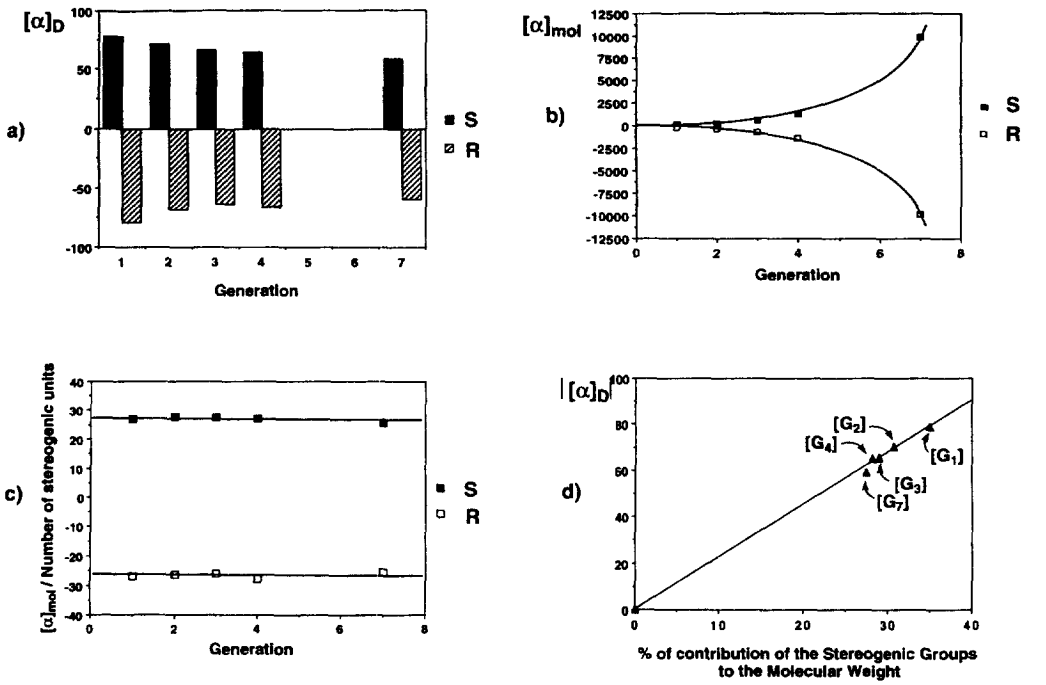


Figure 2. (a) Specific rotation $[\alpha]_D$ versus generation for dendrimers **3*S*-[Gn]** and **3*R*-[Gn]**; (b) molar rotation $[\alpha]_{mol}$ versus generation for dendrimers **3*S*-[Gn]** and **3*R*-[Gn]**; (c) molar rotation $[\alpha]_{mol}$ divided by the number of stereogenic groups versus generation for dendrimers **3*S*-[Gn]** and **3*R*-[Gn]**; (d) absolute value of the specific rotation $|[\alpha]_D|$ versus the percentage of contribution of the stereogenic groups to the molecular weight for dendrimers **3*S*-[Gn]** and **3*R*-[Gn]**.

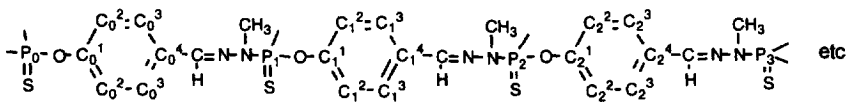
of the stereogenic dendrimer. It can be inferred from these results that each terminal stereogenic group of non-hindered dendrimers behaves like an isolated molecule.

Experimental section

General remarks

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on Bruker AC 200 or WM 250 spectrometers. ^{31}P NMR chemical shifts are reported in ppm relative to 85% H_3PO_4. Specific rotations were measured in THF (c=0.1 g/mL) on a polarimeter Perkin Elmer 241 (λ=589 nm). (*S*)-(−)-α-methylbenzylamine ($[\alpha]_D^{20} = -39$) and (*R*)-(+)-α-methylbenzylamine ($[\alpha]_D^{20} = +38$) were purchased from Aldrich.

The numbering used for ^{13}C and ^{31}P NMR is depicted on the following scheme:



General procedure for the synthesis of imine-terminated dendrimers 3-[Gn]

To a solution of 0.500 g of dendrimer **1-[Gn]** (**n**=1, 0.351 mmol; **n**=2, 0.146 mmol; **n**=3, 0.0675 mmol; **n**=4, 0.0325 mmol, **n**=7, 0.0039 mmol) in THF (20 mL) is added (*R*)-(+)-α-methylbenzylamine **2*R*** or (*S*)-(−)-α-methyl benzylamine **2*S*** (**n**=1, 0.271 mL; **n**=2, 0.226 mL; **n**=3, 0.209 mL; **n**=4, 0.201 mL, **n**=7, 0.195 mL). The resulting mixture is stirred for 24 h at 40°C, then evaporated to dryness. The powder thus obtained is washed with pentane (3×30 mL).

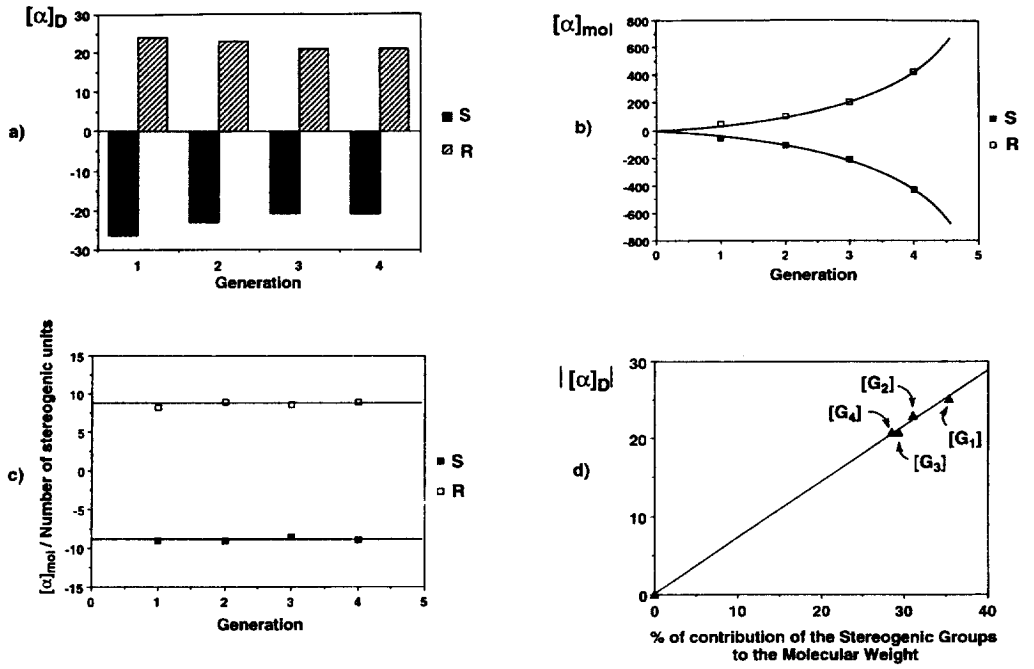


Figure 3. (a) Specific rotation $[\alpha]_D$ versus generation for dendrimers **4*S*-[Gn]** and **4*R*-[Gn]**; (b) molar rotation $[\alpha]_{mol}$ versus generation for dendrimers **4*S*-[Gn]** and **4*R*-[Gn]**; (c) molar rotation $[\alpha]_{mol}$ divided by the number of stereogenic groups versus generation for dendrimers **4*S*-[Gn]** and **4*R*-[Gn]**; (d) absolute value of the specific rotation $|[\alpha]_D|$ versus the percentage of contribution of the stereogenic groups to the molecular weight for dendrimers **4*S*-[Gn]** and **4*R*-[Gn]**.

3-[G_1]: White powder, yield: 90% (**3*S*-[G_1]**), 88% (**3*R*-[G_1]**). ^{31}P {^1H} NMR ($CDCl_3$): δ 52.0 (s, P_0), 61.7 (s, P_1); ^1H NMR ($CDCl_3$): δ 1.53 (d, $^3J_{HH}$=6.6 Hz, 18 H, C*H*$_3$-CH*), 3.32 (d, $^3J_{HP1}$=10.5 Hz, 9 H, CH_3-N-P_1), 4.48 (q, $^3J_{HH}$=6.6 H, 6 H, CH_3-C*H**), 7.28–7.77 (m, 69 H, C_6H_4 CH=N-N and C_6H_5), 8.27 (s, 6 H, C*H*=N-CH*); ^{13}C {^1H} NMR ($CDCl_3$): δ 24.6 (s, *C*H_3-CH*), 32.9 (d, $^2J_{CP1}$=13.4 Hz, CH_3-N-P_1), 69.5 (s, CH_3-*C*H*), 121.4 (br s, C_0^2, C_1^2), 126.4 (s, o-C_6H_5), 126.7 (s, p-C_6H_5), 128.3 (s, m-C_6H_5 and C_0^3), 129.4 (s, C_1^3), 132.4 (s, C_0^4), 133.6 (s, C_1^4), 138.4 (d, $^3J_{CP1}$=13.1 Hz, CH=N-N), 144.9 (s, i-C_6H_5), 151.0 (d, $^2J_{CP0}$=7.0 Hz, C_0^1), 152.1 (d, $^2J_{CP1}$=6.8 Hz, C_1^1), 158.0 (s, *C*H=N-CH*). IR (KBr): 1644 (m, $\upsilon_{C=N}$) cm^{-1}. Anal. Calcd for $C_{114}H_{108}N_{12}O_9P_4S_4$: C, 67.04; H, 5.33; N, 8.23. Found: (**3*S*-[G_1]**): C, 66.89; H, 5.25; N, 8.24. Found (**3*R*-[G_1]**): C, 69.93; H, 5.27; N, 8.18. $[\alpha]_D^{20}$(THF)=+79.0 (**3*S*-[G_1]**); $[\alpha]_D^{20}(THF) = -79.2$ (**3*R*-[G_1]**).

3-[G_2]: White powder, yield: 88% (**3*S*-[G_2]**), 89% (**3*R*-[G_2]**). ^{31}P {^1H} NMR ($CDCl_3$): δ 51.8 (s, P_0), 61.5 (s, P_2); 61.6 (s, P_1) ^1H NMR ($CDCl_3$): δ 1.54 (d, $^3J_{HH}$=6.5 Hz, 36 H, C*H*$_3$-CH*), 3.29 (d, $^3J_{HP2}$=10.6 Hz, 18 H, CH_3-N-P_2), 3.34 (d, $^3J_{HP1}$=10.8 Hz, 9 H, CH_3-N-P_1), 4.48 (q, $^3J_{HH}$=6.5 Hz, 12 H, CH_3C*H**), 7.20–7.75 (m, 153 H, C_6H_4 CH=N-N and C_6H_5), 8.28 (s, 12 H, C*H*=N-CH*); ^{13}C {^1H} NMR ($CDCl_3$): δ 24.9 (s, *C*H_3-CH*), 33.0 (d, $^2J_{CP1\text{-}2}$=13.0 Hz, CH_3-N-$P_{1\text{-}2}$), 69.7 (s, CH_3-*C*H*), 121.7 (m, C_0^2, C_1^2, C_2^2), 126.6 (s, o-C_6H_5), 126.9 (s, p-C_6H_5), 128.3 (s, C_0^3, C_1^3), 128.4 (s, m-C_6H_5), 129.6 (s, C_2^3), 132.2 (s, C_1^4), 132.6 (s, C_0^4), 133.8 (s, C_2^4), 138.9 (d, $^3J_{CP1\text{-}2}$=12.9 Hz, CH=N-N). 145.0 (s, i-C_6H_5), 151.4 (d, $^2J_{CP0\text{-}1}$=7.2 Hz, C_0^1, C_1^1), 152.3 (d, $^2J_{CP2}$=6.5 Hz, C_2^1), 158.2 (s, *C*H=N-CH*). IR (KBr): 1644 (m, $\upsilon_{C=N}$) cm^{-1}. Anal. Calcd for $C_{252}H_{240}N_{30}O_{21}P_{10}S_{10}$: C, 65.02; H, 5.20; N, 9.03. Found: (**3*S*-[G_2]**): C, 64.92; H, 5.14; N, 8.95. Found (**3*R*-[G_2]**): C, 64.89; H, 5.12; N, 8.93. $[\alpha]_D^{20}$(THF)=+71.7 (**3*S*-[G_2]**); $[\alpha]_D^{20}$(THF)=−68.4 (**3*R*-[G_2]**).

3-[G_3]: White powder, yield: 89% (**3*S*-[G_3]**), 87% (**3*R*-[G_3]**). ^{31}P {^1H} NMR ($CDCl_3$): δ 51.8 (s, P_0), 61.5 (s, P_3); 61.7 (s, P_2) 62.0 (s, P_1); ^1H NMR ($CDCl_3$): δ 1.50 (d, $^3J_{HH}$=6.3 Hz, 72 H, C*H*$_3$-

CH*), 3.27 (m, 63 H, CH_3-N-$P_{1\text{-}2\text{-}3}$), 4.44 (q, $^3J_{HH}$=6.3 Hz, 24 H, CH_3CH^*), 7.19–7.70 (m, 321 H, C_6H_4 CH=N-N and C_6H_5), 8.24 (s, 24 H, C*H*=N-CH*); ^{13}C {^1H} NMR ($CDCl_3$): δ 25.3 (s, *C*H_3-CH*), 33.4 (d, $^2J_{CP1\text{-}2\text{-}3}$=12.4 Hz, CH_3-N-$P_{1\text{-}2\text{-}3}$), 70.0 (s, CH_3-*C*H*), 122.1 (m, C_0^2, C_1^2, C_2^2, C_3^2), 126.9 (s, o-C_6H_5), 127.2 (s, p-C_6H_5), 128.8 (br s, C_0^3, C_1^3, C_2^3), m-C_6H_5), 129.9 (s, C_3^3), 132.5 (br s, C_0^4, C_1^4, C_2^4), 134.1 (s, C_3^4), 139.3 (d, $^3J_{CP1\text{-}2\text{-}3}$=13.0 Hz, CH=N-N), 145.4 (s, i-C_6H_5), 151.7 (d, $^2J_{CP0\text{-}1\text{-}2}$=6.7 Hz, C_0^1, C_1^1, C_2^1), 152.6 (d, $^2J_{CP3}$=6.1 Hz, C_3^1), 158.5 (s, *C*H=N-CH*). IR (KBr): 1644 (m, $\upsilon_{C=N}$) cm^{-1}. Anal. Calcd for $C_{528}H_{504}N_{66}O_{45}P_{22}S_{22}$: C, 64.18; H, 5.14; N, 9.36. Found: (**3*S*-[G$_3$]**): C, 64.15; H, 5.09; N, 9.34. Found (**3*R*-[G$_3$]**): C, 64.21; H, 5.17; N, 9.33. $[\alpha]_D^{20}$(THF)=+66.9 (**3*S*-[G$_3$]**); $[\alpha]_D^{20}$(THF)=−63.8 (**3*R*-[G$_3$]**).

3-[G$_4$]: White powder, yield: 85% (**3*S*-[G$_4$]**), 87% (**3*R*-[G$_4$]**). ^{31}P {^1H} NMR ($CDCl_3$): δ 61.4 (s, P_4), 61.6 (s, P_3); 61.9 (s, P_2) 62.3 (s, P_1); ^1H NMR ($CDCl_3$): δ 1.48 (d, $^3J_{HH}$=5.9 Hz, 144 H, C*H*$_3$-CH*), 3.23 (m, 135 H, CH_3-N-$P_{1\text{-}2\text{-}3\text{-}4}$), 4.43 (m, 48 H, CH_3CH^*), 7.17–7.68 (m, 657 H, C_6H_4 CH=N-N and C_6H_5), 8.22 (s, 48 H, C*H*=N-CH*); ^{13}C {^1H} NMR ($CDCl_3$): δ 24.8 (s, *C*H_3-CH*), 33.0 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4}$=12.5 Hz, CH_3-N-$P_{1\text{-}2\text{-}3\text{-}4}$), 69.6 (s, CH_3-*C*H*), 121.7 (m, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2), 126.5 (s, o-C_6H_5), 126.8 (s, p-C_6H_5), 128.4 (br s, C_0^3, C_1^3, C_2^3, C_3^3), m-C_6H_5), 129.5 (s, C_4^3), 132.1 (br s, C_0^4, C_1^4, C_2^4, C_3^4), 133.7 (s, C_4^4), 138.9 (d, $^3J_{CP1\text{-}2\text{-}3\text{-}4}$=12.9 Hz, CH=N-N), 145.0 (s, i-C_6H_5), 151.4 (d, $^2J_{CP0\text{-}1\text{-}2\text{-}3}$=7.9 Hz, C_0^1, C_1^1, C_2^1, C_3^1), 152.2 (d, $^2J_{CP4}$=7.4 Hz, C_4^1), 158.1 (s, *C*H=N-CH*). ppm. IR (KBr): 1644 (m, $\upsilon_{C=N}$) cm^{-1}. Anal. Calcd for $C_{1080}H_{1032}N_{138}O_{93}P_{46}S_{46}$: C, 63.80; H, 5.12; N, 9.51. Found: (**3*S*-[G$_4$]**): C, 63.71; H, 5.07; N, 9.45. Found (**3*R*-[G$_4$]**): C, 63.75; H, 5.08; N, 9.47. $[\alpha]_D^{20}$(THF)=+64.3 (**3*S*-[G$_4$]**); $[\alpha]_D^{20}$(THF)=−65.6 (**3*R*-[G$_4$]**).

3-[G$_7$]: White powder, yield: 85% (**3*S*-[G$_7$]**), 86% (**3*R*-[G$_7$]**). ^{31}P {^1H} NMR ($CDCl_3$): δ 61.4 (s, P_7), 61.6 (s, P_6); 61.9 (s, P_5) 62.2 (s, P_4, P_3, P_2, P_1); ^1H NMR ($CDCl_3$): δ 1.45 (m, 1152 H, C*H*$_3$-CH*), 3.21 (m, 1143 H, CH_3-N-$P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$), 4.40 (m, 384 H, CH_3-C*H*), 7.18–7.63 (m, 5361 H, C_6H_4, CH=N-N and C_6H_5), 8.18 (s, 384 H, C*H*=N-CH*); ^{13}C {^1H} NMR ($CDCl_3$): δ 24.9 (s, *C*H_3-CH*), 33.0 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$=13.0 Hz, CH_3-N-$P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$), 69.5 (s, CH_3-*C*H*), 121.7 (m, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2, C_7^2), 126.5 (s, o-C_6H_5), 126.8 (s, p-C_6H_5), 128.4 (m, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3, C_6^3 and m-C_6H_5), 129.5 (s, C_7^3), 132.1 (m, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4, C_6^4), 133.7 (s, C_7^4), 138.9 (m, CH=N-N), 145.0 (s, i-C_6H_5), 151.4 (d, $^2J_{CP0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$=7.9 Hz, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1, C_6^1), 152.2 (d, $^2J_{CP7}$=7.0 Hz, C_7^1), 158.1 (s, *C*H=N-CH*). IR (KBr): 1644 (m, $\upsilon_{C=N}$) cm^{-1}. Anal. Calcd for $C_{8808}H_{8424}N_{1146}O_{765}P_{382}S_{382}$: C, 63.48; H, 5.09; N, 9.63. Found: (**3*S*-[G$_7$]**): C, 63.25; H, 4.97; N, 9.59. Found (**3*R*-[G$_7$]**): C, 63.32; H, 5.00; N, 9.55. $[\alpha]_D^{20}$(THF)=+59.3 (**3*S*-[G$_7$]**); $[\alpha]_D^{20}$(THF)=−58.9 (**3*R*-[G$_7$]**).

General procedure for the synthesis of amine-terminated dendrimers ***4-[G$_n$]***

To a solution of 0.500 g of dendrimer **3-[G$_n$]** (**n**=1, 0.245 mmol; **n**=2, 0.107 mmol; **n**=3, 0.0506 mmol; **n**=4, 0.0246 mmol) in THF (20 mL) are added an excess of sodium cyanoborohydride (**n**=1, 0.185 g, 2.94 mmol; **n**=2, 0.162 g, 2.57 mmol; **n**=3, 0.153 g, 2.43 mmol; **n**=4, 0.149 g, 2.36 mmol) and a few drops of water. The resulting heterogeneous mixture is stirred for 5 days at 70°C, then centrifuged. The solution is evaporated to dryness and the resulting residue is extracted with chloroform (15 mL). This solution is evaporated to dryness and chloroform is added to the resulting precipitate. If the solution is clear, dendrimer **4-[G$_n$]** is considered to be pure; if a precipitate remains, the solution is filtered, then evaporated to dryness and the same procedure is repeated until the solution in chloroform is clear.

4-[G$_1$]: White powder, yield: 55% (**4*S*-[G$_1$]**), 54% (**4*R*-[G$_1$]**). ^{31}P {^1H} NMR ($CDCl_3$): δ 51.6 (s, P_0), 62.0 (s, P_1); ^1H NMR ($CDCl_3$): δ 1.33 (d, $^3J_{HH}$=6.6 Hz, 18 H, C*H*$_3$-CH*), 1.96 (s, 6 H, NH), 3.33 (d, $^3J_{HP1}$=10.3 Hz, 9 H, CH_3-N-P_1), 3.54 (s, 12 H, CH_2), 3.76 (q, $^3J_{HH}$=6.6 Hz, 6 H, CH_3-C*H*), 7.11–7.77 (m, 69 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^1H} NMR ($CDCl_3$): δ 24.3 (s, *C*H_3-CH*), 32.9 (d, $^2J_{CP1}$=12.8 Hz, CH_3-N-P_1), 50.8 (s, CH_2), 57.4 (s, CH_3-*C*H*), 121.1 (br s, C_0^2, C_1^2), 126.4 (s, o-C_6H_5), 126.8 (s, p-C_6H_5), 128.3 (s, m-C_6H_5 and C_0^3), 129.0 (s, C_1^3), 130.8 (s, C_0^4), 132.6 (s, C_1^4), 137.7 (d, $^3J_{CP1}$=12.8 Hz, CH=N-N), 145.1 (s, i-C_6H_5), 149.2 (d, $^2J_{CP1}$=7.5 Hz, C_1^1), 150.9 (d,

$^2J_{CP0}$=7.0 Hz, C_0^1), Anal. Calcd for $C_{114}H_{120}N_{12}O_9P_4S_4$: C, 66.65; H, 5.89; N, 8.18. Found: (**4*S*-[G$_1$]**): C, 66.60; H, 5.81; N, 8.10. Found (**4*R*-[G$_1$]**): C, 66.71; H, 5.89; N, 8.09. $[\alpha]_D^{20}$(THF)=−26.4 (**4*S*-[G$_1$]**); $[\alpha]_D^{20}$(THF)=+24.0 (**4*R*-[G$_1$]**).

4-[G$_2$]: White powder, yield: 60% (**4*S*-[G$_2$]**), 59% (**4*R*-[G$_2$]**). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 51.7 (s, P_0), 61.7 (s, P_1); 62.2 (s, P_2); ^{1}H NMR ($CDCl_3$): δ 1.32 (d, $^3J_{HH}$=6.4 Hz, 36 H, C*H*$_3$-CH*), 1.65 (br s, 12 H, NH), 3.29 (d, $^3J_{HP2}$=10.4 Hz, 18 H, CH_3-N-P_2), 3.36 (d, $^3J_{HP1}$=10.7 Hz, 9 H, CH_3-N-P_1) 3.53 (s, 24 H CH_2), 3.75 (q, $^3J_{HH}$=6.5 Hz, 12 H, CH_3-C*H**), 7.10–7.76 (m, 153 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 24.3 (s, *C*H$_3$-CH*), 32.9 (d, $^2J_{CP1-2}$=13.0 Hz, CH_3-N-P_{1-2}), 50.8 (s, CH_2), 57.4 (s, CH_3-*C*H*), 121.1 (d, $^3J_{CP2}$=4.5 Hz, C_2^2), 121.7 (br s, C_0^2, C_1^2), 126.5 (s, o-C_6H_5), 126.8 (s, p-C_6H_5), 128.1 (s, C_0^3, C_1^3), 128.3 (s, m-C_6H_5), 129.0 (s, C_2^3), 132.2 (s, C_1^4), 132.5 (s, C_0^4), 137.6 (s, C_2^4), 138.2 (d, $^3J_{CP1-2}$=14.5 Hz, CH=N-N), 145.2 (s, i-C_6H_5), 149.2 (d, $^2J_{CP2}$=7.1 Hz, C_2^1), 151.1 (d, $^2J_{CP0-1}$=7.7 Hz, C_0^1, C_1^1), Anal. Calcd for $C_{252}H_{264}N_{30}O_{21}P_{10}S_{10}$: C, 64.68; H, 5.69; N, 8.98. Found: (**4*S*-[G$_2$]**): C, 64.57; H, 5.62; N, 8.91. Found (**4*R*-[G$_2$]**): C, 64.71; H, 5.70; N, 8.90. $[\alpha]_D^{20}$(THF)=−23.0 (**4*S*-[G$_2$]**); $[\alpha]_D^{20}$(THF)=+28.8 (**4*R*-[G$_2$]**).

4-[G$_3$]: White powder, yield: 57% (**4*S*-[G$_3$]**), 60% (**4*R*-[G$_3$]**). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 51.8 (s, P_0), 61.8 (s, P_2); 62.0 (s, P_1); 62.2 (s, P_3); ^{1}H NMR ($CDCl_3$): δ 1.30 (d, $^3J_{HH}$=6.5 Hz, 72 H, C*H*$_3$-CH*), 1.56 (br s, 24 H, NH), 3.27 (m, 63 H, CH_3-N-P_{1-2-3}), 3.51 (s, 48 H, CH_2), 3.74 (q, $^3J_{HH}$=6.5 Hz, 24 H, CH_3-C*H**), 7.08–7.68 (m, 321 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 24.4 (s, *C*H$_3$-CH*), 32.9 (d, $^2J_{CP1-2-3}$=12.7 Hz, CH_3-N-P_{1-2-3}), 50.8 (s, CH_2), 57.4 (s, CH_3-*C*H*), 121.1 (m, C_3^2), 121.7 (m, C_0^2, C_1^2, C_2^2), 126.5 (s, o-C_6H_5), 126.8 (s, p-C_6H_5), 128.1 (br s, C_0^3, C_1^3, C_2^3), 128.3 (s, m-C_6H_5), 129.0 (s, C_3^3), 132.2 (m, C_0^4, C_1^4, C_2^4), 137.6 (s, C_3^4), 138.3 (d, $^3J_{CP1-2-3}$=11.8 Hz, CH=N-N), 145.2 (s, i-C_6H_5), 149.2 (d, $^2J_{CP3}$=8.3 Hz, C_3^1), 151.1 (d, $^2J_{CP0-1-2}$=6.0 Hz, C_0^1, C_1^1, C_2^1), Anal. Calcd for $C_{528}H_{552}N_{66}O_{45}P_{22}S_{22}$: C, 63.87; H, 5.60; N, 9.31. Found: (**4*S*-[G$_3$]**): C, 63.81; H, 5.57; N, 9.26. Found (**4*R*-[G$_3$]**): C, 63.78; H, 5.55; N, 9.28. $[\alpha]_D^{20}$(THF)=−20.8 (**4*S*-[G$_3$]**); $[\alpha]_D^{20}$(THF)=+20.8 (**4*R*-[G$_3$]**).

4-[G$_4$]: White powder, yield: 58% (**4*S*-[G$_4$]**), 55% (**4*R*-[G$_4$]**). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 51.8 (s, P_0), 61.7 (s, P_3); 62.0 (s, P_1, P_2); 62.1 (s, P_4); ^{1}H NMR ($CDCl_3$): δ 1.28 (d, $^3J_{HH}$=5.9 Hz, 144 H, C*H*$_3$-CH*), 1.64 (br s, 48 H, NH), 3.28 (m, 135 H, CH_3-N-$P_{1-2-3-4}$), 3.50 (s, 96 H, CH_2), 3.72 (m, 48 H, CH_3-C*H**), 7.07–7.66 (m, 657 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 24.5 (s, *C*H$_3$-CH*), 33.1 (d, $^2J_{CP1-2-3-4}$=12.4 Hz, CH_3-N-$P_{1-2-3-4}$), 51.0 (s, CH_2), 57.6 (s, CH_3-*C*H*), 121.3 (d, $^3J_{CP4}$=3.1 Hz, C_4^2), 121.9 (br s, C_0^2, C_1^2, C_2^2, C_3^2), 126.6 (s, o-C_6H_5), 127.0 (s, p-C_6H_5), 128.3 (br s, C_0^3, C_1^3, C_2^3, C_3^3), 128.5 (s, m-C_6H_5), 129.2 (s, C_4^3), 132.2 (br s, C_0^4, C_1^4, C_2^4), 132.3 (s, C_3^4), 137.8 (s, C_4^4), 138.5 (d, $^3J_{CP1-2-3-4}$=14.0 Hz, CH=N-N), 145.4 (s, i-C_6H_5), 149.4 (d, $^2J_{CP4}$=7.4 Hz, C_4^1), 151.3 (d, $^2J_{CP0-1-2-3}$=7.2 Hz, C_0^1, C_1^1, C_2^1, C_3^1), Anal. Calcd for $C_{1080}H_{1128}N_{138}O_{93}P_{46}S_{46}$: C, 63.49; H, 5.56; N, 9.46. Found: (**4*S*-[G$_4$]**): C, 63.33; H, 5.49; N, 9.40. Found (**4*R*-[G$_4$]**): C, 63.40; H, 5.51; N, 9.39. $[\alpha]_D^{20}$(THF)=−20.8 (**4*S*-[G$_4$]**); $[\alpha]_D^{20}$(THF)=+20.8 (**4*R*-[G$_4$]**).

*General procedure for the synthesis of phosphine terminated dendrimers **5-[G$_n$]***

A solution of 0.500 g of dendrimer **4-[G$_n$]** (**n**=1, 0.243 mmol; **n**=2, 0.107 mmol; **n**=3, 0.050 mmol; **n**=4, 0.024 mmol) in THF (20 mL) is added at room temperature to a 20% excess of Ph_2PCH_2OH, obtained by reaction of neat Ph_2PH (**n**=1, 0.31 mL, 1.75 mmol; **n**=2, 0.27 mL, 1.54 mmol; **n**=3, 0.25 mL, 1.45 mmol; **n**=4, 0.25 mL, 1.41 mmol) with paraformaldehyde (**n**=1, 0.052 g, **n**=2, 0.046 g; **n**=3, 0.044 g; **n**=4, 0.042 g) heated for 90 min. at 120°C. The resulting mixture is stirred for 48 h at room temperature, then evaporated to dryness. The residue thus obtained is washed with 3×20 mL of pentane/ether (1:1) to afford dendrimer **5-[G$_n$]**.

5-[G$_1$]: White powder, yield: 70% (**5*S*-[G$_1$]**), 65% (**5*R*-[G$_1$]**). ^{31}P {^{1}H} NMR ($CDCl_3$): δ −26.8 (s, $P(C_6H_5)_2$), 52.2 (s, P_0), 62.5 (s, P_1); ^{1}H NMR ($CDCl_3$): δ 1.36 (d, $^3J_{HH}$=6.7 Hz, 18 H, C*H*$_3$-CH*), 3.30 (s, 12H, N-C*H*$_2$-$P(C_6H_5)_2$), 3.36 (d, $^3J_{HP1}$=10.3 Hz, 9 H, CH_3-N-P_1), 3.71 (s, 12 H, C_6H_4-CH_2-N), 4.34 (m, 6 H, CH_3-C*H**), 7.10–7.82 (m, 129 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.4 (d, $^4J_{CP}$=10.9 Hz, *C*H$_3$-CH*), 33.2 (d, $^2J_{CP1}$=11.6 Hz, CH_3-N-P_1), 52.7 (s, C_6H_4-C*H*$_2$-N), 54.3

(d, $^{1}J_{CP}$=7.7 Hz, N-*C*H_2-P(C_6H_5)$_2$), 58.0 (d, $^{3}J_{CP}$=9.9 Hz, CH_3-*C*H*), 121.0 (d, $^{3}J_{CP1}$=3.7 Hz, C_1^2), 121.6 (s, o-C_0^2), 126.8 (s, o-*C*$_6H_5$-C, p-*C*$_6H_5$-C), 128.3 (m, m-*C*$_6H_5$-C, m-*C*$_6H_5$-P, p-*C*$_6H_5$-P), 129.8 (s, C_0^3, C_1^3), 132.5 (s, C_1^4), 132.7 (s, C_0^4), 133.1 (d, $^{2}J_{CP}$=18.2 Hz, o-*C*$_6H_5$-P), 137.0 (s, C_1^4), 137.6 (d, $^{3}J_{CP1}$=12.0 Hz, CH=N-N), 138.3 (d, $^{3}J_{CP1}$=11.1 Hz, i-*C*$_6H_5$-P),142.7 (d, $^{4}J_{CP}$=6.1 Hz, i-*C*$_6H_5$-C), 149.4 (d, $^{2}J_{CP1}$=6.5 Hz, C_1^1), 151.2 (d, $^{2}J_{CP0}$=6.4 Hz, C_0^1). Anal. Calcd for $C_{192}H_{186}N_{12}O_9P_{10}S_4$: C, 71.09; H, 5.78; N, 5.18. Found: (**5*S*-[G$_1$]**): C, 70.87; H, 5.71; N, 5.10. Found (**5*R*-[G$_1$]**): C, 70.81; H, 5.69; N, 5.11. $[\alpha]_D^{20}$(THF)=+22.4 (**5*S*-[G$_1$]**).

5-[G$_2$]: White powder, yield: 63% (**5*S*-[G$_2$]**), 61% (**5*R*-[G$_2$]**). ^{31}P {^{1}H} NMR ($CDCl_3$): δ −26.8 (s, P(C_6H_5)$_2$), 52.3 (s, P_0), 62.3 (s, P_1), 62.5 (s, P_2); ^{1}H NMR ($CDCl_3$): δ 1.37 (d, $^{3}J_{HH}$=6.3 Hz, 36 H, *C*H_3-CH*), 3.31 (s, 24H, N-*C*H_2-P(C_6H_5)$_2$), 3.33 (m, 27H, CH_3-N-$P_{1\text{-}2}$), 3.71 (s, 24 H, C_6H_4-*C*H_2-N), 4.35 (m, 12 H, CH_3-*C*H*), 7.10–7.77 (m, 273 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.4 (d, $^{4}J_{CP}$=12.4 Hz, *C*H_3-CH*), 33.1 (d, $^{2}J_{CP1\text{-}2}$=13.0 Hz, CH_3-N-$P_{1\text{-}2}$), 52.7 (s, C_6H_4-*C*H_2-N), 54.3 (d, $^{1}J_{CP}$=9.1 Hz, N-*C*H_2-P(C_6H_5)$_2$), 58.0 (d, $^{3}J_{CP}$=9.8 Hz, CH_3-*C*H*), 121.0 (d, $^{3}J_{CP2}$=3.7 Hz, C_2^2), 121.6 (s, C_0^2), 121.9 (s, C_1^2), 126.8 (s, o-*C*$_6H_5$-C, p-*C*$_6H_5$-C), 128.0–128.5 (m, C_0^3, C_1^3, m-*C*$_6H_5$-C, m-*C*$_6H_5$-P, p-*C*$_6H_5$-P), 129.8 (s, C_2^3), 132.5 (s,C_1^4), 132.7 (s, C_0^4), 133.2 (d, $^{2}J_{CP}$=18.4 Hz, o-*C*$_6H_5$-P), 137.0 (s, C_2^4), 137.6 (d, $^{3}J_{CP1\text{-}2}$=15.0 Hz, CH=N-N), 138.3 (d, $^{1}J_{CP}$=12.0 Hz, i-*C*$_6H_5$-P), 142.7 (d, $^{4}J_{CP}$=6.1 Hz, i-*C*$_6H_5$-C), 149.4 (d, $^{2}J_{CP2}$=7.2 Hz, C_2^1), 151.3 (d, $^{2}J_{CP0\text{-}1}$=5.7 Hz, C_0^1, C_1^1). Anal. Calcd for $C_{408}H_{396}N_{30}O_{21}P_{22}S_{10}$: C, 69.43; H, 5.65; N, 5.95. Found: (**5*S*-[G$_2$]**): C, 69.23; H, 5.58; N, 5.89. Found (**5*R*-[G$_2$]**): C, 69.21; H, 5.56; N, 5.88.

5-[G$_3$]: White powder, yield: 61% (**5*S*-[G$_3$]**), 63% (**5*R*-[G$_3$]**). ^{31}P {^{1}H} NMR ($CDCl_3$): δ −26.8 (s, P(C_6H_5)$_2$), 52.3 (s, P_0), 62.4 (m, P_1, P_2, P_3); ^{1}H NMR ($CDCl_3$): δ 1.29 (d, $^{3}J_{HH}$=6.1 Hz, 72 H, *C*H_3-CH*), 3.23 (m, 111 H, N-*C*H_2-P(C_6H_5)$_2$ and CH_3-N-$P_{1\text{-}2\text{-}3}$), 3.63 (s, 48 H, C_6H_4-*C*H_2-N), 4.30 (m, 24 H, CH_3-*C*H*), 7.02–7.69 (m, 561 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.4 (d, $^{4}J_{CP}$=11.2 Hz, *C*H_3-CH*), 33.1 (d, $^{2}J_{CP1\text{-}2\text{-}3}$=12.1 Hz, CH_3-N-$P_{1\text{-}2\text{-}3}$), 52.6 (s, C_6H_4-*C*H_2-N), 54.2 (d, $^{1}J_{CP}$=7.5 Hz, N-*C*H_2-P(C_6H_5)$_2$), 57.9 (d, $^{3}J_{CP}$=7.8 Hz, CH_3-*C*H*), 121.0 (d, $^{3}J_{CP3}$=3.6 Hz, C_3^2), 121.9 (br s, C_0^2, C_1^2, C_2^2), 126.8 (s, o-*C*$_6H_5$-C, p-*C*$_6H_5$-C), 128.0–128.5 (m, C_0^3, C_1^3, C_2^3, m-*C*$_6H_5$-C, m-*C*$_6H_5$-P, p-*C*$_6H_5$-P), 129.8 (s, C_3^3), 132.2 (m, C_0^4, C_1^4, C_2^4), 133.0 (d, $^{2}J_{CP}$=18.4 Hz, o-*C*$_6H_5$-P), 136.9 (s, C_3^4), 137.4 (d, $^{3}J_{CP1\text{-}2\text{-}3}$=14.2 Hz, CH=N-N), 138.2 (d, $^{1}J_{CP}$=12.4 Hz, i-*C*$_6H_5$-C), 142.7 (d, $^{4}J_{CP}$=4.3 Hz, i-*C*$_6H_5$-C), 149.4 (d, $^{2}J_{CP3}$=6.1 Hz, C_3^1), 151.3 (m, C_0^1, C_1^1, C_2^1). Anal. Calcd for $C_{840}H_{816}N_{66}O_{45}P_{46}S_{22}$: C, 68.70; H, 5.60; N, 6.29. Found: (**5*S*-[G$_3$]**): C, 68.53; H, 5.51; N, 6.18. Found (**5*R*-[G$_3$]**): C, 68.59; H, 5.54; N, 6.20.

5-[G$_4$]: White powder, yield: 66% (**5*S*-[G$_4$]**), 62% (**5*R*-[G$_4$]**). ^{31}P {^{1}H} NMR ($CDCl_3$): δ −27.2 (s, P(C_6H_5)$_2$), 61.5 (m, P_1, P_2, P_3, P_4); ^{1}H NMR ($CDCl_3$): δ 1.33 (m, 144 H, *C*H_3-CH*), 3.26 (m, 231 H, N-*C*H_2-P(C_6H_5)$_2$ and CH_3-N-$P_{1\text{-}2\text{-}3\text{-}4}$), 3.66 (s, 96 H, C_6H_4-*C*H_2-N), 4.30 (m, 48 H, CH_3-*C*H*), 7.05–7.68 (m, 1137 H, C_6H_4, CH=N-N and C_6H_5); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.2 (d, $^{4}J_{CP}$=9.6 Hz, *C*H_3-CH*), 32.9 (d, $^{2}J_{CP1\text{-}2\text{-}3\text{-}4}$=12.2 Hz, CH_3-N-$P_{1\text{-}2\text{-}3\text{-}4}$), 52.5 (s, C_6H_4-*C*H_2-N), 54.0 (d, $^{1}J_{CP}$=8.5 Hz, N-*C*H_2-P(C_6H_5)$_2$), 57.8 (d, $^{3}J_{CP}$=9.6 Hz, CH_3-*C*H*), 120.8 (d, $^{3}J_{CP4}$=4.0 Hz, C_4^2), 121.7 (m, C_0^2, C_1^2, C_2^2, C_3^2), 126.6 (s, o-*C*$_6H_5$-C, p-*C*$_6H_5$-C), 127.8–128.2 (m, C_0^3, C_1^3, C_2^3, m-*C*$_6H_5$-C, m-*C*$_6H_5$-P, p-*C*$_6H_5$-P), 129.6 (s, C_4^3), 131.2 (s, C_3^4), 132.2 (m, C_0^4, C_1^4, C_2^4), 132.9 (d, $^{2}J_{CP}$=18.4 Hz, o-*C*$_6H_5$-P), 136.8 (s, C_4^4), 137.4 (d, $^{3}J_{CP1\text{-}2\text{-}3\text{-}4}$=13.6 Hz, CH=N-N), 138.0 (d, $^{1}J_{CP}$=12.9 Hz, i-*C*$_6H_5$-P), 142.5 (d, $^{4}J_{CP}$=3.5 Hz, i-*C*$_6H_5$-C), 149.2 (d, $^{2}J_{CP4}$=7.3 Hz, C_4^1), 151.1 (m, C_0^1, C_1^1, C_2^1, C_3^1). Anal. Calcd for $C_{1704}H_{1656}N_{138}O_{93}P_{94}S_{46}$: C, 68.35; H, 5.57; N, 6.46. Found: (**5*S*-[G$_4$]**): C, 68.19; H, 5.49; N, 6.37. Found (**5*R*-[G$_4$]**): C, 68.22; H, 5.50; N, 6.38. $[\alpha]_D^{20}$(THF)=+17.8 (**5*S*-[G$_4$]**).

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References

1. For reviews on dendrimers see for example: (a) Tomalia, D. A.; Naylor, A. M.; Goddart III, W. A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138. (b) Tomalia, D. A.; Durst, H. D. in *Topics*

in Current Chemistry, Vol. 165 (Ed.: Weber, E.) Springer Verlag, Berlin, Heidelberg, **1993**, pp. 193. (c) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413. (d) Moorefield, C. N.; Newkome, G. R. in *Advances in Dendritic Molecules*, Vol. 1 (Ed.; Newkome, G. R.) JAI Press, Greenwich CT, USA **1994**, pp. 1. (e) Caminade, A.-M.; Majoral, J.-P. *Main Group Chemistry News* **1995**, *3*, 14. (f) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 876. (g) Majoral, J.-P.; Caminade, A.-M. *Act. Chim.* **1996**, *4*, 13. (h) Fréchet, J. M. J.; Hawker, C. J. in *Comprehensive Polymer Science*, 2nd suppl., **1996**, chap. 3, pp 71. (i) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. in *Dendritic Molecules*, VCH Weinheim **1996**.

2. (a) Brunner, H.; Fürst, J. *Tetrahedron*, **1994**, *50*, 4303. (b) Brunner, H.; Altmann, S.; *Chem Ber*, **1994**, *127*, 2285. (c) Brunner, H.; Bublack, P. *Synthesis*, **1995**, 36. (d) Bolm, C.; Derrien, N.; Seger, A. *Synlett* **1996**, 387.
3. (a) Denkewalter, R. G.; Kolc, J. F.; Lukasavage, W. J. US Pat. 4289872, **1981** (*CA* **102**, 79324q). (b) Denkewalter, R. G.; Kolc, J. F.; Lukasavage, W. J. US Pat. 4410688, **1983** (*CA* **100**, 103907p). (c) Aharoni, S. M.; Crosby III, C. R.; Walsh, E. K. *Macromolecules*, **1982**, *15*, 1093 (*CA* **97**, 73219r). (d) Aharoni, S. M.; Murthy, N. S. *Polym. Commun.* **1983**, 24, 132 (*CA* **99**, 140362 p). (e) Posnett, D. N.; McGrath, H.; Tam, J. P. *J. Biol. Chem.* **1988**, *263*, 1719. (f) Rao, C.; Tam, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 6975. (g) Shao, J.; Tam, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 3893. (h) Hudson, R. H. E.; Damha, M. J. *J. Am Chem. Soc.* **1993**, *115*, 2119. (i) Roy, R.; Zanini, D.; Meunier, S. J.; Romanowska, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1869. (j) Roy, R.; Park, W. C. K.; Wu, Q.; Wang, S. N. *Tetrahedron Letters* **1995**, *36*, 4377. (k) Zanini, D.; Park, W. C. K.; Roy, R. *Tetrahedron Letters* **1995**, *36*, 7383. (l) Chapman, T. M.; Hillyer, G. L.; Mahan E. J.; Shaffer, K. A. *J. Am. Chem. Soc* **1994**, *116*, 11195. (m) Twyman, L. J.; Beezer, A. E.; Mitchell, J. C. *Tetrahedron Letters* **1994**, *35*, 4423. (n) Aoi, K.; Itoh, K.; Okada, M. *Macromolecules*, **1995**, *28*, 5391.
4. (a) Kremers, J. A.; Meijer, E. W. *J. Org. Chem.* **1994**, *59*, 4262. (b) Kremers, J. A.; Meijer, E. W., *Macromol. Symp.* **1995**, *98*, 491. (c) Kremers, J. A.; Meijer, E. W. Elsevier Science **1995**, *Reactive and Functional Polymers 26*, 137.
5. (a) Chow, H. F.; Fok, L. F.; Mak, C. C. *Tetrahedron Letters*, **1994**, *35*, 3547. (b) Chow, H. F.; Mak, C. C. *J. Chem. Soc. Perkin Trans.* **1994**, 2223.
6. (a) Seebach, D.; Lapierre, J. M.; Skobridis, K.; Greiveldinger, G. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 440. (b) Seebach D.; Lapierre, J. M.; Skobridis, K.; Greiveldinger, G. *Helv. Chim. Acta*, **1994**, *77*, 1673.
7. Murer, P.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2116.
8. Chang, H. T.; Chen, C. C.; Kondo, T.; Siuzdak, G.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 182.
9. (a) McGrath, D. V.; Wu, M. J.; Chaudhry, U. *Tetrahedron Lett.* **1996**, *37*, 6077. (b) McElhanon, J. R.; Wu, M. J.; Escobar, M.; McGrath, D. V. *Macromolecules* **1996**, *29*, 8979. (c) McElhanon, J. R.; Wu, M. J.; Escobar, M.; Chaudhry, U.; Hu, C. H.; McGrath, D. V. *J. Org. Chem.* **1997**, *62*, 908.
10. Newkome, G. R.; Lin, X.; Weis, C. D. *Tetrahedron Asym.* **1991**, I, 957.
11. (a) Jansen, J. F. G. A.; Peerlings, H. W. I.; de Brabander-van den Berg, E. M. M.; Meijer; E. W. *Angew. Chem. Int. Ed. Eng.* **1995**, *34*, 1206. (b) Peerlings, H. W. J.; Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Polymer Mater. Sci.* **1995**, *73*, 342. (c) Jansen, J. F. G. A.; Meijer, W. W.; de Brabander van den Berg, E. M. M. *Macromol Symp.* **1996**, *102*, 27.
12. (a) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226. (b) Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. *J. Am. Chem. Soc.* **1995**, *117*, 4417. (c) Bosman, A. W.; Jansen, J. F. G. A.; Janssen, R. A. J.; Meijer, E. W. *Polymer Mater. Sci.* **1995**, 340.
13. Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Rec. Trav. Chim Pays-Bas* **1995**, *114*, 225.

14. Issberner, J.; Böhme, M.; Grimmes, S.; Nieger, M.; Paulus, W.; Vögtle, F. *Tetrahedron Asym.* **1996**, *7*, 2223.
15. (a) Launay, N.; Caminade, A. M.; Lahana, R.; Majoral, J. P. *Angew. Chem. Int. Ed. Eng.* **1994**, *33*, 1589. (b) Launay, N.; Caminade, A. M.; Majoral, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 3282. (c) Slany, M.; Bardaji, M.; Casanove, M. J.; Caminade, A. M.; Majoral, J. P.; Chaudret, B. *J. Am. Chem. Soc.* **1995**, *117*, 9764.
16. (a) Launay, N.; Slany, M.; Caminade, A. M.; Majoral, J. P. *J. Org. Chem.* **1996**, *61*, 3799. (b) Lartigue, M. L.; Slany, M.; Caminade, A. M.; Majoral, J. P. *Chem. Eur. J.* **1996**, *2*, 1417. (c) Slany, M.; Caminade, A. M.; Majoral, J. P. *Tetrahedron Lett.* **1996**, 9053. (d) Bardaji, M.; Kustos, M.; Caminade, A. M.; Majoral, J. P.; Chaudret, B. *Organometallics* **1997**, *16*, 403. (e) Larré, C.; Caminade, A. M.; Majoral, J. P. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 596. (f) Slany, M.; Bardaji, M.; Caminade, A. M.; Chaudret, B.; Majoral, J. P. *Inorg. Chem.* **1997**, *36*, 1939.
17. Hellmann, H.; Bader, J.; Birkner, H.; Schumacher, O. *Liebigs Ann Chem* **1962**, *659*, 49.

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