Behavior of an Optically Active Ferrocene Chiral Shell Located within Phosphorus-Containing Dendrimers

Cédric-Olivier Turrin, Jérôme Chiffre, Dominique de Montauzon,[†]
Gilbert Balavoine, Eric Manoury,* Anne-Marie Caminade,* and
Jean-Pierre Majoral*

*Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne,
31077 Toulouse Cedex 4, France*

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Three families of phosphorus-containing dendrimers having chiral ferrocenic subunits precisely placed at one individual shell within their skeleton are synthesized. The influence of the progressive "burying" of the chiral ferrocene derivatives upon their electrochemical and chiroptical properties is reported. It is shown that both properties depend mainly on the chemical environment of the chiral organometallic centers. However, they differ in the sensitivity to the "burying"; the chiroptical properties do not appear to be sensitive to where the chiral units are positioned within the dendrimer, whereas the electrochemical properties are.

Introduction

The introduction of chirality in dendritic architectures[1] dates back to the very beginning of this field, when Denkewalter described in 1979 the synthesis of hyperbranched compounds based on the amino acid lysine as a building block, but no mention of chirality was made in this original patent.[2] Since that time, a lot of work has been devoted to the synthesis of various types of chiral dendritic macromolecules, having the chirality either at the level of the core, or within the branching units, or at the end groups, or at two or three of these levels.[3] Besides expected applications for asymmetric catalysis, sensor technology, or enantioselective clathration, this work developed mainly the basic understanding of fundamental stereochemistry. For instance, we[4,5] and others[6] have demonstrated that the optical activity per end group is generally roughly constant whatever the generation is, when chirality is introduced only by the end groups, provided the chiral groups are not sensitive to differences in packing. On the other hand, first studies of dendrimers having chirality at the core, the branching units, and the end groups at the same time seem to indicate that the optical activity of a building block depends on where the unit is positioned within the dendrimer. However, recent results indicate that the differences are mainly due to constitutional differences instead of ordered substructures.[7] To the best of our knowledge, there has been no report to date studying the properties of chiral groups placed at only one individual shell within a large dendrimer, even if this type of work was described for relatively small (fourth-generation) dendrons.[8,9]

We recently grafted on the surface of phosphorus-containing dendrimers[10] several groups whose chirality was issued from the planar chirality of ferrocene derivatives.[5,11] One of them, being functionalized by an aldehyde group, appears particularly suitable to grow

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* Corresponding authors. Fax: 33 5 61 55 30 03. E-mail: caminade@lcc-toulouse.fr (A.-M.C.); majoral@lcc-toulouse.fr (J.-P.M.); manoury@lcc-toulouse.fr (E.M.).

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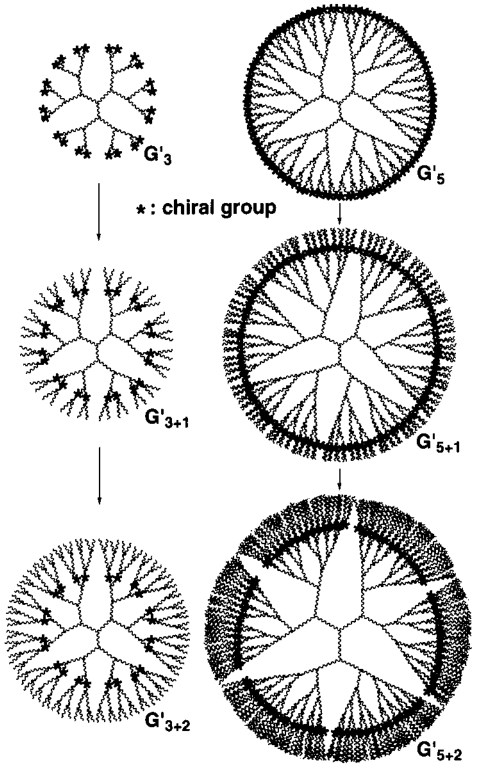

Figure 1. Optically active groups positioned at various places in dendrimers.

further generations. This should lead to dendrimers having chiral groups precisely placed at one individual shell within their skeleton (Figure 1). We report here the synthesis of these new chiral dendrimers, as well as their electrochemical and chiroptical properties, depending on the generation, up to the eleventh generation.

Results and Discussion

The synthesis is carried out starting from dendrimers $\mathbf{1\text{-}G'_n}$, having ferrocene aldehyde end groups, whose synthesis was previously described for $\mathbf{n} = 3$ (24 CHO end groups), $\mathbf{n} = 5$ (96 CHO end groups), and $\mathbf{n} = 9$ (1536 CHO end groups, theoretically).[5] Starting from dendrimer $\mathbf{1\text{-}G'_3}$, the condensation with the phosphorhydrazide $H_2NNMeP(S)Cl_2$ affords as expected the next generation $\mathbf{1\text{-}G_{3+1}}$ (Scheme 1). The condensation rate does not appear to be slower than usual, i.e., when using parahydroxybenzaldehyde derivatives.[10] This is in accordance with the low steric hindrance of the aldehyde part of the ferrocene shown by X-ray crystallography for the parent (*R*)-2-(4-methoxyphenyl)ferrocenecarboxaldehyde, despite the presence of aryl and aldehyde groups in the 1,2 positions.[5] The condensation goes to completion, as shown by the total disappearance of the signal corresponding to aldehydes in ^1H and ^{13}C NMR and IR spectroscopies. The synthesis is pursued from dendrimer $\mathbf{1\text{-}G_{3+1}}$ by reacting successively hydroxybenzaldehyde sodium salt, leading to $\mathbf{1\text{-}G'_{3+1}}$, then $H_2NNMeP(S)Cl_2$ leading to the next generation $\mathbf{1\text{-}G_{3+2}}$. Finally, hydroxybenzaldehyde sodium salt is added, leading to dendrimer $\mathbf{1\text{-}G'_{3+2}}$, a fifth generation having 96 CHO end groups. An absolutely similar sequence of reactions is applied to dendrimers $\mathbf{1\text{-}G'_5}$ and $\mathbf{1\text{-}G'_9}$, leading finally to dendrimers $\mathbf{1\text{-}G'_{5+2}}$ (generation 7, theoretically 384 end groups) and $\mathbf{1\text{-}G'_{9+2}}$ (generation 11, theoretically 6144 end groups), respectively (Scheme 2).

In all cases, the reactions are monitored by NMR. ^{31}P NMR is used for the reaction of hydroxybenzaldehyde, which induces the usual shielding ($\Delta\delta \cong 2$ ppm) of the signal corresponding to the phosphorus atoms that underwent the reaction. ^1H NMR is used for the condensation reaction of the aldehydes, inducing the total disappearance of the signal at $\delta \cong 9.9$ ppm. It is worth noting that the signals of the *C*-H atoms (ortho and meta) of the benzaldehyde end groups are split into two on the ^{13}C NMR spectra of compounds $\mathbf{1\text{-}G'_{n+1}}$. For instance, two doublets with an equal intensity are observed for P−O(ArC_{ortho}) at $\delta = 121.7$ ppm ($^3J_{CP} = 5.2$ Hz) and 122.0 ppm ($^3J_{CP} = 6.1$ Hz) for $\mathbf{1\text{-}G'_{3+1}}$. This phenomenon is also observed for the same groups in compounds $\mathbf{1\text{-}G_{n+2}}$ and presumably also in $\mathbf{1\text{-}G'_{n+2}}$. An overlapping of signals by the outermost aromatic groups precludes making a conclusion in the later case, but it is not observed for the external layer of benzaldehyde groups. Despite the long distance between the CH aromatic groups and the planar chiral group (7 to 8 bonds), diastereotopicity seems the most likely to account for the phenomenon of splitting observed in the ^{13}C NMR. In addition to NMR characterization, size exclusion chromatography is used to determine the polydispersity (found between 1.03 and 1.08), the MALDI-TOF technique being unusable to check the purity of dendrimers having conjugated hydrazone linkages, as we already demonstrated.[12]

Thus, we have on hand several families of chiral organometallic dendrimers, analyzable by electrochemistry and chiroptical measurements. Both techniques could furnish information concerning the behavior of active groups placed either at the external layer of dendrimers of various size or more or less deeply within their skeleton. First experiments are conducted in electrochemistry, for all nine dendrimers having aldehyde end groups. All the data concerning electrochemistry and coulometry are gathered in Table 1. They were determined in 0.1 M $[^nBu_4N^+][BF_4^-]$ acetone/THF (1:2) solutions, using a conventional three-electrode cell with a Pt working electrode. The concentration in dendrimer used is different for each family, but chosen in order to have 10^{-4} mol L^{-1} in ferrocene units in all cases. The cyclic voltammograms show a single oxidation wave corresponding to a multielectronic transfer of the equivalent and electrochemically independent ferrocenyl groups, for the oxidation process $[Fe^{II} \rightarrow Fe^{III}]$ (Figure 2). Such behavior was already demonstrated by us[5,13] and others.[14] As expected, the value of the half-wave potential strongly depends on the direct chemical environment of the metallic center. The replacement of the aldehyde by the hydrazone induces a shift of ∼160 mV toward

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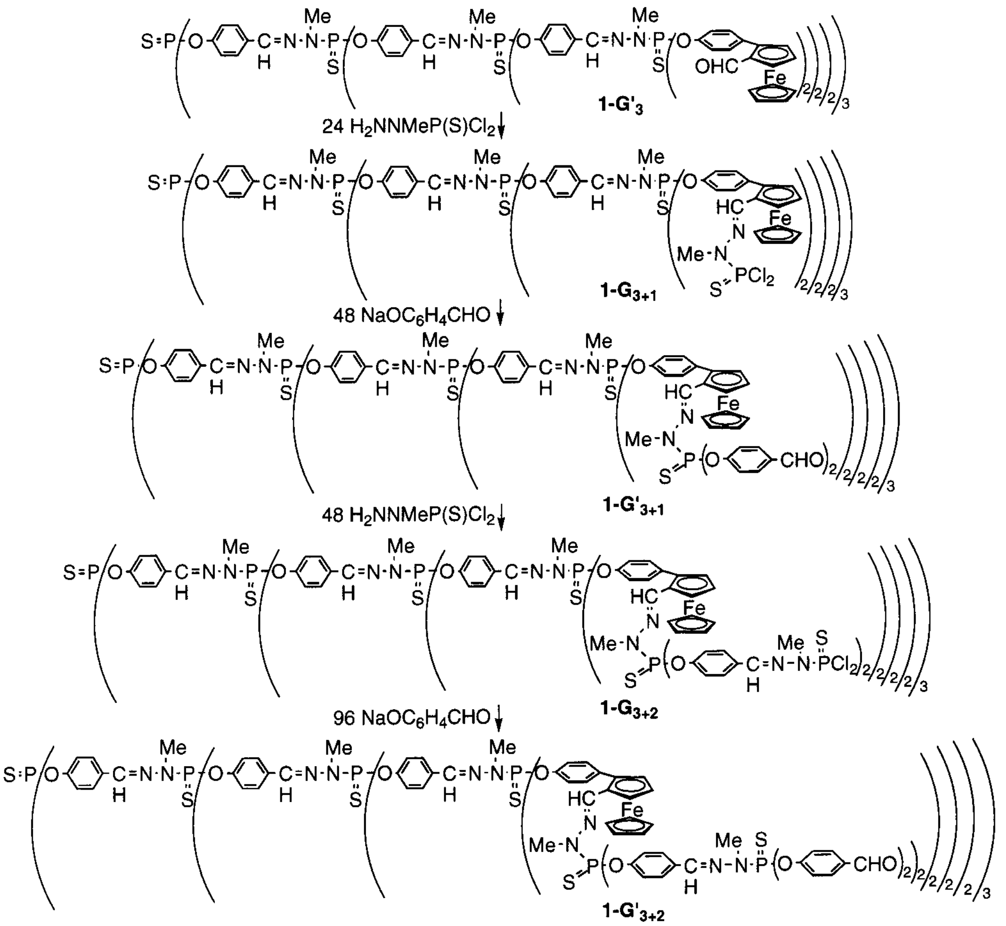
Scheme 1



anodic potentials, from ~0.81 V to ~0.64 V, whatever the size of the dendrimer considered. On the other hand, two phenomena have to be noted. First, the rate of the electronic transfer decreases when the redox centers are more confined within the interior of the dendrimer; this is shown by the increase of the ΔEp values, within each series of dendrimers **1-G′$_{\mathbf{n}}$** → **1-G′$_{\mathbf{n}+1}$** → **1-G′$_{\mathbf{n}+2}$**. Second, the reversibility of the system decreases with the increase of the generation of the dendrimer within the same series, as shown by the decrease of the I_{pc}/I_{pa} values (Table 1 and Figure 2). The reduction wave for compounds having ferrocenes on the surface (**1-G′$_{\mathbf{n}}$**) presents a typical striping shape, corresponding to changes in solubility properties of the oxidation state; indeed, a blue conducting film deposits onto the Pt electrode during oxidation. Such behavior is not observed when the ferrocene units are located within the dendrimer (compounds **1-G′$_{\mathbf{n}+1}$** and **1-G′$_{\mathbf{n}+2}$**). These phenomena can be explained by a decrease of the accessibility of the electrode for the redox centers, which become gradually excluded from the electronic transfers. These findings were already shown by us[13] and others,[14−16] but generally for smaller dendrimers. In addition, a new trend can be inferred from all these data: if the initial dendrimer is large, the irreversibility of the oxidation of the redox center is more pronounced when adding a first, then a second layer (compare values for **1-G′$_{\mathbf{3}+1}$**, **1-G′$_{\mathbf{5}+1}$**, and **1-G′$_{\mathbf{9}+1}$**, or for **1-G′$_{\mathbf{3}+2}$**, **1-G′$_{\mathbf{5}+2}$**, and **1-G′$_{\mathbf{9}+2}$**). This can be deduced from the larger modification of ΔE_p and I_{pc}/I_{pa} for the highest generations, leading even to the absence of a definite return signal for **1-G′$_{\mathbf{9}+2}$** (I_{pc} undetermined). This increased irreversibility can explain the lower percentage of electrolysis measured for **1-G′$_{\mathbf{9}+2}$** by coulometry compared to the other dendrimers. Such an increased irreversibility was already observed for dendrimers having electroactive moieties located at the core.[17]

Thus, electrochemistry furnishes interesting information about steric accessibility of ferrocenes buried at several levels within a dendrimer, but chiroptical properties could add information about conformational order within the dendrimer. For this purpose, we studied the variation of the optical rotation at 20 °C in THF, for all nine compounds previously characterized by electrochemistry. All the data concerning the chiroptical properties are gathered in Table 2. First, it can be noted that the specific rotation, $[\alpha]_D$, value depends almost exclusively on the chemical environment and not on the generation considered, for a similar degree of burying. The very slight decrease observed on going from **1-G′$_{\mathbf{3}}$** to **1-G′$_{\mathbf{9}}$**, or from **1-G′$_{\mathbf{3}+1}$** to **1-G′$_{\mathbf{9}+1}$**, or from **1-G′$_{\mathbf{3}+2}$** to **1-G′$_{\mathbf{9}+2}$** can be directly related to the variation of the percentage in weight of the chiral groups reported to the dendrimer overall weight (Table 2), the chiral

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Scheme 2

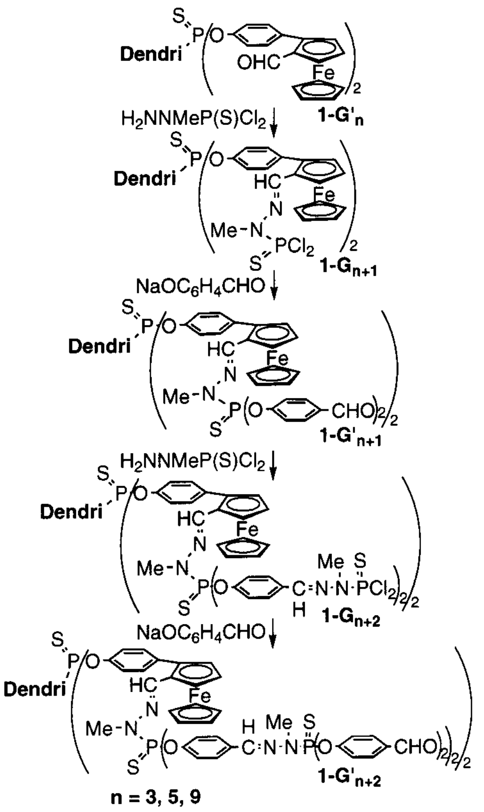

Table 1. Electrochemical Data

compound	theoretical number of e$^-$	E_{pc}	E_{pa}	$E^{1/2}$	ΔE_p	I_{pc}/I_{pa}	electrolysis %
1-G′$_3$	24	0.81	0.87	0.84	0.06	2	99
1-G′$_{3+1}$	24	0.65	0.71	0.68	0.06	1	91
1-G′$_{3+2}$	24	0.65	0.72	0.68	0.07	0.9	81
1-G′$_5$	96	0.82	0.88	0.85	0.06	2	97
1-G′$_{5+1}$	96	0.64	0.70	0.67	0.06	0.9	95
1-G′$_{5+2}$	96	0.59	0.73	0.66	0.14	0.7	71
1-G′$_9$	1536	0.82	0.88	0.85	0.06	2	85
1-G′$_{9+1}$	1536	0.65	0.71	0.68	0.06	0.9	91
1-G′$_{9+2}$	1536	undefined	0.72				50

group being arbitrary considered to be constituted of $OC_6H_4C_5H_3FeC_5H_5CHO$ for **1-G′$_n$** and of $OC_6H_4C_5H_3$-$FeC_5H_5CH{=}NNMePS$ for **1-G′$_{n+1}$** and **1-G′$_{n+2}$**. We have previously reported such behavior for chiral methylbenzylamine derivatives linked to the surface of dendrimers.[4] On the other hand, the chemical environment has a dramatic influence on the $[\alpha]_D$ values, as shown by the comparison of the data obtained for the series **1-G′$_n$** → **1-G′$_{n+1}$** → **1-G′$_{n+2}$** (Figure 3). If the first modification is easily understandable, the chemical environment being changed from aldehyde to hydrazone (step **1-G′$_n$** → **1-G′$_{n+1}$**), the second modification is obviously not related to chemical changes, which occurs very far from the chiral centers. In fact, it is again related to the percentage in weight of the chiral groups. Indeed, if the percentage of chiral groups in **1-G′$_{3+2}$** was 47.6 (as in **1-G′$_{3+1}$**) instead of 26.4, the $[\alpha]_D$ value for **1-G′$_{3+2}$** would be 425, a value that compares well with the value found for **1-G′$_{3+1}$** (415.1). The slight difference observed could be due to experimental errors (for instance, due to the presence of variable traces of solvents in the powdered dendrimers). Similar remarks can be done for the other **1-G′$_{n+2}$** compounds.

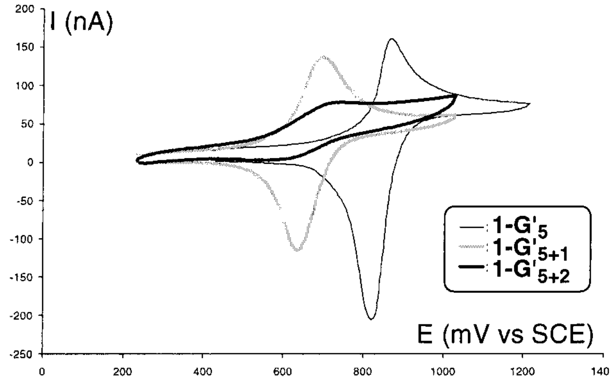

Figure 2. Cyclic voltammograms (scan rate 100 mV s^{-1}) obtained for dendrimers **1-G′$_5$**, **1-G′$_{5+1}$**, and **1-G′$_{5+2}$**.

The molar rotation, the $[\alpha]_{mol}$ value, confirms all the conclusions drawn previously, particularly the large variation between the **1-G′$_n$** and **1-G′$_{n+1}$** series, and the very small variation between the **1-G′$_{n+1}$** and **1-G′$_{n+2}$** series (Figure 4). In addition, the expected increase of the $[\alpha]_{mol}$ value is observed on going from **1-G′$_3$** to **1-G′$_9$**, as well as from **1-G′$_{3+1}$** to **1-G′$_{9+1}$**, or from **1-G′$_{3+2}$** to **1-G′$_{9+2}$**. This increase is related only to the number of chiral groups within one molecule. Indeed, the $[\alpha]_{mol}$ value divided by the number of chiral units is a constant for each series considered in the previous sentence (Figure 5). The coherence of these data is an indication concerning the absence of important defects in the structure of these dendrimers. Figure 5 proves that the relative burying of a chiral shell within the interior of the dendrimer has no influence upon its chiroptical properties for high generations.

Conclusion

Thus, this work demonstrates for the first time that, as far as chirality is concerned, high-generation dendrimers behave like “traditional” polymers: only the number of chiral groups and their chemical environment influence the chiroptical properties and not their placement within the dendrimer. On the other hand, a very different behavior is observed for the electrochemical properties of the same chiral groups. The electrochemical behavior is extremely dependent on the generation considered and on the degree of burying within the dendrimer. Thus, the behavior of particular groups precisely placed at one layer within a dendrimer is different, depending on what property is considered.

Experimental Section

General Procedures. All reactions were carried out in the absence of air, using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried before use. Instrumentation: Bruker AM250 and DPX300 (^1H, ^{13}C, and ^{31}P NMR); Perkin-Elmer 1725X (FT-IR). $[\alpha]_D$ were measured on a PE 241 Perkin-Elmer polarimeter. SEC data were obtained using a Waters 410 differential diffractometer. The numbering used for NMR data of dendrimers is depicted in Figure 6. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^1H and ^{13}C NMR. The assignment of ^{13}C NMR signals was carried out using J_{mod}, two-dimensional HMBC, and HMQC, broad-band, or CW ^{31}P-decoupling experiments when necessary. Dendrimers **1-G′$_n$**[5] were prepared in our lab, according to the procedures we developed.

Table 2. Chiroptical Data

compound	theoretical number of chiral groups	MW (g mol^{-1})	contribution of chiral groups (%)	$[\alpha]_D$	$[\alpha]_{mol}$	$[\alpha]_{mol}$/chiral units
1-G′$_3$	24	11 821	61.9	+224.5	+2654	111
1-G′$_5$	96	48 998	59.7	+217.1	+10 637	111
1-G′$_9$	1536	792 524	59.1	+214.5	+169 996	111
1-G′$_{3+1}$	24	19 797	47.6	+415.1	+8218	342
1-G′$_{5+1}$	96	80 900	46.6	+404.3	+32 708	341
1-G′$_{9+1}$	1536	1 302 964	46.3	+402.1	+523 922	341
1-G′$_{3+2}$	24	35 748	26.4	+236.1	+8440	352
1-G′$_{5+2}$	96	144 705	26.1	+232.2	+33 601	350
1-G′$_{9+2}$	1536	2 323 865	26.0	+231.0	+536 813	349

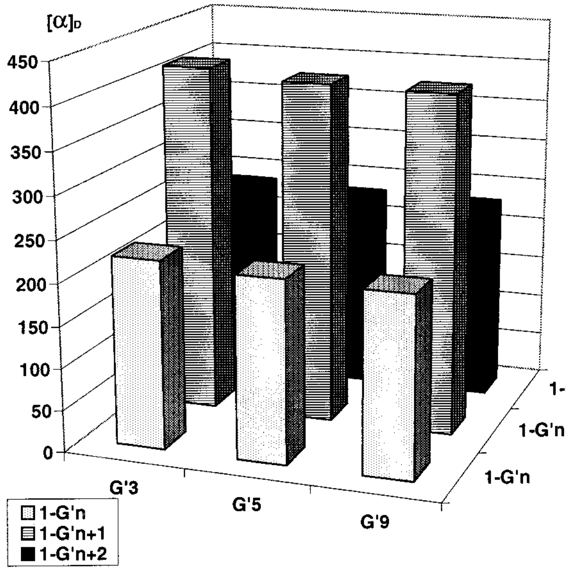

Figure 3. Specific rotation $[\alpha]_D$ versus generation for dendrimers **1-G′$_n$**, **1-G′$_{n+1}$**, and **1-G′$_{n+2}$** (**n** = 3, 5, 9).

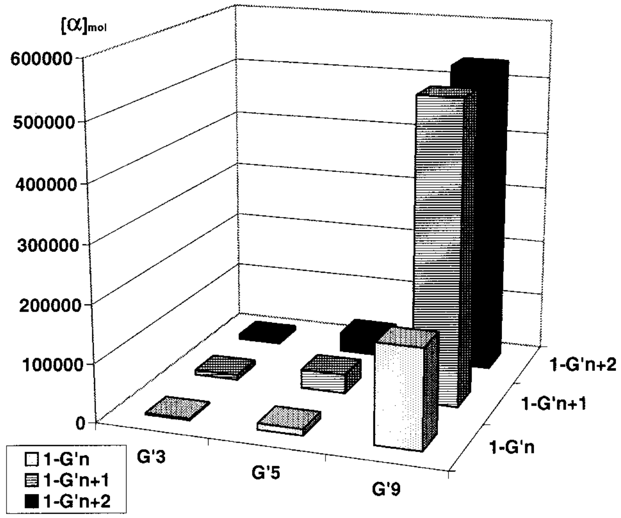

Figure 4. Molar rotation $[\alpha]_{mol}$ versus generation for dendrimers **1-G′$_n$**, **1-G′$_{n+1}$**, and **1-G′$_{n+2}$** (**n** = 3, 5, 9).

Electrochemical Measurements. Voltammetric and electrolytic measurements were carried out with a homemade potentiostat using the interrupt method to minimize the uncompensated resistance (*iR*) drop. Experiments were performed at room temperature in an airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted in a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a spiral of ca. 1 cm^2 apparent surface, made of a platinum wire, 8 cm in length and 0.5 cm in diameter. The working electrode was a Pt electrode (1 mm diameter) for cycling voltammetry and a Pt gauze electrode for bulk electrolysis. $E^{1/2}$ values were determined as the average of the cathodic and the anodic peak potentials. The supporting electrolyte [nBu$_4$N][BF$_4$] (Fluka, electrochemical grade) was used as received.

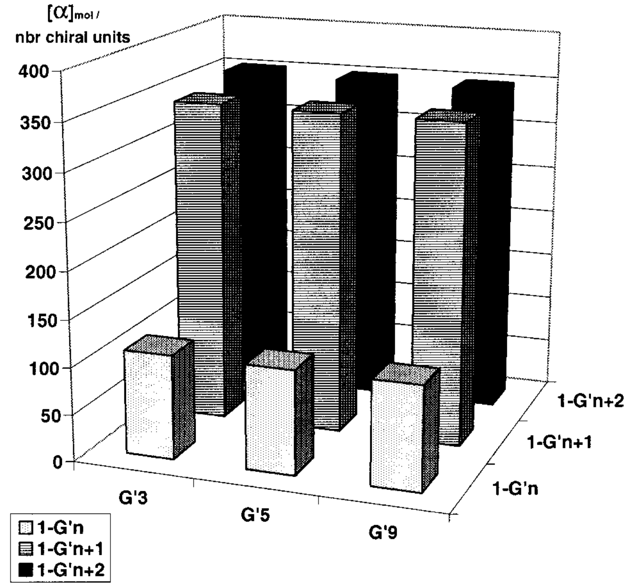

Figure 5. Molar rotation $[\alpha]_{mol}$ divided by the number of stereogenic groups versus generation for dendrimers **1-G′$_n$**, **1-G′$_{n+1}$**, and **1-G′$_{n+2}$** (**n** = 3, 5, 9).

General Procedure for the Synthesis of Dendrimers 1-G$_{n+1}$. To a solution of 250 mg of dendrimer **1-G′$_n$** (**n** = 3, 0.021 mmol; **n** = 5, 5.1 × 10^{-3} mmol; **n** = 9, 3.1 × 10^{-4} mmol) in THF (5 to 10 mL) at room temperature was added a slight excess of a solution of dichlorothiophosphorhydrazide in chloroform (0.3 M). The resulting solution was stirred overnight, then evaporated to dryness. The residue was washed twice with ether to afford dendrimers **1-G$_{n+1}$**.

1-G$_{3+1}$: maroon powder (90% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 52.5 (s, P$_0$), 62.0 (s, P$_3$), 62.8 (s, P$_{1-2-4}$). ^{1}H NMR (CDCl$_3$): δ 3.27 (br s, 135H, P$_{1-2-3-4}$-N-CH$_3$), 4.08 (s, 120H, Cp-H), 4.44 (s, 24H, Cp-H), 4.53 (s, 24H, Cp-H), 4.94 (s, 24H, Cp-H), 7.15–7.76 (m, 225H, C$_6$H$_4$, CH=N). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 32.2 (d, $^2J_{CP4}$ = 12.2 Hz, P$_4$-N-CH$_3$), 32.9 (d, $^2J_{CP1-2-3}$ = 13.3 Hz, P$_{1-2-3}$-N-CH$_3$), 67.5 (s, Cp), 69.7 (s, Cp), 70.8 (s, C$_5$H$_5$), 72.1 (s, Cp), 77.2 (s, Cp^{quat}), 88.4 (s, Cp^{quat}), 121.1 (d, $^3J_{CP3}$ = 3.0 Hz, C$_3{}^2$), 121.7 (br s, C$_{0-1-2}{}^2$), 128.3 (s, C$_{0-1-2}{}^3$), 130.6 (s, C$_3{}^3$), 132.3 (s, C$_{0-1-2}{}^4$), 134.6 (s, C$_3{}^4$), 138.8 (d, $^3J_{CP1-2-3}$ = 14.2 Hz, CH=N), 143.0 (d, $^3J_{CP4}$ = 18.2 Hz, CH=N), 149.5 (d, $^2J_{CP3}$ = 7.1 Hz, C$_3{}^1$), 151.3 (d, $^2J_{CP0-1-2}$ = 7.4 Hz, C$_{0-1-2}{}^1$). Anal. Calcd for $C_{600}H_{552}Cl_{48}Fe_{24}N_{90}O_{45}P_{46}S_{46}$ (15685.4 g mol^{-1}): C, 45.94; H, 3.55; N, 8.04. Found: C, 45.88; H, 3.67; N, 7.92.

1-G$_{5+1}$: maroon powder (88% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 53.6 (s, P$_0$), 62.0 (s, P$_5$), 62.7 (s, P$_{1-2-3-4-6}$). ^{1}H NMR (CDCl$_3$): δ 3.34 (br s, 567H, P$_{1-2-3-4-5-6}$-N-CH$_3$), 4.08 (s, 288H, Cp-H), 4.44 (s, 96H, Cp-H), 4.53 (s, 96H, Cp-H), 4.94 (s, 96H, Cp-H), 7.12–7.68 (m, 945H, C$_6$H$_4$, CH=N). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 32.1 (d, $^2J_{CP6}$ = 12.1 Hz, P$_6$-N-CH$_3$), 32.8 (d,

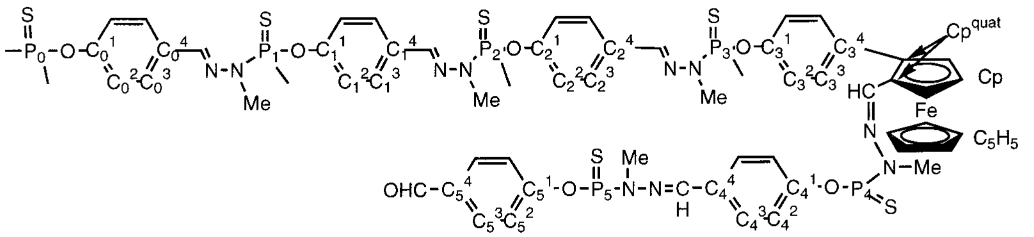

Figure 6. Numbering scheme used for NMR.

$^{2}J_{\mathrm{CP1-2-3-4-5}}$ = 13.3 Hz, $\mathrm{P_{1-2-3-4-5}}$-N-$\mathrm{CH_3}$), 67.5 (s, Cp), 69.7 (s, Cp), 70.8 (s, $\mathrm{C_5H_5}$), 72.1 (s, Cp), 77.2 (s, $\mathrm{Cp^{quat}}$), 88.4 (s, $\mathrm{Cp^{quat}}$), 121.2 (br s, $\mathrm{C_5{}^2}$), 121.7 (br s, $\mathrm{C_{0-1-2-3-4}{}^2}$), 128.3 (s, $\mathrm{C_{0-1-2-3-4}{}^3}$), 130.6 (s, $\mathrm{C_5{}^3}$), 132.3 (s, $\mathrm{C_{0-1-2-3-4}{}^4}$), 134.6 (s, $\mathrm{C_5{}^4}$), 138.8 (br d, $^{3}J_{\mathrm{CP1-2-3-4-5}}$ = 14.2 Hz, CH=N), 143.1 (d, $^{3}J_{\mathrm{CP6}}$ = 18.2 Hz, CH=N), 149.6 (d, $^{2}J_{\mathrm{CP5}}$ = 7.2 Hz, $\mathrm{C_5{}^1}$), 151.2 (d, $^{2}J_{\mathrm{CP0-1-2-3-4}}$ = 7.4 Hz, $\mathrm{C_{0-1-2-3-4}{}^1}$). Anal. Calcd for $\mathrm{C_{2472}H_{2280}Cl_{192}Fe_{96}N_{378}O_{189}P_{190}S_{190}}$ (64453.3 g $\mathrm{mol^{-1}}$): C, 46.07; H, 3.56; N, 8.21. Found: C, 46.12; H, 3.61; N, 8.19.

1-G$_{9+1}$: maroon powder (86% yield). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 62.0 (s, $\mathrm{P_{10}}$), 62.7 (s, $\mathrm{P_{1-2-3-4-5-6-7-8-9}}$), $\mathrm{P_0}$ undetectable. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.34 (br s, 9207H, $\mathrm{P_{1-2-3-4-5-6-7-8-9-10}}$-N-$\mathrm{CH_3}$), 4.03–4.89 (s, 12288H, Cp-H), 7.12–7.68 (m, 15345H, $\mathrm{C_6H_4}$, CH=N). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 32.1 (d, $^{2}J_{\mathrm{CP10}}$ = 13.0 Hz, $\mathrm{P_{10}}$-N-$\mathrm{CH_3}$), 32.8 (d, $^{2}J_{\mathrm{CP1-2-3-4-5-6-7-8-9}}$ = 13.2 Hz, $\mathrm{P_{1-2-3-4-5-6-7-8-9}}$-N-$\mathrm{CH_3}$), 67.5 (s, Cp), 69.7 (s, Cp), 70.8 (s, $\mathrm{C_5H_5}$), 72.1 (s, Cp), 77.2 (s, $\mathrm{Cp^{quat}}$), 88.4 (s, $\mathrm{Cp^{quat}}$), 121.1 (br s, $\mathrm{C_9{}^2}$), 121.7 (br s, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^2}$), 128.3 (s, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^3}$), 130.6 (s, $\mathrm{C_9{}^3}$), 132.2 (s, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^4}$), 134.6 (s, $\mathrm{C_9{}^4}$), 138.8 (br d, $^{3}J_{\mathrm{CP1-2-3-4-5-6-7-8-9}}$ = 14.1 Hz, CH=N), 143.1 (d, $^{3}J_{\mathrm{CP10}}$ = 18.1 Hz, CH=N), 149.5 (d, $^{2}J_{\mathrm{CP9}}$ = 7.1 Hz, $\mathrm{C_9{}^1}$), 151.3 (d, $^{2}J_{\mathrm{CP0-1-2-3-4-5-6-7-8}}$ = 7.2 Hz, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^1}$). Anal. Calcd for $\mathrm{C_{39912}H_{36840}Cl_{3072}Fe_{1536}N_{6138}O_{3069}P_{3070}S_{3070}}$ (1039811 g $\mathrm{mol^{-1}}$): C, 46.10; H, 3.57; N, 8.27. Found: C, 46.39; H, 3.55; N, 8.15.

General Procedure for the Synthesis of Dendrimers 1-G′$_{n+1}$. To a solution of 250 mg of dendrimer **1-G$_{n+1}$** (**n** = 3, 0.0159 mmol; **n** = 5, 3.87 × 10^{-3} mmol; **n** = 9, 2.4 × 10^{-4} mmol) in THF (10 to 20 mL) at room temperature was added a slight excess of 4-hydroxybenzaldehyde sodium salt (**n** = 3, 121 mg, 0.841 mmol; **n** = 5, 118 mg, 0.817 mmol; **n** = 9, 107 mg, 0.737 mmol). The resulting solution was stirred overnight, then centrifuged, and evaporated to dryness. The residue was washed twice with ether to afford dendrimers **1-G′$_{n+1}$**.

1-G′$_{3+1}$: orange powder (89% yield). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 52.6 (s, $\mathrm{P_0}$), 60.2 ($\mathrm{P_4}$), 62.0 (s, $\mathrm{P_3}$), 62.8 (s, $\mathrm{P_{1-2}}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.27 (m, 135H, $\mathrm{P_{1-2-3-4}}$-N-$\mathrm{CH_3}$), 3.97 (s, 120H, Cp-H), 4.39 (s, 24H, Cp-H), 4.51 (s, 24H, Cp-H), 4.84 (s, 24H, Cp-H), 7.15–7.76 (m, 417H, $\mathrm{C_6H_4}$, CH=N), 9.99 (s, 48H, CHO). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 33.1 (d, $^{2}J_{\mathrm{CP1-2-3-4}}$ = 12.9 Hz, $\mathrm{P_{1-2-3-4}}$-N-$\mathrm{CH_3}$), 66.9 (s, Cp), 69.4 (s, Cp), 70.6 (s, $\mathrm{C_5H_5}$), 72.0 (s, Cp), 77.2 (s, $\mathrm{Cp^{quat}}$), 88.1 (s, $\mathrm{Cp^{quat}}$), 121.1 (d, $^{3}J_{\mathrm{CP3}}$ = 4.0 Hz, $\mathrm{C_3{}^2}$), 121.7 (d, $^{3}J_{\mathrm{CP4}}$ = 5.2 Hz, $\mathrm{C_4{}^2}$), 121.8 (br s, $\mathrm{C_{0-1-2}{}^2}$), 122.0 (d, $^{3}J_{\mathrm{CP4}}$ = 6.1 Hz, $\mathrm{C_4{}^2}$), 128.3 (s, $\mathrm{C_{0-1-2}{}^3}$), 130.6 (s, $\mathrm{C_3{}^3}$), 131.3 (s, $\mathrm{C_4{}^3}$), 131.4 (s, $\mathrm{C_4{}^3}$), 132.3 (s, $\mathrm{C_{0-1-2}{}^4}$), 133.5 (s, $\mathrm{C_4{}^4}$), 134.6 (s, $\mathrm{C_3{}^4}$), 138.9 (m, CH=N-N-$\mathrm{P_{1-2-3}}$), 140.8 (d, $^{3}J_{\mathrm{CP4}}$ = 13 Hz, CH=N-N-$\mathrm{P_4}$), 149.4 (d, $^{2}J_{\mathrm{CP3}}$ = 6.7 Hz, $\mathrm{C_3{}^1}$), 151.3 (d, $^{2}J_{\mathrm{CP0-1-2}}$ = 5.5 Hz, $\mathrm{C_{0-1-2}{}^1}$), 155.4 (br s, $\mathrm{C_4{}^1}$), 190.7 (s, CHO). IR (KBr): 1703 $\mathrm{cm^{-1}}$ (C=O). Anal. Calcd for $\mathrm{C_{936}H_{792}Fe_{24}N_{90}O_{141}P_{46}S_{46}}$ (19797 g $\mathrm{mol^{-1}}$): C, 56.79; H, 4.03; N, 6.37. Found: C, 56.93; H, 4.13; N, 6.32.

1-G′$_{5+1}$: orange powder (86% yield). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 60.2 (s, $\mathrm{P_6}$), 62.1 (s, $\mathrm{P_{3-4-5}}$), 62.7 (s, $\mathrm{P_{1-2}}$), $\mathrm{P_0}$ undetectable. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.34 (br d, 567H, $\mathrm{P_{1-2-3-4-5-6}}$-N-$\mathrm{CH_3}$), 3.96 (s, 288H, Cp-H), 4.39 (s, 96H, Cp-H), 4.51 (s, 96H, Cp-H), 4.84 (s, 96H, Cp-H), 7.12–7.69 (m, 1713H, $\mathrm{C_6H_4}$, CH=N), 9.89 (s, 3072H, CHO). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 33.2 (d, $^{2}J_{\mathrm{CP1-2-3-4-5-6}}$ = 12.8 Hz, $\mathrm{P_{1-2-3-4-5-6}}$-N-$\mathrm{CH_3}$), 66.9 (s, Cp), 69.4 (s, Cp), 70.6 (s, $\mathrm{C_5H_5}$), 72.0 (s, Cp), 77.2 (s, $\mathrm{Cp^{quat}}$), 88.1 (s, $\mathrm{Cp^{quat}}$), 121.2 (br s, $\mathrm{C_5{}^2}$), 121.7 (d, $^{3}J_{\mathrm{CP0-1-2-3-4-6}}$ = 5.1 Hz, $\mathrm{C_6{}^2}$, $\mathrm{C_{0-1-2-3-4}{}^2}$), 122.0 (br s, $\mathrm{C_6{}^2}$), 128.3 (s, $\mathrm{C_{0-1-2-3-4}{}^3}$), 130.5 (s, $\mathrm{C_5{}^3}$), 131.3 (br s, $\mathrm{C_6{}^3}$), 132.3 (s, $\mathrm{C_{0-1-2-3-4}{}^4}$), 133.4 (s, $\mathrm{C_6{}^4}$), 134.6 (s, $\mathrm{C_5{}^4}$), 138.9 (m, CH=N-N-$\mathrm{P_{1-2-3-4-5}}$), 140.8 (d, $^{3}J_{\mathrm{CP6}}$ = 13.1 Hz, CH=N-N-$\mathrm{P_6}$), 149.4 (d, $^{2}J_{\mathrm{CP5}}$ = 6.6 Hz, $\mathrm{C_5{}^1}$), 151.3 (br s, $\mathrm{C_{0-1-2-3-4}{}^1}$), 155.3 (br s, $\mathrm{C_6{}^1}$), 190.7 (s, CHO). IR (KBr): 1703 $\mathrm{cm^{-1}}$ (C=O). Anal. Calcd for $\mathrm{C_{3816}H_{3240}Fe_{96}N_{378}O_{573}P_{190}S_{190}}$ (80900 g $\mathrm{mol^{-1}}$): C, 56.65; H, 4.03; N, 6.54. Found: C, 56.73; H, 4.15; N, 6.49.

1-G′$_{9+1}$: orange powder (86% yield). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 62.0 (s, $\mathrm{P_{1-6}}$), 62.7 (s, $\mathrm{P_{2-3-4-5}}$), $\mathrm{P_0}$ undetectable. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.34 (br s, 9207H, $\mathrm{P_{1-2-3-4-5-6-7-8-9-10}}$-N-$\mathrm{CH_3}$), 4.03–4.89 (m, 12288H, Cp-H), 7.12–7.68 (m, 15345H, $\mathrm{C_6H_4}$, CH=N). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 32.8 (d, $^{2}J_{\mathrm{CP1-2-3-4-5-6-7-8-9-10}}$ = 13.2 Hz, $\mathrm{P_{1-2-3-4-5-6-7-8-9-10}}$-N-$\mathrm{CH_3}$), 66.9 (s, Cp), 69.4 (s, Cp), 70.6 (s, $\mathrm{C_5H_5}$), 72.0 (s, Cp), 77.2 (s, $\mathrm{Cp^{quat}}$), 88.1 (s, $\mathrm{Cp^{quat}}$), 121.1 (br s, $\mathrm{C_9{}^2}$), 121.7 (br s, $\mathrm{C_{10}{}^2}$, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^2}$), 122.1 (br s, $\mathrm{C_{10}{}^2}$), 128.3 (s, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^3}$), 130.6 (s, $\mathrm{C_9{}^3}$), 131.4 (br s, $\mathrm{C_{10}{}^3}$), 132.2 (s, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^4}$), 133.5 (s, $\mathrm{C_{10}{}^4}$), 134.6 (s, $\mathrm{C_9{}^4}$), 138.8 (br d, $^{3}J_{\mathrm{CP1-2-3-4-5-6-7-8-9}}$ = 14.2 Hz, CH=N), 142.1 (br d, $^{3}J_{\mathrm{CP10}}$ = 14.1 Hz, CH=N-N-$\mathrm{P_{10}}$), 149.5 (d, $^{2}J_{\mathrm{CP9}}$ = 7.1 Hz, $\mathrm{C_9{}^1}$), 151.4 (m, $\mathrm{C_{0-1-2-3-4-5-6-7-8}{}^1}$), 152.5 (d, $^{2}J_{\mathrm{CP10}}$ = 7.3 Hz, $\mathrm{C_{10}{}^1}$). IR (KBr): 1703 $\mathrm{cm^{-1}}$ (C=O). Anal. Calcd for $\mathrm{C_{61416}H_{52200}Fe_{1536}N_{6138}O_{9213}P_{3070}S_{3070}}$ (1302964 g $\mathrm{mol^{-1}}$): C, 56.60; H, 4.04; N, 6.60. Found: C, 56.69; H, 4.16; N, 6.52.

General Procedure for the Synthesis of Dendrimers 1-G$_{n+2}$. To a solution of 250 mg of dendrimer **1-G′$_{n+1}$** (**n** = 3, 1.3 × 10^{-2} mmol; **n** = 5, 3.18 × 10^{-3} mmol; **n** = 9, 1.98 × 10^{-4} mmol) in THF (5 to 10 mL) at room temperature was added a slight excess of a solution of dichlorothiophosphorhydrazide in chloroform (0.3 M). The resulting solution was stirred overnight, then evaporated to dryness. The residue was washed twice with ether to afford dendrimers **1-G$_{n+2}$**.

1-G$_{3+2}$: maroon powder (88% yield). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 52.6 (s, $\mathrm{P_0}$), 60.8 (s, $\mathrm{P_4}$), 62.2 (s, $\mathrm{P_3}$), 62.8 (s, $\mathrm{P_{1-2}}$), 63.1 (s, $\mathrm{P_6}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.25–3.34 (m, 216H, $\mathrm{P_{1-2-3-4-5}}$-N-$\mathrm{CH_3}$), 4.08 (br s, 120H, Cp-H), 4.45 (br s, 24H, Cp-H), 4.55 (br s, 24H, Cp-H), 4.99 (br s, 24H, Cp-H), 7.11–7.79 (m, 465H, $\mathrm{C_6H_4}$, CH=N). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 32.2 (d, $^{3}J_{\mathrm{CP5}}$ = 13.6 Hz, $\mathrm{P_5}$-N-$\mathrm{CH_3}$), 32.9–33.2 (m, $\mathrm{P_{1-2-3-4}}$-N-$\mathrm{CH_3}$), 67.0 (s, Cp), 69.3 (s, Cp), 70.7 (s, $\mathrm{C_5H_5}$), 71.9 (s, Cp), 77.2 (s, $\mathrm{Cp^{quat}}$), 88.0 (s, $\mathrm{Cp^{quat}}$), 121.1 (br s, $\mathrm{C_3{}^2}$), 121.6 (br s, $\mathrm{C_4{}^2}$, $\mathrm{C_{0-1-2}{}^2}$), 121.9 (br s, $\mathrm{C_4{}^2}$), 128.3 (s, $\mathrm{C_{0-1-2}{}^3}$), 128.7 (br s, $\mathrm{C_4{}^3}$), 130.5 (br s, $\mathrm{C_3{}^3}$), 131.4 (s, $\mathrm{C_4{}^4}$), 132.2 (s, $\mathrm{C_{0-1-2}{}^4}$), 134.7 (s, $\mathrm{C_3{}^4}$), 138.9 (br s, CH=N-N-$\mathrm{P_{1-2-3}}$), 140.2 (br s, CH=N-N-$\mathrm{P_4}$), 141.1 (br s, CH=N-N-$\mathrm{P_5}$), 149.4 (d, $^{2}J_{\mathrm{CP3}}$ = 7.0 Hz, $\mathrm{C_3{}^1}$), 151.3 (br s, $\mathrm{C_{0-1-2}{}^1}$), 151.8 (br s, $\mathrm{C_4{}^1}$). Anal. Calcd for $\mathrm{C_{984}H_{936}Cl_{96}Fe_{24}N_{186}O_{93}P_{94}S_{94}}$ (27524 g $\mathrm{mol^{-1}}$): C, 42.94; H, 3.43; N, 9.46. Found: C, 43.03; H, 3.53; N, 9.42.

1-G$_{5+2}$: maroon powder (87% yield). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 61.6 (s, $\mathrm{P_6}$), 62.0 (br s, $\mathrm{P_{1-2-3-4-5}}$), 63.1 (s, $\mathrm{P_7}$), $\mathrm{P_0}$ undetectable. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.35 (br s, 1143H, $\mathrm{P_{1-2-3-4-5-6}}$-N-$\mathrm{CH_3}$), 4.02 (br s, 288H, Cp-H), 4.41 (br s, 96H, Cp-H), 4.52 (br s, 96H, Cp-H), 4.89 (br s, 96H, Cp-H), 7.19–7.82 (m, 1805H, $\mathrm{C_6H_4}$, CH=N). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 31.8 (d, $^{3}J_{\mathrm{CP7}}$ = 13.4 Hz, $\mathrm{P_7}$-N-$\mathrm{CH_3}$), 33.2 (br d, $^{3}J_{\mathrm{CP1-2-3-4-5-6}}$ = 13.4 Hz, $\mathrm{P_{1-2-3-4-5-6}}$-N-$\mathrm{CH_3}$), 67.0 (s, Cp), 69.3 (s, Cp), 70.7 (s, $\mathrm{C_5H_5}$), 71.9 (s, Cp), 77.2 (s, $\mathrm{Cp^{quat}}$), 88.0 (s, $\mathrm{Cp^{quat}}$), 121.1 (br s, $\mathrm{C_5{}^2}$), 121.6 (br s, $\mathrm{C_6{}^2}$, $\mathrm{C_{0-1-2-4}{}^2}$), 122.0 (br s, $\mathrm{C_6{}^2}$), 128.3 (s, $\mathrm{C_{0-1-2-3-4}{}^3}$), 128.6 (br s, $\mathrm{C_6{}^3}$), 130.5 (br s, $\mathrm{C_5{}^3}$), 131.4 (s, $\mathrm{C_6{}^4}$), 132.3 (s, $\mathrm{C_{0-1-2-3-4}{}^4}$), 134.7 (s, $\mathrm{C_5{}^4}$), 138.5–139.1 (m, CH=N-N-$P_{1-2-3-4-5}$), 139.8 (br s, CH=N-N-P_6), 140.7 (br s, CH=N-N-P_7), 149.4 (d, $^2J_{CP3} = 7.8$ Hz, $C_5{}^1$), 151.3−152.0 (m, $C_{0-1-2-3-4-6}{}^1$). Anal. Calcd for $C_{4008}H_{3816}Cl_{384}Fe_{96}N_{762}O_{381}P_{382}S_{382}$ (111811 g mol^{-1}): C, 43.06; H, 3.44; N, 9.57. Found: C, 42.98; H, 3.57; N, 9.50.

1-G$_{9+2}$: maroon powder (86% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.6 (s, P_{10}), 62.0 (s, $P_{1-2-3-4-5-6-7-8-9}$), 63.1 (s, P_{11}), P_0 undetectable. ^1H NMR ($CDCl_3$): δ 3.35 (br s, 18423H, $P_{1-2-3-4-5-6-7-8-9-10-11}$-N-$CH_3$), 4.01−4.99 (m, 12288H, Cp-H), 7.22−7.78 (m, 18417H, C_6H_4, CH=N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.6 (d, $^3J_{CP11} = 13.5$ Hz, P_{11}-N-CH_3), 32.9−33.2 (m, $P_{1-2-3-4-5-6-6-7-8-9-10}$-N-$CH_3$), 67.0 (s, Cp), 69.3 (s, Cp), 70.7 (s, C_5H_5), 71.9 (s, Cp), 77.2 (s, Cp^{quat}), 88.0 (s, Cp^{quat}), 121.1 (br s, $C_9{}^2$), 121.6 (br s, $C_{10}{}^2$, $C_{0-1-2-3-4-5-6-7-8}{}^2$), 128.3 (s, $C_{0-1-2-3-4-5-6-7-8}{}^3$), 128.6 (br s, $C_{10}{}^3$), 130.5 (br s, $C_9{}^3$), 131.4 (s, $C_{0-1-2-3-4-5-6-7-8-10}{}^4$), 134.6 (s, $C_9{}^4$), 138.5−138.9 (m, CH=N-N-$P_{1-2-3-4-5-6-7-8-9}$), 139.9 (br s, CH=N-N-P_{10}), 140.6 (br s, CH=N-N-P_{11}), 149.4−152.1 (m, $C_{0-1-2-3-4-5-6-7-8-9-10}{}^1$). Anal. Calcd for $C_{64488}H_{61416}Cl_{6144}Fe_{1536}N_{12282}O_{6141}P_{6142}S_{6142}$ (1797538 g mol^{-1}): C, 43.09; H, 3.44; N, 9.57. Found: C, 43.15; H, 3.54; N, 9.51.

General Procedure for the Synthesis of Dendrimers 1-G′$_{n+2}$. To a solution of 250 mg of dendrimer **1-G$_{n+2}$** (**n** = 3, 9.28 × 10^{-3} mmol; **n** = 5, 2.28 × 10^{-3} mmol; **n** = 9, 1.42 × 10^{-4} mmol) in THF (10 to 20 mL) at room temperature was added a slight excess of 4-hydroxybenzaldehyde sodium salt (**n** = 3, 141 mg, 0.980 mmol; **n** = 5, 139 mg, 0.963 mmol; **n** = 9, 138 mg, 0.960 mmol). The resulting solution was stirred overnight, then centrifuged, and evaporated to dryness. The residue was washed twice with ether to afford dendrimers **1-G′$_{n+2}$**.

1-G′$_{3+2}$: orange powder (85% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.6 (s, P_0), 60.5 (br s, P_5), 61.6 (s, P_4), 62.2 (br s, P_{1-2-3}). ^1H NMR ($CDCl_3$): δ 3.32 (m, 216H, $P_{1-2-3-4-5}$-N-CH_3), 4.07 (br s, 120H, Cp-H), 4.41 (br s, 24H, Cp-H), 4.52 (br s, 24H, Cp-H), 4.98 (br s, 24H, Cp-H), 7.11−7.79 (m, 849H, C_6H_4, CH=N), 9.92 (s, 96H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.3 (d, $^3J_{CP1-2-3-4-5} = 13.6$ Hz, $P_{1-2-3-4-5}$-N-CH_3), 66.8 (s, Cp), 69.4 (s, Cp), 70.7 (s, C_5H_5), 71.9 (s, Cp), 77.2 (s, Cp^{quat}), 88.0 (s, Cp^{quat}), 121.2 (d, $^3J_{CP3} = 3.3$ Hz, $C_3{}^2$), 121.5 (d, $^3J_{CP0-1-2-4} = 3.0$ Hz, $C_4{}^2$, $C_{0-1-2}{}^2$), 121.7 (d, $^3J_{CP4} = 3.1$ Hz, $C_4{}^2$), 122.1 (br s, $C_5{}^2$), 128.5 (br s, $C_4{}^3$, $C_{0-1-2}{}^3$), 130.5 (s, $C_3{}^3$), 131.5 (br s, $C_5{}^3$, $C_4{}^4$), 132.3 (s, $C_{0-1-2}{}^4$), 133.5 (s, $C_5{}^4$), 134.7 (s, $C_3{}^4$), 138.8−140.7 (m, CH=N-N-$P_{1-2-3-4-5}$), 149.4 (br s, $C_3{}^1$), 151.4−151.9 (m, $C_{0-1-2-4}{}^1$), 155.0 (br s, $C_5{}^1$), 190.8 (s, CHO). IR (KBr): 1702 cm^{-1} (C=O). Anal. Calcd for $C_{1656}H_{1416}Fe_{24}N_{186}O_{285}P_{94}S_{94}$ (35748 g mol^{-1}): C, 55.64; H, 3.99; N, 7.29. Found: C, 55.77; H, 4.06; N, 7.17.

1-G′$_{5+2}$: orange powder (86% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.6 (br s, P_7), 61.6 (s, P_6), 62.3 (br s, $P_{1-2-3-4-5}$), P_0 undetectable. ^1H NMR ($CDCl_3$): δ 3.36 (br s, 1143H, $P_{1-2-3-4-5-6-7}$-N-CH_3), 4.00 (br s, 288H, Cp-H), 4.38 (br s, 96H, Cp-H), 4.51 (br s, 96H, Cp-H), 4.99 (br s, 96H, Cp-H), 7.18−7.92 (m, 3341H, C_6H_4, CH=N), 9.83 (s, 384H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.5 (br d, $^3J_{CP1-2-3-4-5-6-7} = 13.4$ Hz, $P_{1-2-3-4-5-6-7}$-N-CH_3), 66.8 (s, Cp), 69.4 (s, Cp), 70.7 (s, C_5H_5), 71.9 (s, Cp), 77.2 (s, Cp^{quat}), 88.0 (s, Cp^{quat}), 121.2 (br s, $C_5{}^2$), 121.5 (br s, $C_6{}^2$, $C_{0-1-2-3-4}{}^2$), 121.9 (br s, $C_6{}^2$, $C_7{}^2$), 128.3 (br s, $C_6{}^3$, $C_{0-1-2-3-4}{}^3$), 130.5 (s, $C_5{}^3$), 131.5 (s, C_6,^{4} $C_7{}^3$), 132.3 (s, $C_{0-1-2-3-4}{}^4$), 133.6 (s, $C_7{}^4$), 134.7 (s, $C_5{}^4$), 138.7−140.4 (m, CH=N-N-$P_{1-2-3-4-5-6-7}$), 149.3 (d, $^3J_{CP5} = 7.1$ Hz, $C_5{}^1$), 151.4−151.9 (m, $C_{0-1-2-3-4-6}{}^1$), 155.5 (d, $^3J_{CP7} = 6.9$ Hz, $C_7{}^1$), 190.8 (s, CHO). IR (KBr): 1702 cm^{-1} (C=O). Anal. Calcd for $C_{6696}H_{5736}Fe_{96}N_{762}O_{1149}P_{382}S_{382}$ (144705 g mol^{-1}): C, 55.58; H, 3.99; N, 7.38. Found: C, 55.70; H, 4.07; N, 7.26.

1-G′$_{9+2}$: orange powder (85% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.6 (br s, P_{11}), 61.5 (s, P_{10}), 62.2 (br s, $P_{1-2-3-4-5-6-7-8-9}$), P_0 undetectable. ^1H NMR ($CDCl_3$): δ 3.33 (br s, 18423H, $P_{1-2-3-4-5-6-7-8-9-10-11}$-N-$CH_3$), 4.01−4.98 (m, 12288H, Cp-H), 7.12−7.98 (m, 42993H, C_6H_4, CH=N), 9.84 (s, 6144H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.4 (br d, $^3J_{CP1-2-3-4-5-6-7-8-9-10-11} = 13.2$ Hz, $P_{1-2-3-4-5-6-7-8-9-10-11}$-N-$CH_3$), 66.8 (s, Cp), 69.4 (s, Cp), 70.7 (s, C_5H_5), 71.9 (s, Cp), 77.2 (s, Cp^{quat}), 88.0 (s, Cp^{quat}), 121.2 (br s, $C_9{}^2$), 121.6 (br s, $C_{10}{}^2$, $C_{0-1-2-3-4-5-6-7-8}{}^2$), 122.1 (br s, $C_{10}{}^2$, $C_{11}{}^2$), 128.4 (br s, $C_{10}{}^3$, $C_{0-1-2-3-4-5-6-7-8}{}^3$), 130.6 (s, $C_9{}^3$), 131.6 (s, $C_{10}{}^4$, $C_{11}{}^3$), 132.4 (s, $C_{0-1-2-3-4-5-6-7-8}{}^4$), 133.7 (s, $C_{11}{}^4$), 134.6 (s, $C_9{}^4$), 138.6−140.4 (m, CH=N-N-$P_{1-2-3-4-5-6-7-8-9-10-11}$), 149.6 (d, $^3J_{CP9} = 7.2$ Hz, $C_9{}^1$), 151.1−151.9 (m, $C_{0-1-2-3-4-5-6-7-8-10}{}^1$), 155.4 (d, $^3J_{CP11} = 6.9$ Hz, $C_{11}{}^1$), 190.7 (s, CHO). IR (KBr) = 1702 cm^{-1} (C=O). Anal. Calcd for $C_{107496}H_{92156}Fe_{1536}N_{12282}O_{18429}P_{6142}S_{6142}$ (2323865 g mol^{-1}): C, 55.56; H, 3.99; N, 7.40. Found: C, 56.64; H, 4.14; N, 7.31.

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