Chemistry within Megamolecules: Regiospecific Functionalization after Construction of Phosphorus Dendrimers

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Abstract: The synthesis of dendrimers including P═N−P═S linkages specifically placed at some generations within the dendrimeric architecture allows the grafting of several types of functional groups at site- and depth-specific locations in the internal layers. The synthesis is carried out up to the fourth generation starting from a difunctional core, or up to the third generation starting from a hexafunctional core. These dendrimers include 2, 6, or 18 P═N−P═S groups, depending on the type of core and the generation considered. The functional groups are introduced by several types of reactions. First, the strong polarization of the P═N−P═S linkage induces a facile reactivity with various alkyl triflates such as methyl, allyl, and propargyl triflates, leading to the formation of functionalized phosphonium salts $[P{=}N{=}P{-}S{-}R]^+$. The alkylation induces a weakening of the P−S bond which is cleaved with $P(NMe_2)_3$, leading to the formation of internal aminophosphite groups [P═N−P:]. These highly reactive tricoordinated phosphorus atoms are alkylated by methyl or allyl iodide, leading to a second series of functionalized dendrimers including phosphonium salts at some precise internal layers. A third series of internally functionalized dendrimers is obtained by the Staudinger reaction of functionalized azides with the aminophosphite internal groups. Isothiocyanate, aldehyde, and primary amine derivatives have been grafted regiospecifically in this way [P═N−P═N−R]. The reactivity of the aldehyde internal functions leading to the grafting of azides or crown-ethers is also described.

Introduction

The study of mesoscopic systems and nanostructures receives increasing attention, and among them, the study of dendrimers[1] appears as a very dynamic topic. Indeed, these highly branched oligomers with precise molecular architectures built by repetitive synthetic cycles, offer a range of applications and properties. Up to now, most of the work devoted to dendrimers concerned the synthesis and the transformation of surface functional groups.[1,2] In addition, some specific reactions at the level of the core have been reported,[3] but very few papers deal with the reactivity of internal functions after the synthesis of the dendrimer. Furthermore, most of these reactions concerning lithiation,[4] protonation,[5] complexation,[6] or the obtention of polyradicals[7] are not layer-specific. In fact, only one group has reported site- and depth-specific reactions[8] before our own work.

In preliminary reports, we have demonstrated the permeability of phosphorus containing dendrimers toward small molecules such as alkyltriflates, even for high generations.[9,10] Indeed, the presence of polar P═N−P═S linkages, precisely placed at some generations within the dendrimeric superstructure, allows the regiospecific grafting of methylium groups only at the generations containing this linkage, even at the core of the seventh generation.[9] Furthermore, we have shown that the dendrimeric structure is sufficiently flexible to accommodate very bulky

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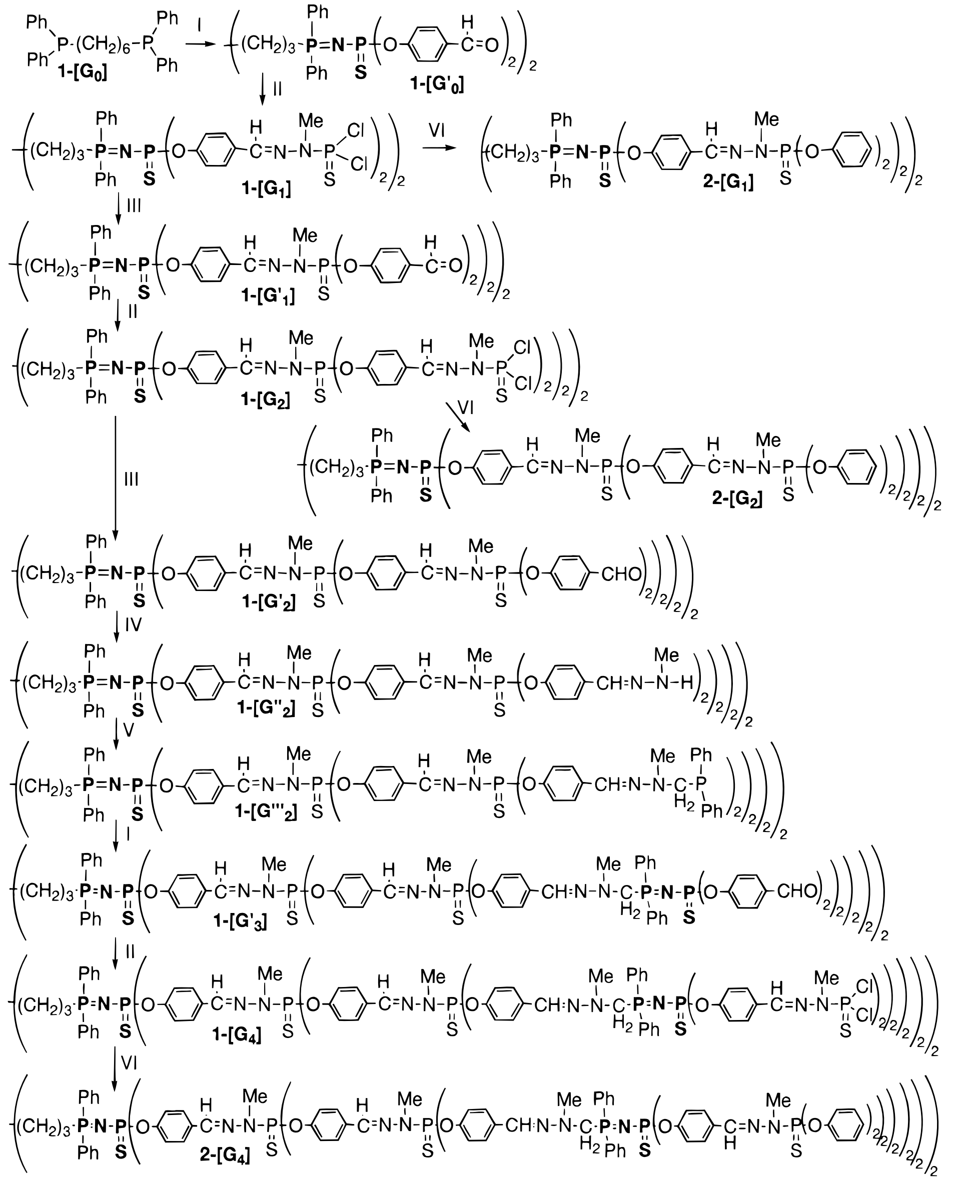
10.1021/ja982778e CCC: $15.00

Scheme 1



I) $N_3P(S)(OC_6H_4CHO)_2$ II) $Cl_2P(S)NMeNH_2$ III) $NaOC_6H_4CHO$ IV) H_2NNHMe V) Ph_2PCH_2OH VI) $NaOC_6H_5$

entities: six dendrons have been grown up to the third generation inside a main dendrimer which had been chemically modified at well-defined sites in the network.[11]

We report here an extension of these preliminary results, the grafting of various functional groups when and where desired within the dendrimer after its construction, without any branch degradation.

Results and Discussion

Synthesis of Dendrimers. The design of dendrimers is carried out with the aim of including P═N−P═S groups in precise sites which could be activated after the synthesis of the dendrimer. For this purpose, two different cores are used: the 1,6-bis(diphenylphosphinohexane) **1-[G$_0$]** and the hexachlorocyclotriphosphazene **3-[G$_0$]**.

Starting from **1-[G$_0$]**, P═N−P═S linkages are obtained directly by a Staudinger reaction with $N_3P(S)[OC_6H_4CHO]_2$ which affords **1-[G′$_0$]** (Scheme 1). The growing of the dendrimeric structure is pursued up to the formation of compound **1-[G′$_2$]** by using alternatively the condensation of aldehyde functions with $H_2NNMeP(S)Cl_2$ and the reaction of 4-hydroxybenzaldehyde sodium salt with $P(S)Cl_2$ end groups.[2a] Starting from **1-[G′$_2$]** other P═N−P═S linkages are introduced in three steps: (i) condensation of aldehyde end groups with methylhydrazine, (ii) Mannich type condensation with Ph_2PCH_2OH, and (iii) Staudinger reaction with $N_3P(S)[OC_6H_4CHO]_2$. This sequence of reactions induces the formation of 16 P═N−P═S groups at the level of the third generation. Condensation with $H_2NNMeP(S)Cl_2$ affords dendrimer **1-[G$_4$]** which possess 64 Cl on the surface of the dendrimer and 18 P═N−P═S linkages: two at the core and 16 at the third generation. To

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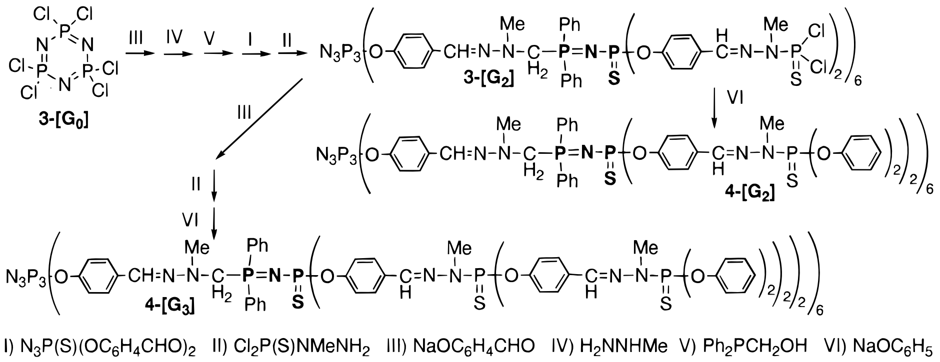
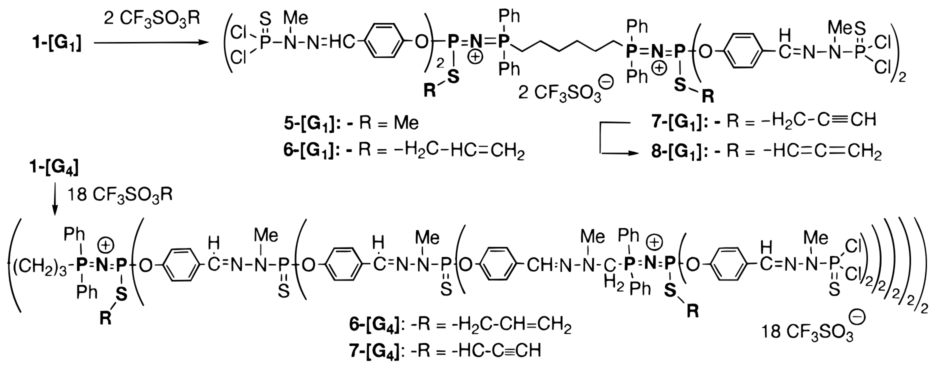
Scheme 2



Scheme 3



avoid side reactions with the $P(S)Cl_2$ groups which could occur when studying the reactivity of the P=N−P=S linkages, phenol sodium salt is added to **1-[G$_1$]**, **1-[G$_2$]**, and **1-[G$_4$]** leading to **2-[G$_1$]**, **2-[G$_2$]**, and **2-[G$_4$]**, respectively.

A similar reaction scheme is also applied starting from the hexachloro cyclotriphosphazene **3-[G$_0$]**. In this case, the P=N−P=S groups are included at the level of the first generation, using the procedure already described in Scheme 1. Reactions with $NaOC_6H_4CHO$, H_2NNMeH, Ph_2PCH_2OH, $N_3P(S)[OC_6H_4CHO]_2$, and $H_2NNMeP(S)Cl_2$ successively, afford compound **3-[G$_2$]**. Starting from compound **3-[G$_2$]**, the alternate use of $NaOC_6H_4CHO$ and $H_2NNMeP(S)Cl_2$ finally leads to dendrimer **3-[G$_3$]** which possess 6 P=N−P=S linkages at the level of the first generation and 48 Cl on the surface. In this case also, the surface of the dendrimer is inactivated by reacting **3-[G$_2$]** and **3-[G$_3$]** with $NaOC_6H_5$, to afford dendrimers **4-[G$_2$]** and **4-[G$_3$]**, respectively (Scheme 2).

All the dendrimers are obtained in quantitative yields as crude products and in >90% yield after work up. All the reactions are monitored by ^{31}P NMR, which, in addition to ^1H and ^{13}C NMR, and IR spectra is a unique and irreplaceable tool to characterize all these compounds.[2a,f,n,11]

Reactions with Alkyl Triflates. The first phosphonium-containing dendrimers were built with phosphonium salts at all the branching points of each generation.[12] For our part, we have described dendrimers in which phosphonium salts were created only at specific generations after the synthesis of the dendrimer.[9] Indeed, the strong polarity of the P=N−P=S linkage ($P^+−N=P−S^−$) allows the regiospecific alkylation of the sulfur atom of this linkage, whereas the other P=S bonds of the molecule do not react. This reaction was illustrated first with methyltriflate on compound **1-[G$_1$]**[9] (Scheme 3). The monitoring of this reaction by ^{31}P NMR indicated the total disappearance of both doublets corresponding to the P=N−P=S linkages of **1-[G$_1$]** (δ = 20.9 (Ph_2P=N), and 51.9 ppm (P=S), $^2J_{PP}$ = 35 Hz) on behalf of two new doublets for the $[P−N−P−S−Me]^+$ linkages of **5-[G$_1$]** (δ = 22.1 (P−S−Me), and 27.6 ppm (Ph_2P−N), $^2J_{PP}$ = 17 Hz), whereas the signal corresponding to the $P(S)Cl_2$ groups remains identical (δ = 62.1 for **1-[G$_1$]**, 62.5 ppm for **5-[G$_1$]**). This result is now unambiguously confirmed by the X-ray diffraction determination of the structure of **5-[G$_1$]** (Table 1). The CAMERON drawing is represented in Figure 1, together with selected bond lengths and bond angles. The four $O−C_6H_4−CH=N−N(Me)P(S)$ arms are flat, a tendency which was already observed for other dendrimers incorporating this linkage.[2n,13] One methyl group is linked to the sulfur atom of each P=N−P=S group, whereas the four $P(S)Cl_2$ end groups remain unchanged. The P(1)−N(2) (1.52(1) Å), N(2)−P(2) (1.60(1) Å), P(1)−S(1) (2.035(4) Å), and S(1)−C(4) (1.86(2) Å) bond

Table 1. Crystal Data for Dendrimers **5-[G$_1$]** and **8-[G$_1$]**

compound	**5-[G$_1$]**	**8-[G$_1$]**
formula	$[C_{64}H_{70}N_{10}O_4S_6P_8Cl_8]$-$[CF_3SO_3]_2$, 6 (CH_2Cl_2)	$[C_{68}H_{70}N_{10}O_4S_6P_8Cl_8]$-$[CF_3SO_3]_2$, 2 (CH_2Cl_2), 4 (CH_3OH)
molecular weight	2574.8	2288
space group	$P\bar{1}$	$P\bar{1}$
crystal system	triclinic	triclinic
a, Å	13.235(2)	13.290(2)
b, Å	13.738(2)	14.060(2)
c, Å	17.145(2)	17.048(2)
α, deg	84.18(2)	83.13(1)
β, deg	69.82(1)	68.44(1)
γ, deg	70.04(1)	73.21(1)
V, Å^3	2750(2)	2798(2)
Z	1	1
D_{calcd}, g cm^{-3}	1.56	1.40
μ, cm^{-1}	8.24	6.11
T (K)	130	293
crystal size, mm	0.50 × 0.10 × 0.05	0.60 × 0.35 × 0.20

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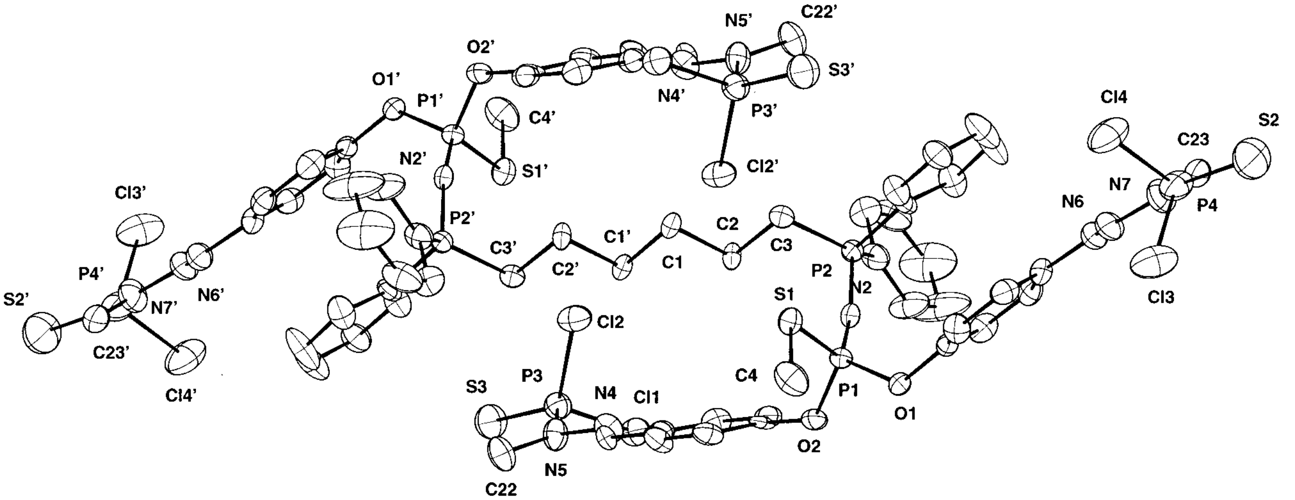

Figure 1. CAMERON drawing of dendrimer **5-[G$_1$]**. Selected bond lengths (Å): P(1)−S(1) = 2.035(4); P(1)−N(2) = 1.52(1); P(2)−N(2) = 1.60(1); S(1)−C(4) = 1.86(2); P(3)−S(3) = 1.906(5); P(3)−N(5) = 1.65(1); P(4)−S(2) = 1.882(6); P(4)−N(7) = 1.62(1). Selected bond angles (deg): P(1)−N(2)−P(2) = 152.1(7); S(1)−P(1)−N(2) = 110.9(4); P(1)−S(1)−C(4) = 102.2(5).

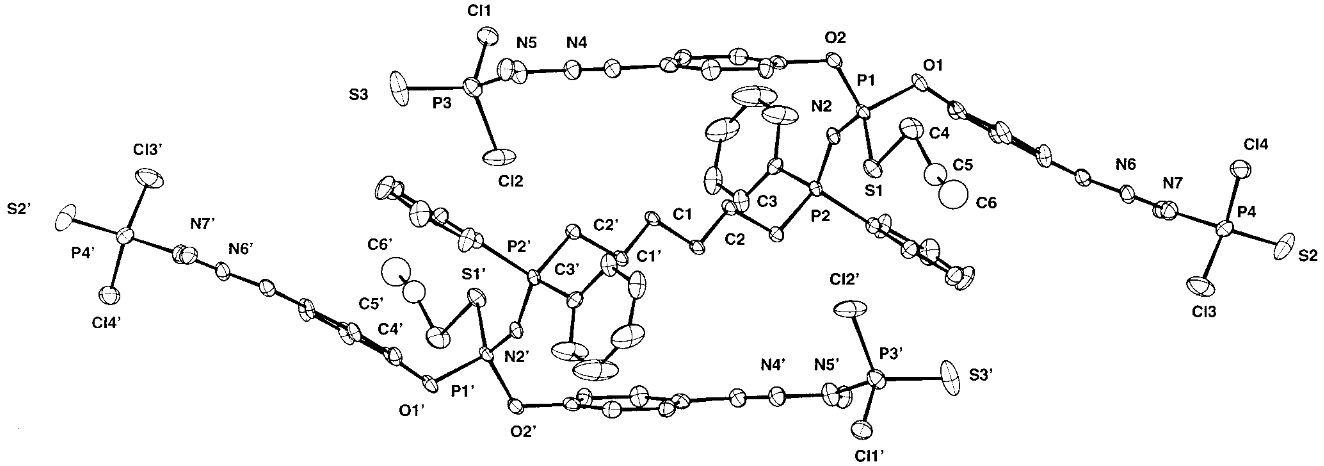

Figure 2. CAMERON drawing of dendrimer **8-[G$_1$]**. Selected bond lengths (Å): P(1)−S(1) = 2.03 (3); P(1)−N(2) = 1.53(6); P(2)−N(2) = 1.59(6); S(1)−C(4) = 1.85(9); C(4)−C(5) = 1.45(9); C(5)−C(6) = 1.40(9); P(3)−S(3) = 1.90(4); P(3)−N(5) = 1.66(7); P(4)−S(2) = 1.88(5); P(4)−N(7) = 1.63(7). Selected bond angles (deg): P(1)−N(2)−P(2) = 148(5); S(1)−P(1)−N(2) = 111(3); P(1)−S(1)−C(4) = 101(3); S(1)−C(4)−C(5) = 102(4).

distances reflect the partial delocalization of the positive charge along this linkage. Indeed, all these bond lengths lie between the distances commonly found for single and double bonds between these elements: for instance, the distances for the N−P(S)Cl$_2$ fragments of **5-[G$_1$]** are 1.62−1.65 Å for the P−N bonds and 1.882−1.906 Å for the P=S bonds. The bond lengths of the [P=N=P]$^+$ fragments of **5-[G$_1$]** are comparable to the values generally determined for the well-known bis(triphenylphosphine)imminium cations [Ph$_3$P=N=PPh$_3$]$^+$ which has found extensive use for the crystallization of anionic species.[14]

The dialkylation of **1-[G$_1$]** has been extended to functionalized triflates such as allyltriflate and propargyltriflate.[15] In both cases, the alkylation reaction occurs on the sulfur of the P=N−P=S bonds to afford **6-[G$_1$]** and **7-[G$_1$]**, respectively.[10] Two new doublets appear on the ^{31}P NMR spectra at δ = 20.4 (P−S−allyl) and 26.9 ppm (Ph$_2$P−N), $^2J_{PP}$ = 17 Hz, for **6-[G$_1$]**, or at δ = 18.8 (P−S−propargyl) and 27.5 ppm (Ph$_2$P−N), $^2J_{PP}$ = 13 Hz, for **7-[G$_1$]**, beside signals corresponding to the other P=S groups of the molecule, which remain unchanged. The structure of compound **6-[G$_1$]** has been determined by X-ray diffraction.[10] The bond lengths and angles corresponding to the [P=N=P−S]$^+$ linkages are very close to those determined for **5-[G$_1$]**, as could be expected (Scheme 3).

A slow evolution of compound **6-[G$_1$]** (unpurified) is observed when left in solution for 3 months. The new compound **8-[G$_1$]** exhibits in ^{31}P NMR two new doublets (δ = 19.0 (P−S−C) and 27.3 ppm (Ph$_2$P−N), $^2J_{PP}$ = 14 Hz) very slightly different from those detected for **6-[G$_1$]**. Changes are mainly detected in ^{1}H and ^{13}C NMR, exclusively on signals corresponding to the S−allyl linkages. For instance, the presence of a highly deshielded signal on the ^{13}C NMR spectrum of **8-[G$_1$]** (δ = 203 ppm), characteristic of HC=$\underline{C}$=CH$_2$ linkages, corresponds to the well-known transformation CH$_2$−C≡CH → HC=C=CH$_2$ in the presence of a base. The X-ray diffraction study of compound **8-[G$_1$]** (Figure 2, Table 1) confirms the structure, even if the determination of the bond lengths and angles for the S−HC=C=CH$_2$ linkages is not very accurate, due to the fact that the allenic chains are highly disordered. The values determined for the [P=N=P−S]$^+$ linkages compare well with those found for **5-[G$_1$]** and **7-[G$_1$]**.

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[14] See for instance: (a) Wei, C. Y.; Marks, M. W.; Ban, R.; Kirtley, S. W.; Bisson, D. E., Henderson, M. E., Koetzle, T. F. *Inorg. Chem.* **1982**, *21*, 2556. (b) Blake, A. J.; Freeman, G.; Johnson, B. F. G.; McDougall, G. S. *Acta Crystallogr.* **1994**, *C50*, 1301.

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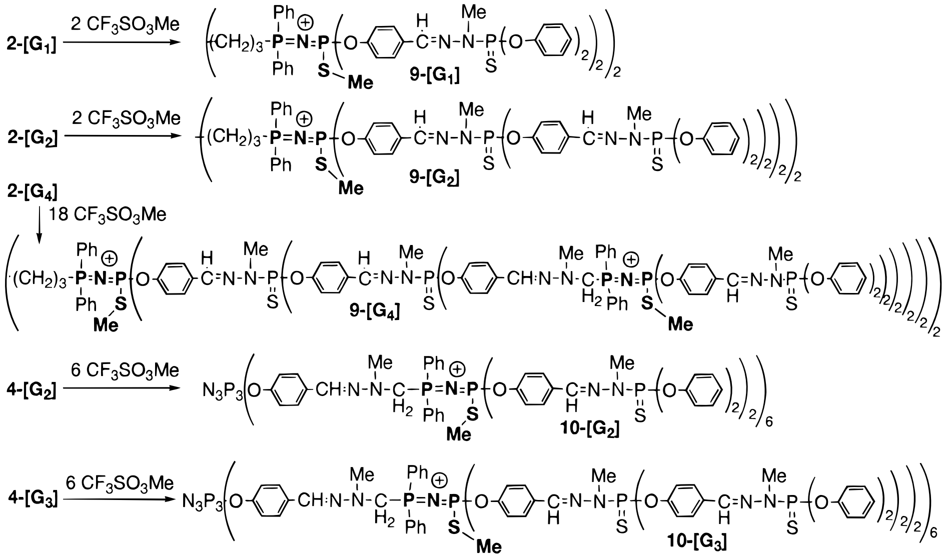
Scheme 4



The alkylation reactions have been extended to higher generations of the dendrimer **1-[Gn]**, particularly to the fourth generation **1-[G$_4$]**. This dendrimer possesses 2 P=N−P=S groups at the core and 16 P=N−P=S groups at the third generation. The reaction with 18 equiv of allyl triflate gives dendrimer **6-[G$_4$]**, whereas the reaction with 18 equiv of propargyltriflate gives dendrimer **7-[G$_4$]** (Scheme 3). In both cases, the reactions are monitored by ^{31}P NMR which indicates, besides the signals of the N−N−P=S groups, the presence of two sets of two doublets in an approximative ratio 1/8: δ = 20.5 (P−S−allyl) and 26.7 ppm (Ph$_2$P−N), $^2J_{PP}$ = 15 Hz at the level of the core, 19.7 (Ph$_2$P−N) and 21.3 ppm (P−S−allyl), $^2J_{PP}$ = 11 Hz at the level of the third generation for **6-[G$_4$]**; δ = 18.8 (P−S−propargyl) and 27.4 ppm (Ph$_2$P−N), $^2J_{PP}$ = 12 Hz at the level of the core, 19.6 (Ph$_2$P−N) and 20.5 ppm (P−S−propargyl), $^2J_{PP}$ = 8 Hz at the level of the third generation for **7-[G$_4$]**. ^{1}H and ^{13}C NMR spectra of both compounds confirm their structure.

The methylation reaction with methyltriflate has been used also with dendrimers possessing O−Ph groups on the surface (Scheme 4). Dendrimers **9-[G$_1$]** (2 P=N=P−S−Me groups), **9-[G$_2$]** (2 P=N=P−S−Me groups), and **9-[G$_4$]** (18 P=N=P−S−Me groups) are obtained from the dendrimers with the diphosphine core, **2-[G$_1$]**, **2-[G$_2$]**, and **2-[G$_4$]**, respectively. Dendrimers **10-[G$_2$]** (6 P=N=P−S−Me groups), and **10-[G$_3$]** (6 P=N=P−S−Me groups) are obtained from the dendrimers with the cyclotriphosphazene core, **4-[G$_2$]**, and **4-[G$_3$]**, respectively. Methylation of all these compounds induces the same type of shielding of the signal corresponding to the P=N−P=S groups and the slight deshielding of the signal corresponding to the Ph$_2$P=N−P=S groups already observed by ^{31}P NMR for all the alkylated dendrimers described above (Figure 3). In all cases, the attribution of the signals to each phosphorus is done by running a ^{31}P NMR experiment with proton couplings: the PPh$_2$ signal gives a broad singlet, whereas each line of the doublet corresponding to the P−S−Me groups is splitted into four lines.

Desulfurization Reactions. It has been shown already that the alkylation of P=S bonds induces a weakening of the strength of this bond which can lead to its cleavage, for instance in the presence of tris(dimethylamino)phosphine, to give tricoordinated phosphorus atoms.[16] We have tried to apply this reaction to various dendrimers obtained after alkylation with methyltriflate. To demonstrate the feasability of this reaction with P=N=P−S−Me linkages, in first experiments, we have carried out this reaction with the first generation **9-[G$_1$]** (Scheme 5). Reaction with P(NMe$_2$)$_3$ induces the appearance of one singlet on the ^{31}P NMR spectrum at δ = 68 ppm, corresponding to [Me−S−P(NMe$_2$)$_3$]$^+$, and the disappearance of the signals corresponding to the [P=N=P−S−Me]$^+$ linkages, on behalf of two new doublets at δ = 14.5 (Ph$_2$P=N) and 144.2 ppm (N−P:) ($^2J_{PP}$ = 40.2 Hz). This last signal is characteristic of tricoordinated phosphorus atoms, and shows that the desulfurization has occurred to yield the dendrimer **11-[G$_1$]** which possess two [P=N−P:] linkages. **11-[G$_1$]** is soluble in toluene, whereas [Me-S−P(NMe$_2$)$_3$]$^+$ is not, thus **11-[G$_1$]** is isolated by extraction with toluene, and used without further purification. Indeed, this compound is extremely sensitive to oxidation, and we have been unable to obtain reliable ^{1}H and ^{13}C NMR spectra. However, the ^{31}P NMR spectrum of compound **11-[G$_1$]** is unambiguous.

The same desulfurization procedure applied to dendrimers **9-[G$_2$]**, **9-[G$_4$]** (diphosphine core), and **10-[G$_2$]**, **10-[G$_3$]** (cyclotriphosphazene core) yields compounds **11-[G$_2$]**, **11-[G$_4$]**, **12-[G$_2$]**, and **12-[G$_3$]**, respectively (Scheme 5, Figure 3). Among them, one can notice the obtention of dendrimer **11-[G$_4$]**, which possess two [P=N−P:] linkages at the level of the core (characterized on the ^{31}P NMR spectrum by the appearance of two doublets at δ = 14.2 (Ph$_2$P=N) and 144.1 ppm (N−P:), $^2J_{PP}$ = 41 Hz), and 16 [P=N−P:] linkages at the level of the third generation (characterized on the ^{31}P NMR spectrum by the appearance of two doublets at δ = 8.7 (Ph$_2$P=N) and 144.3 ppm (N−P:), $^2J_{PP}$ = 40 Hz).

Reactions of [P=N−P:] Internal Linkages with Alkyl Halides. The presence of tricoordinated phosphorus atoms in the internal layers of dendrimers 11-[Gn] and 12-[Gn] should confer to these compounds a versatile reactivity. We have focused our attention on the obtention of phosphonium salts (reactivity with alkyl halides) and P=N bonds (reactivity with azides). Both methods can lead to the grafting of new types of internal functions.

In first attempts, we tried to react alkyl bromides with dendrimer **11-[G$_2$]**: no reaction occurs, except oxidation. On

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[16] (a) Omelanczuk, J.; Mikolajczyk, M. *Tetrahedron Lett.* **1984**, *25*, 2493. (b) Omelanczuk, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1718. (c) Prévôté, D.; Galliot, C.; Caminade, A. M.; Majoral, J. P. *Heteroatom Chem.* **1995**, *6*, 313.

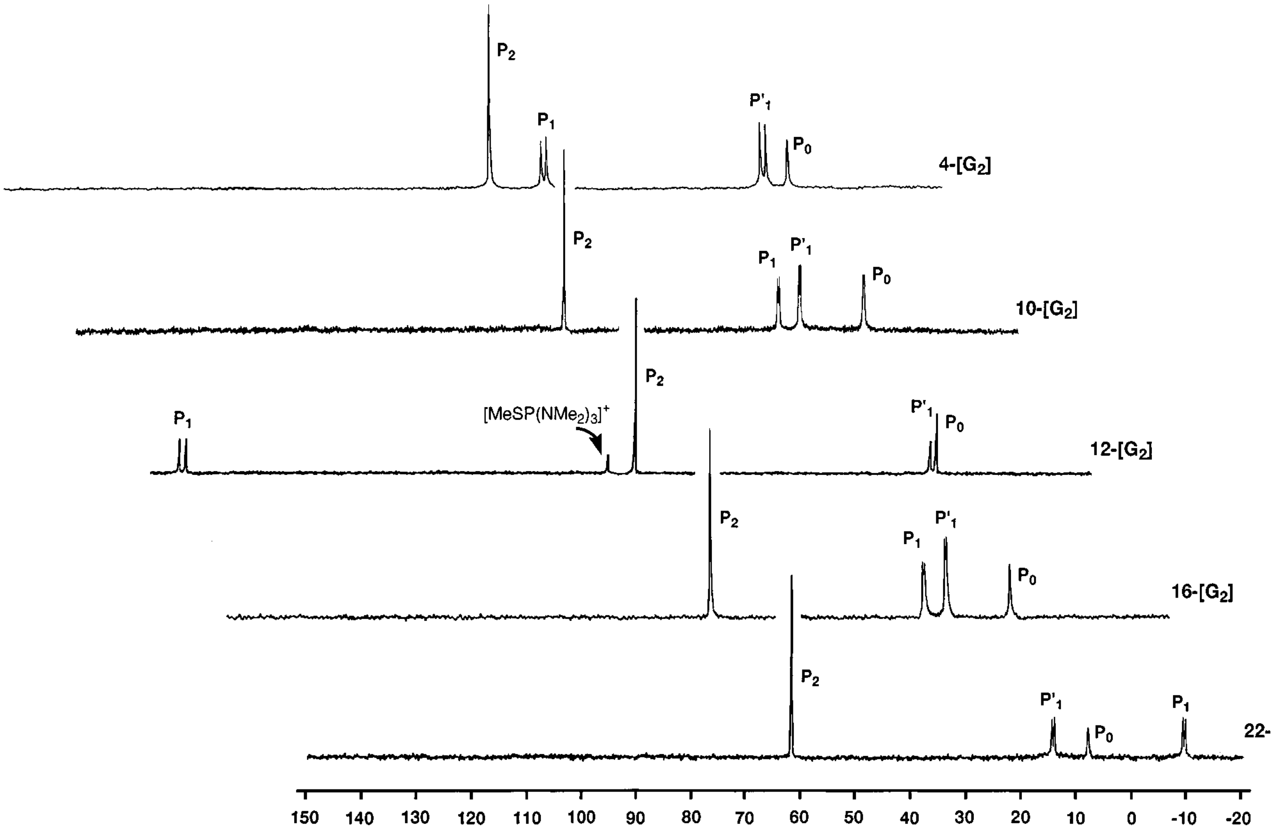
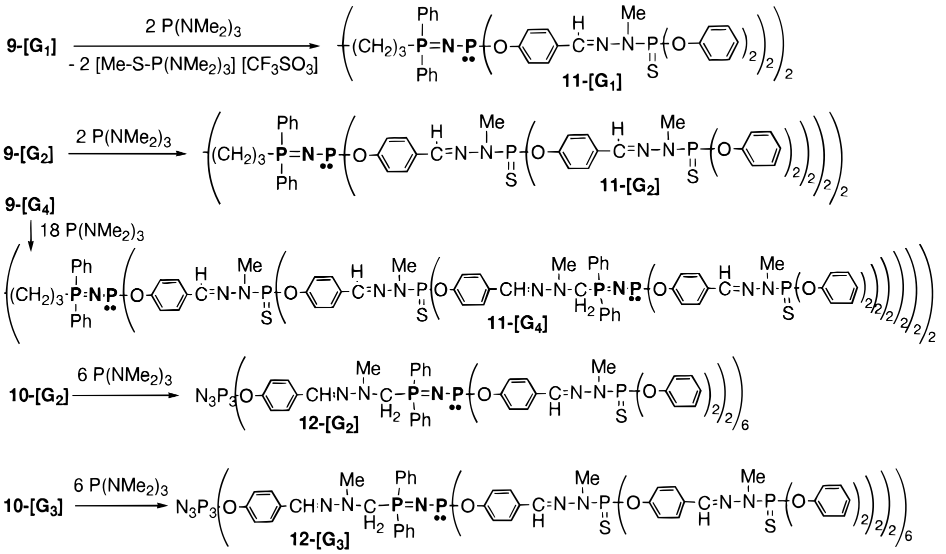


Figure 3. ^{31}P NMR spectra of dendrimers **4-[G$_2$]**, **10-[G$_2$]**, **12-[G$_2$]**, **16-[G$_2$]**, and **22-[G$_2$]**.

Scheme 5

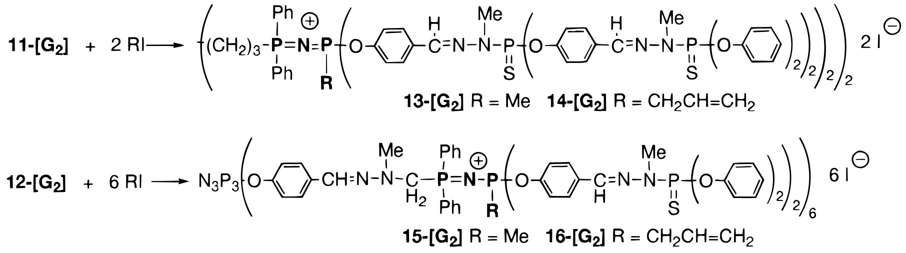


the other hand, alkyl iodides react easily at room temperature to yield the corresponding phosphonium salts. The reaction with methyl iodide leads to dendrimer **13-[G$_2$]** (Scheme 6), which is characterized by the appearance of two doublets corresponding to the [$Ph_2P{=}N{=}P{-}Me]^+$ linkages at $\delta = 26.5$ and 26.9 ppm, $^2J_{PP} = 23$ Hz, on the ^{31}P NMR spectrum. Analogous experiments have been carried out with dendrimer **12-[G$_2$]**, leading to the methylated dendrimer **15-[G$_2$]** which possess 6 [$Ph_2P{=}N{=}P{-}Me]^+$ internal linkages.

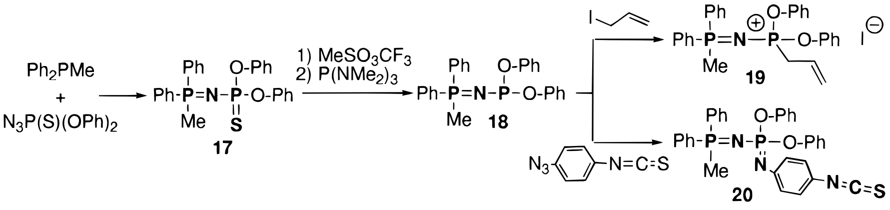
Allylic functions are introduced in the same way, reacting allyl iodide with dendrimers **11-[G$_2$]** and **12-[G$_2$]**, to yield dendrimers **14-[G$_2$]** and **16-[G$_2$]**, respectively. The allylation induces the appearance of two doublets on the ^{31}P NMR spectrum of both compounds, characteristic of the [$Ph_2P{=}N{=}P{-}C]^+$ linkages (Figure 3). To ascertain the attribution of signals in ^{1}H and ^{13}C NMR spectra, the "small" compound **19**, possessing all the functional groups of dendrimers **14-[Gn]** and **15-[Gn]** was also synthesized as shown in Scheme 7.

Reactions of [P=N−P:] Internal Linkages with Azides. The Staudinger reaction of functionalized azides with the aminophosphite groups of dendrimers **11-[Gn]** and **12-[Gn]** should be the best method to introduce new functions at some specific layers within the dendrimer. Indeed, these reactions are generally quantitative and proceed with evolution of nitrogen as sole byproduct.

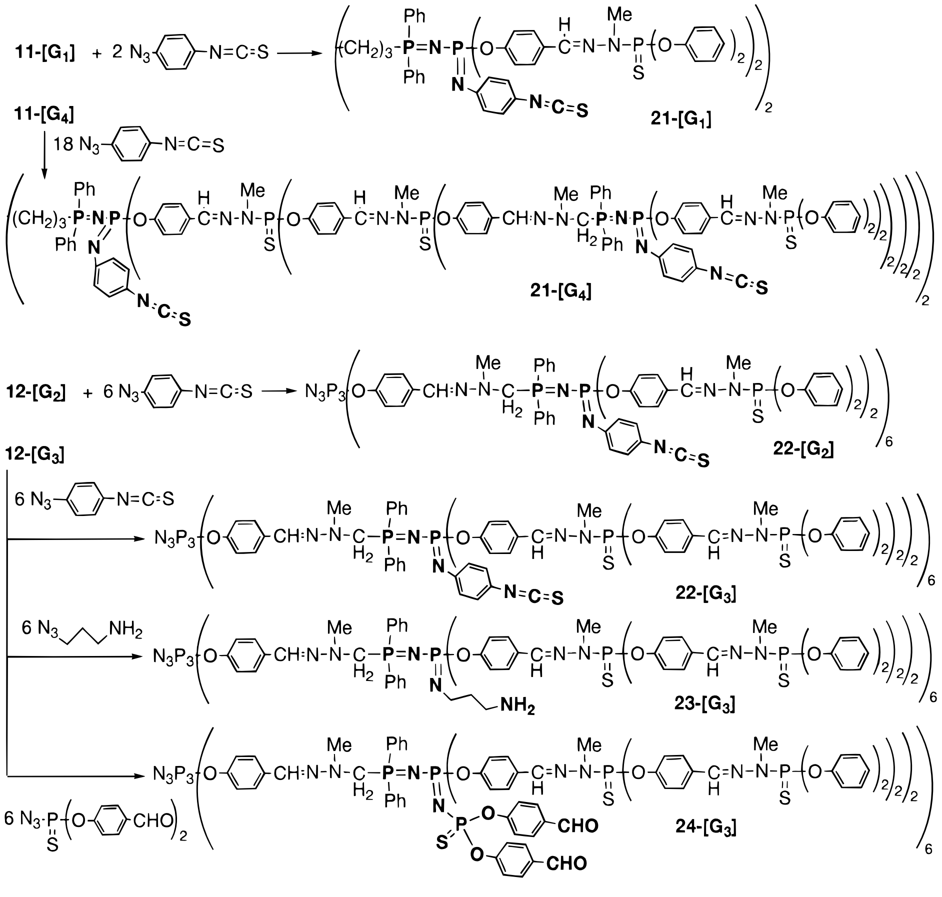
Scheme 6



Scheme 7



Scheme 8



The reaction was first tested with the small compound **18** and 4-azidophenylisothiocyanate, leading to the quantitative formation of compound **20** (Scheme 7). The reaction was then applied to the first generation of the dendrimer **11-[G$_1$]**. It proceeds rapidly at room temperature to yield compound **21-[G$_1$]** (Scheme 8). The formation of the Ph$_2$P=N−P=N−Ar linkages induces the appearance of two doublets on the ^{31}P NMR spectrum at $\delta = -8.3$ (P=N−Ar) and 20.6 ppm (Ph$_2$P=N), $^2J_{PP} = 22$ Hz. The bright orange color of this dendrimer indicates a large delocalization of electrons along the P=N−P=N−C$_6$H$_4$−N=C=S linkages. The same experiment carried out with 18 equiv of 4-azidophenylisothiocyanate and dendrimer **11-[G$_4$]** affords dendrimer **21-[G$_4$]** which possesses 2 isocyanate linkages at the core and 16 at the third generation. Both P=N−P=S types of linkages induce the appearance of two different sets of two doublets on the ^{31}P NMR spectrum: $\delta = -8.6$ (P=N−Ar) and 17.5 ppm (Ph$_2$P=N) ($^2J_{PP} = 30.5$ Hz) for the core, and $\delta = -10.4$ (P=N−Ar) and 18.2 ppm (Ph$_2$P=N) ($^2J_{PP} = 31.1$ Hz) for the third generation.

Dendrimers **12-[G$_2$]** and **12-[G$_3$]** obtained from the cyclotriphosphazene core behave alike with 4-azidophenylisothiocyanate to give compounds **22-[G$_2$]** and **22-[G$_3$]**, respectively (Scheme 8).

Figure 3 demonstrates how useful is ^{31}P NMR to monitor rigorously the P=N−P=S → P=N=P−S−Me → P=N−P: → P=N=P−allyl or P=N−P=N−R transformations (**4-[G$_2$]** →

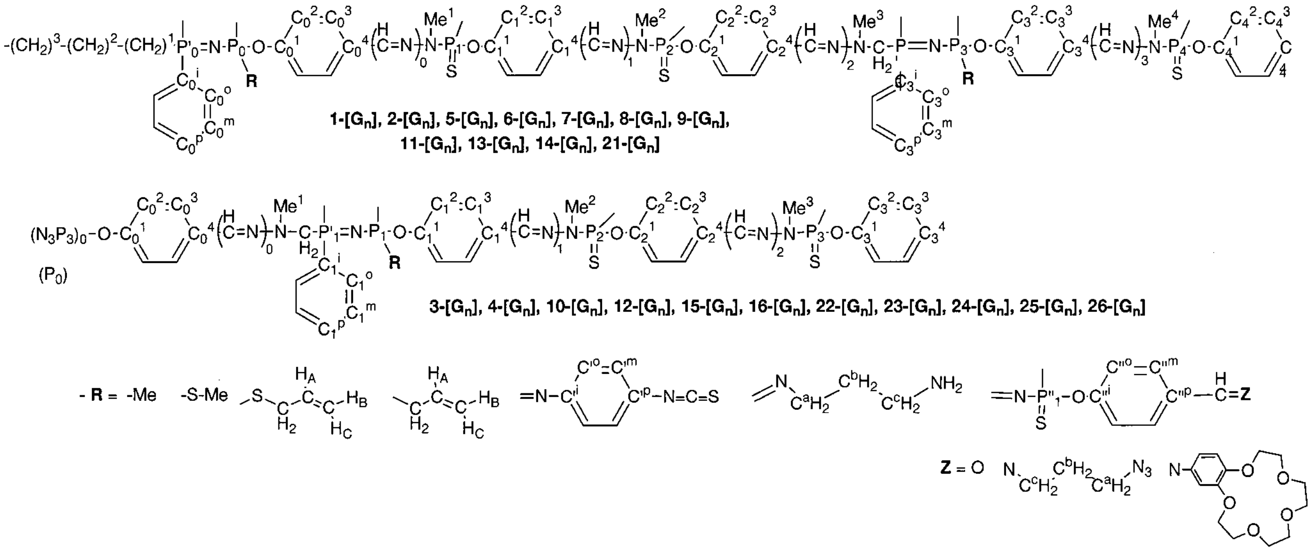
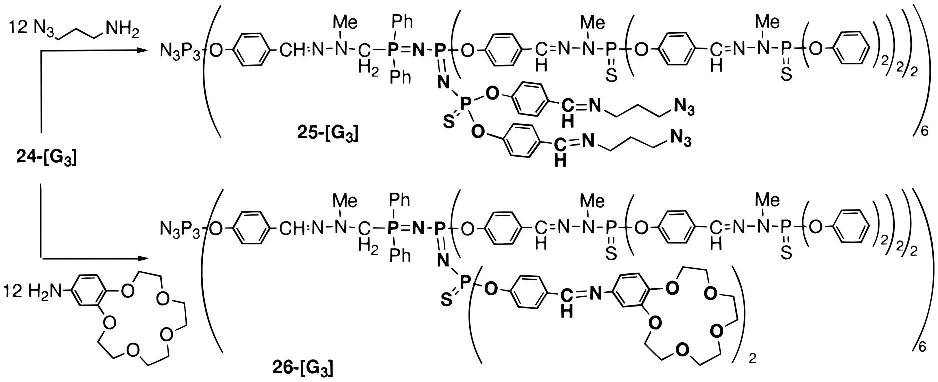


Figure 4. Numbering schemes used for ^{31}P, ^{1}H, and ^{13}C NMR.

Scheme 9



10-[G$_2$] → **12-[G$_2$]** → **16-[G$_2$]** or **22-[G$_2$]**). In all cases, the signals corresponding to the core P_0 and to the phosphorus of the surface P_2 remain unchanged, whereas the doublet corresponding to P'_1 and P_1 are shielded or deshielded, depending on the reagent used (see Figure 4 for the numbering used).

Several other types of azides such as 1-amino-3-azidopropane[17] and $N_3P(S)[OC_6H_4CHO]_2$ react with the aminophosphite internal groups. These reactions, carried out with dendrimer **12-[G$_3$]** induce the grafting of 6 primary amine (**23-[G$_3$]**) or 12 aldehyde (**24-[G$_3$]**) groups in the internal layer of the third generation dendrimer **12-[G$_3$]** (Scheme 8).

Condensation Reactions of Aldehyde Internal Groups. The presence of aldehyde internal groups should confer to dendrimer **24-[G$_3$]** a versatile reactivity, as we have already shown for dendrimers bearing aldehyde groups on the surface.[2] The condensation reaction of primary amines (Schiff reaction) occurs readily at room temperature with alkylamines such as 1-amino-3-azidopropane (Scheme 9). This reaction is monitored by ^{1}H NMR which indicates the total disappearance of the signal due to the CHO groups (δ = 9.73 ppm) on behalf of a signal at δ = 8.10 ppm corresponding to the CH═N groups. The condensation is also confirmed by ^{13}C NMR and IR spectra. This reaction leads to the quantitative grafting of 12 azides in the internal layers of dendrimer **25-[G$_3$]**.

Even a large molecule such as 4′-aminobenzo-15-crown-5 can be incorporated within the dendrimer by condensation, leading to compound 26-[G3] (Scheme 9, Figure 5). This reaction needs one week in refluxing THF to go to completion. The steric hindrance presumably plays a role in the disminishing of the reaction rate when compared to the condensation with 1-amino-3-azidopropane, but the main factor is certainly the fact that the crown ether is connected to an arylamine. Indeed, arylamines are known to be much less reactive than alkylamines; this phenomenon was already observed for the reactivity on the surface of low generation (nonhindered) dendrimers.[2e]

Conclusion

We have shown that the presence of P═N−P═S groups in the internal layers of two series of dendrimers allows the development of a versatile reactivity, due to the fact that the sulfur atom of this linkage can be considered as a protecting group, easy to remove. Indeed, the deprotection of this linkage allows the regiospecific grafting of several types of functional groups such as aminophosphites, allyl or propargyl groups, isothiocyanates, primary amines, azides, or crown-ethers. Furthermore, the use of alkyl triflates or alkyl iodides permits the introduction of charges in different layers, for instance at the core and at the third generation. All these functional groups and/or charges are located at precise sites within the dendrimeric structure, after the synthesis of the dendrimer.

This paper demonstrates that the presence of phosphorus atoms in the skeleton of the dendrimer should make possible for the first time the incorporation in the internal layers of any type of function needed for particular purposes, such as for example molecular recognition or catalysis. Work is in progress

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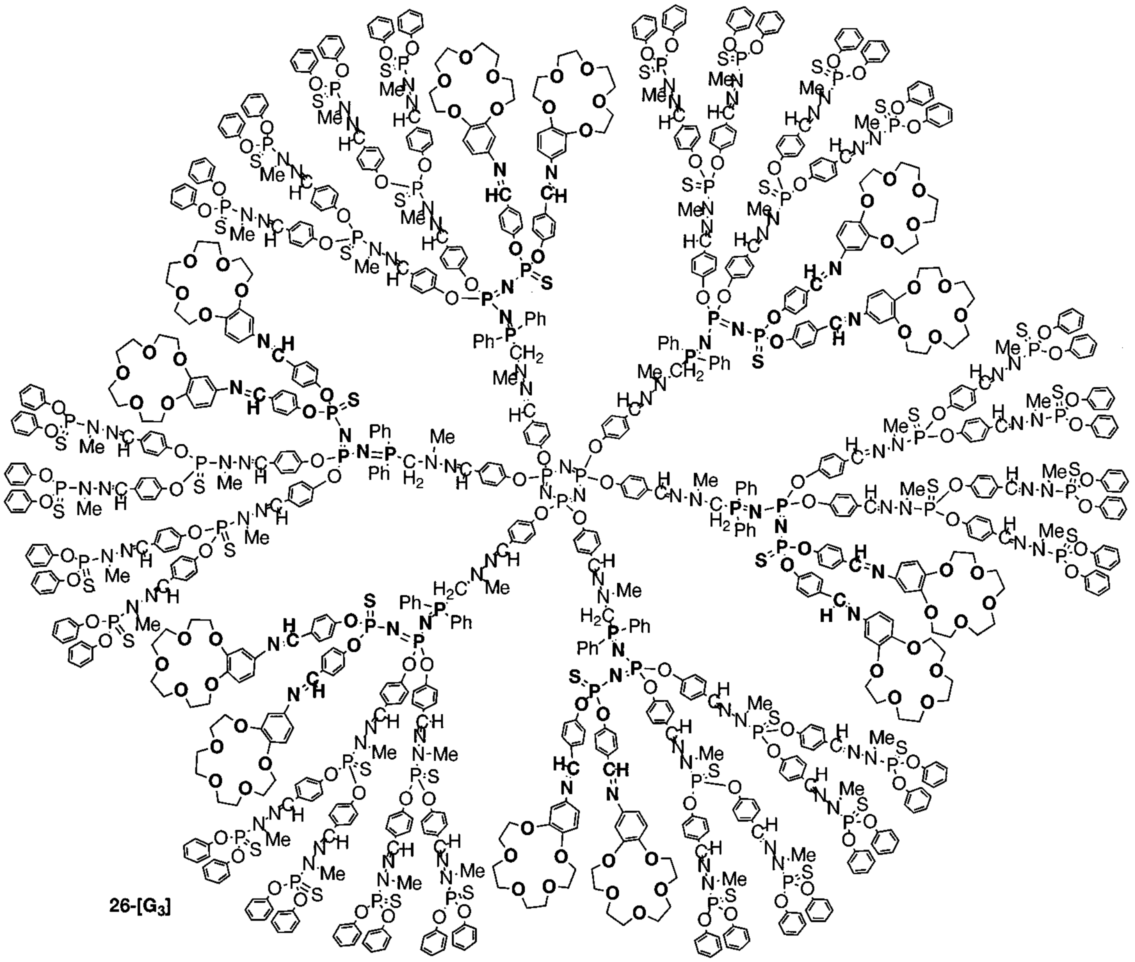
[17] Carboni, B.; Benalil, A.; Vaultier, M. *J. Org. Chem.* **1993**, *58*, 3736.



26-[G$_3$]

Figure 5. Dendrimer **26-[G$_3$]** possessing 12 crown-ether cavities in the internal layers.

to study the complexation ability of crown-ethers toward alkaline metals and of P═N−P═S and P═N−P═N−P═S groups toward transition metals.

Experimental Section

General. All manipulations were carried out with standard high vacuum and dry argon atmosphere techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC200 or AMX 400 spectrometers. ^{31}P NMR chemical shifts were reported in ppm relative to 85% H_3PO_4. The numbering used for NMR is depicted in Figure 4. Compounds $N_3P(S)(OC_6H_4CHO)_2$,[18] Ph_2PCH_2OH,[2g] $CF_3SO_3CH_2{-}CH{=}CH_2$,[14] $CF_3SO_3CH_2{-}C{\equiv}CH$,[14] and $N_3CH_2CH_2CH_2NH_2$,[17] were synthesized according to published procedures.

Synthesis of Dendrimers: Characterization of Compounds. 1-[G$_4$]: 94% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.5 (d, $^2J_{P'_3P_3} = 31.7$ Hz, P'_3), 20.4 (d, $^2J_{P'_0P_0} = 34.0$ Hz, P_0'), 52.5 (br d, $^2J_{P_3P'_3} = {}^2J_{P_0P'_0} = 31$ Hz, P_0, P_3), 62.5 (s, P_1), 63.0 (s, P_2), 63.2 (s, P_4) ppm. ^{1}H NMR ($CDCl_3$): δ 1.40 (br s, 8 H, $(CH_2)_3$, $(CH_2)_2$), 2.60 (br s, 4 H, $(CH_2)^1$), 2.82 (s, 48 H, Me^3), 3.37 (d, $^3J_{HP_1} = {}^3J_{HP_2} = {}^3J_{HP_4} = 14.0$ Hz, 132 H, Me^1, Me^2, Me^4), 4.71 (s, 32 H, $CH_2P'_3$), 6.85−7.70 (m, 480 H, C_6H_4, C_6H_5, CH═N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.7 (d, $^2J_{CP_4} = 13$ Hz, Me^4); 32,9 (d, $^2J_{CP_1} = {}^2J_{CP_2} = 12$ Hz, Me^1, Me^2), 39.1 (d, $^3J_{CP'_3} = 4$ Hz, Me^3), 56.5 (d, $^1J_{CP'_3} = 74$ Hz, $CH_2P'_3$), 121.1 (d, $^1J_{CP_2} = 3$ Hz, $C_2{}^2$), 121.9 (d, $^3J_{CP_0} = {}^3J_{CP_1} = {}^3J_{CP_3} = 4$ Hz, $C_0{}^2$, $C_1{}^2$, $C_3{}^2$), 126.5 (s, $C_2{}^3$), 127.8 (dd, $^1J_{CP'_3} = 104$ Hz, $^3J_{CP_3} = 5$ Hz, $C_3{}^i$), 127.9 (s, $C_0{}^3$), 128.2 (s, $C_1{}^3$, $C_3{}^3$), 128.5 (d, $^3J_{CP'_0} = {}^3J_{CP'_3} = 13$ Hz, $C_0{}^m$, $C_3{}^m$), 130.1 (s, $C_3{}^4$), 130.8 (s, $C_2{}^4$), 131.7 (s, $C_1{}^4$, $C_0{}^4$), 132.0 (d, $^2J_{CP'_0} = {}^2J_{CP'_3} = 10$ Hz, $C_0{}^o$, $C_3{}^o$), 132.4 (s, $C_3{}^p$), 133.4 (s, $\underline{C}H{=}NNCH_2P'_3$), 138.8 (m, $(CH{=}N)^1$), 139.7 (m, $(CH{=}N)^0$), 141.2 (d, $^3J_{CP_4} = 19$ Hz, $(CH{=}N)^3$), 149.6 (d, $^2J_{CP_2} = 7$ Hz, $C_2{}^1$), 151.2 (d, $^2J_{CP_1} = 7$ Hz, $C_1{}^1$), 152.9 (d, $^2J_{CP_0} = 8$ Hz, $C_0{}^1$), 153.2 (d, $^2J_{CP_3} = 9$ Hz, $C_3{}^1$), ($(CH_2)^3$, $(CH_2)^2$, $(CH_2)^1$, and $C_0{}^i$ not detected). Anal. Calcd for $C_{718}H_{704}N_{138}O_{60}P_{80}S_{62}Cl_{64}$: C, 45.48; H, 3.74; N, 10.19. Found: C, 45.71, H, 3.92; N, 9.99.

2-[G$_4$]: 94% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.2 (d, $^2J_{P'_3P_3} = 31.6$ Hz, P'_3), 20.4 (d, $^2J_{P'_0P_0} = 34.5$ Hz, P'_0), 52.1 (br d, $^2J_{P_0P'_0} = {}^2J_{P_3P'_3} = 31.5$ Hz, P_0, P_3), 61.8 (s, P_1), 61.9 (s, P_2), 63.2 (s, P_4) ppm; ^{1}H NMR ($CDCl_3$): 1.38 (br s, 8 H, $(CH_2)^3$, $(CH_2)^2$), 2.60 (br s, 4 H, $(CH_2)^1$), 2.82 (s, 48 H, Me^3), 3.37 (d, $^3J_{HP_1} = {}^3J_{HP_2} = {}^3J_{HP_4} = 14$ Hz, 132 H, Me^1, Me^2, Me^4), 4.71 (s, 32 H, $C\underline{H_2}P'_3$), 6.85−7.70 (m, 800 H, C_6H_4, C_6H_5, CH═N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.9 (d, $^2J_{CP_1} = {}^2J_{CP_2} = {}^2J_{CP_4}$, 12 Hz, Me^1, Me^2, Me^4), 39.1 (d, $^3J_{CP'_3} = 4$ Hz, Me^3), 56.6 (d, $^1J_{CP'_3} = 74$ Hz, $CH_2P'_3$), 121.1 (d, $^1J_{CP_2} = 3$ Hz, $C_2{}^2$), 121.3 (d, $^3J_{CP_4} = 4$ Hz, $C_4{}^2$), 121.8 (d, $^3J_{CP_0} = {}^3J_{CP_1} = {}^3J_{CP_3} = 4$ Hz, $C_0{}^2$, $C_1{}^2$, $C_3{}^2$), 125.2 (s, $C_4{}^4$), 126.5 (s, $C_2{}^3$), 127.8 (dd, $^1J_{CP'_3} = 103$ Hz, $^3J_{CP_3} = 5$ Hz, $C_3{}^i$), 127.9 (s, $C_0{}^3$), 128.1 (br s, $C_1{}^3$, $C_3{}^3$), 128.5 (br d, $^3J_{CP'_0} = {}^3J_{CP'_3} = 13$ Hz, $C_0{}^m$, $C_3{}^m$), 129.4 (s, $C_4{}^3$), 130.5 (s, $C_3{}^4$), 130.8 (s, $C_2{}^4$), 131.7 (s, $C_1{}^4$, $C_0{}^4$), 132.1 (d, $^2J_{CP'_0} = {}^2J_{CP'_3} = 10$ Hz, $C_0{}^o$, $C_3{}^o$), 132.4 (s, $C_0{}^p$, $C_3{}^p$), 133.4 (s, $\underline{C}H{=}NNCH_2P'_3$), 138.4 (d, $^3J_{CP_4} = 19$ Hz, $(CH{=}N)_3$), 138.9 (br d, $(CH{=}N)_1$), 139.7 (br d, $(CH{=}N)_0$), 149.6 (d, $^2J_{CP_2} = 7$ Hz, $C_2{}^1$), 150.4 (d, $^2J_{CP_4} = 7$ Hz, $C_4{}^1$), 151.2 (d, $^2J_{CP_1} = 7$ Hz, $C_1{}^1$), 152.9 (d, $^2J_{CP_0} = 8$ Hz, $C_0{}^1$), 153.1 (d, $^2J_{CP_3} = 9$ Hz, $C_3{}^1$) ppm, ($(CH_2)^3$, $(CH_2)^2$, $(CH_2)^1$, and $C_0{}^i$ not detected). Anal. Calcd for $C_{1102}H_{1024}N_{138}O_{124}P_{80}S_{62}$: C, 58.43; H, 4.56; N, 8.53. Found: C, 58.70; H, 4.68; N, 8.45.

3-[G$_2$]: 92% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.1 (s, P_0), 13.4 (d, $^2J_{P'_1P_1} = 31$ Hz, P'_1), 52.5 (d, $^2J_{P_1P'_1} = 31$ Hz, P_1), 63.2 (s, P_2). ^{1}H NMR ($CDCl_3$): δ 2.82 (s, 18 H, Me^1), 3.40 (d, $^3J_{HP_2} = 15.6$ Hz, 36 H, Me^1), 4.74 (br s, 12 H, CH_2), 6.80−7.80 (m, 150 H, C_6H_5, C_6H_4, HC═N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.7 (d, $^2J_{CP_2} = 13$ Hz, Me^2), 39.1 (d, $^3J_{CP'_1} = 2$ Hz, Me^1), 56.6 (d, $^1J_{CP'_1} = 73$ Hz, CH_2), 120.5 (s, $C_0{}^2$), 121.9 (d, $^3J_{CP_1} = 5$ Hz, $C_1{}^2$), 126.6 (s, $C_0{}^3$), 128.0 (dd, $^1J_{CP'_1} = 115$ Hz, $^3J_{CP_1} =$

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[18] Mitjaville, J.; Caminade, A.-M.; Mathieu, R.; Majoral, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5007.

5 Hz, C_1^{i}), 128.3 (s, C_1^{3}), 128.5 (d, $^{3}J_{CP'_1} = 13$ Hz, C_1^{m}), 130.1 (s, C_1^{4}), 130.9 (s, (HC=N)$_0$), 132.0 (d, $^{2}J_{CP'_1} = 10$ Hz, C_1^{o}), 132.5 (s, C_1^{p}), 133.2 (s, C_0^{4}), 140.2 (d, $^{3}J_{CP_2} = 19$ Hz, (HC=N)$_1$), 149.6 (d, $^{2}J_{CP_0} = 7$ Hz, C_0^{1}), 153.2 (d, $^{2}J_{CP_1} = 9$ Hz, C_1^{1}). Anal. Calcd for $C_{222}H_{216}N_{45}O_{18}P_{27}S_{18}Cl_{24}$: C, 43.95; H, 3.59; N, 10.39. Found: C, 43.54; H, 3.51; N, 10.26.

4-[G_2]: 94% yield. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 8.1 (s, P_0), 13.6 (d, $^{2}J_{P'_1P_1} = 31$ Hz, P'_1), 52.6 (d, $^{2}J_{P_1P'_1} = 31$ Hz, P_1), 62.0 (s, P_2). ^{1}H NMR ($CDCl_3$): δ 2.82 (s, 18 H, Me^{1}), 3.34 (d, $^{3}J_{HP_2} = 10.8$ Hz, 36 H, Me^{2}), 4.77 (br s, 12 H, CH_2), 6.80−7.85 (m, 270 H, C_6H_5, C_6H_4, HC=N). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 32.8 (d, $^{2}J_{CP_2} = 14$ Hz, Me^{2}), 39.0 (s, Me^{1}), 56.7 (d, $^{1}J_{CP'_1} = 73$ Hz, CH_2), 120.5 (s, C_0^{2}), 121.3 (d, $^{3}J_{CP_2} = 4$ Hz, C_2^{2}), 121.8 (d, $^{3}J_{CP_1} = 4$ Hz, C_1^{2}), 125.2 (s, C_2^{4}), 126.5 (s, C_0^{3}), 127.8 (dd, $^{1}J_{CP'_1} = 106$ Hz, $^{3}J_{CP_1} = 5$ Hz, C_1^{i}), 127.9 (s, C_1^{3}), 128.5 (d, $^{3}J_{CP'_1} = 13$ Hz, C_1^{m}), 129.6 (s, C_2^{3}), 130.5 (s, C_1^{4}), 130.7 (s, (HC=N)$_0$), 132.1 (d, $^{2}J_{CP'_1} = 10$ Hz, C_1^{o}), 132.4 (s, C_1^{p}), 133.1 (s, C_0^{4}), 138.6 (d, $^{3}J_{CP_2} = 14$ Hz, (HC=N)$_1$), 149.6 (d, $^{2}J_{CP_0} = 5$ Hz, C_0^{1}), 150.6 (d, $^{2}J_{CP_2} = 6$ Hz, C_2^{1}), 152.9 (d, $^{2}J_{CP_1} = 9$ Hz, C_1^{1}) ppm. Anal. Calcd for $C_{366}H_{336}N_{45}O_{42}P_{27}S_{18}$: C, 59.00; H, 4.55; N, 8.46. Found: C, 59.45; H, 4.51; N, 8.36.

4-[G_3]: 94% yield. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 8.1 (br s, P_0), 13.5 (d, $^{2}J_{P'_1P_1} = 31$ Hz, P'_1), 52.6 (d, $^{2}J_{P_1P'_1} = 31$ Hz, P_1), 62.7 (s, P_2, P_3). ^{1}H NMR ($CDCl_3$): δ 2.77 (s, 18 H, Me^{1}), 3.27 (m, 108 H, Me^{2}, Me^{3}), 4.72 (br s, 12 H, CH_2), 6.75−7.70 (m, 510 H, C_6H_5, C_6H_4, HC=N). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 32.9 (br d, $^{2}J_{CP_2} = {}^{2}J_{CP_3} = 13$ Hz, Me^{2}, Me^{3}), 39.0 (s, Me^{1}), 56.8 (br d, $^{1}J_{CP'_1} = 73$ Hz, CH_2), 120.5 (s, C_0^{2}), 121.2 (d, $^{3}J_{CP_3} = 4$ Hz, C_3^{2}), 121.7 (br s, C_1^{2}, C_2^{2}), 125.2 (s, C_3^{4}), 126.5 (s, C_0^{3}), 127.7 (dd, $^{1}J_{CP'_1} = 109$ Hz, $^{3}J_{CP_1} = 6$ Hz, C_1^{i}), 127.9 (s, C_1^{3}), 128.1 (s, C_2^{3}), 128.4 (d, $^{3}J_{CP'_1} = 12$ Hz, C_1^{m}), 129.4 (s, C_3^{3}), 130.8 (s, C_1^{4}, (HC=N)$_0$), 132.0 (d, $^{2}J_{CP'_1} = 10$ Hz, C_1^{o}), 132.1 (s, C_2^{4}), 132.4 (s, C_1^{p}), 133.2 (s, C_0^{4}), 138.4 (d, $^{3}J_{CP_3} = 13$ Hz, (HC=N)$_2$), 139.4 (d, $^{2}J_{CP_2} = 13$ Hz, (HC=N)$_1$), 149.6 (br s, C_0^{1}), 150.4 (d, $^{2}J_{CP_3} = 7$ Hz, C_3^{1}), 151.1 (d, $^{2}J_{CP_2} = 7$ Hz, C_2^{1}), 152.7 (d, $^{2}J_{CP_1} = 9$ Hz, C_1^{1}). Anal. Calcd for $C_{702}H_{648}N_{93}O_{90}P_{51}S_{42}$: C, 57.15; H, 4.43; N, 8.83. Found: C, 56.98; H, 4.40; N, 8.74.

Reactivity of Dendrimers. Typical experiments were carried out with 0.2 g of dendrimer.

General Procedure for the Reaction of P=N−P=S Linkages with Alkyl Triflates: Synthesis of Dendrimers 5-[G_1], 6-[G_1], 6-[G_4], 7-[G_1], 7-[G_4], 9-[G1], 9-[G_2], 9-[G_4], 10-[G_2], 10-[G_3]. To a solution of dendrimer in dichloromethane was added neat alkyl triflate (alkyl = methyl, allyl, propargyl) in 5% excess with respect to the number of P=N−P=S linkages, at room temperature. The solution was stirred for 1 h, then evaporated to dryness to afford the cationic dendrimers with P−N−P−S−Me linkages as white powders.

General Procedure for the Desulfurization: Synthesis of Dendrimers 11-[G_1], 11-[G_2], 11-[G_4], 12-[G_2], 12-[G_3], and Compound 18. To a solution of the dendrimer with P−N−P−S−Me linkages in dichloromethane was added neat $P(NMe_2)_3$ (20% excess with respect to the number of P−N−P−S−Me linkages) at room temperature. The solution was stirred for 2 h, then evaporated to dryness. The residue was extracted with toluene; the solution was filtered, then evaporated to dryness to afford dendrimers **11-[G_1]**, **11-[G_2]**, and **12-[G_2]**. Dendrimers **11-[G_4]** and **12-[G_3]** are not enough soluble in toluene to be extracted. They are not isolated at this step, the crude solution is used to react immediately with azides. All the dendrimers with aminophosphite internal groups are extremely sensitive to oxidation.

General Procedure for the Reaction with Alkyl Iodides: Synthesis of Dendrimers 13-[G_2], 14-[G_2], 15-[G_2], 16-[G_2], and Compound 19. To a solution of the dendrimer (with aminophosphite internal functions) or compound **18** in toluene was added a 100% excess of neat alkyl iodide (alkyl = methyl, allyl) at room temperature. The solution was stirred for 2 h and then filtered. The residue was recovered and washed with pentane to afford the cationic dendrimers as white powders.

General Procedure for the Reaction with Azides: Synthesis of Compound 20 and Dendrimers 21-[G_1], 21-[G_4], 22-[G_2], 22-[G_3], 23-[G_3], 24-[G_3]. To a solution of compound **18** or the dendrimer (with aminophosphite internal functions) in toluene was added a solution of the azide (4-azidophenylisothiocyanate, 1-amino-3-azidopropane, or $N_3P(S)[OC_6H_4CHO]_2$) in toluene (5% excess) at room temperature. The solution was stirred for 1 h and then evaporated to dryness. The residue thus obtained was washed with pentane to afford the dendrimers as yellow to orange powders.

6-[G_4]: 96% yield. $^{31}P\{^{1}H\}$ NMR (CD_3COCD_3): δ 19.7 (d, $^{2}J_{P'_3P_3} = 11$ Hz, P'_3), 20.5 (d, $^{2}J_{P_0P'_0} = 15$ Hz, P_0), 21.3 (d, $^{2}J_{P_3P'_3} = 11$ Hz, P_3), 26.7 (d, $^{2}J_{P'_0P_0} = 15$ Hz, P'_0), 61.8 (s, P_4), 62.1 (s, P_2), 62.2 (s, P_1) ppm. ^{1}H NMR (CD_3COCD_3): δ 1.40 (br s, 8 H, $(CH_2)^{2}$, $(CH_2)^{3}$), 2.93 (br s, 4 H, $(CH_2)^{1}$), 3.09 (s, 48 H, Me^{3}), 3.64 (br d, $^{3}J_{HP_1} = {}^{3}J_{HP_2} = {}^{3}J_{HP_4} = 15$ Hz, 132 H, Me^{1}, Me^{2}, Me^{4}), 4.05 (m, 36 H, SCH_2), 5.01 (br s, 32 H, $CH_2P'_3$), 5.32 (br d, $^{3}J_{H_BH_A} = 10$ Hz, 18 H, H_B), 5.46 (br d, $^{3}J_{H_CH_A} = 17$ Hz, 18 H, H_C), 6.05 (m, 18 H, H_A), 7.01−8.16 (m, 480 H, C_6H_5, C_6H_4, CH=N) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): 21.3 (br s, $(CH_2)^{3}$), 26.7 (br d, $^{1}J_{CP'_0} = 70$ Hz, $(CH_2)^{1}$), 31.9 (d, $^{2}J_{CP_4} = 13$ Hz, Me^{4}), 33.1 (br d, $^{2}J_{CP_1} = {}^{2}J_{CP_2} = 11$ Hz, Me^{1}, Me^{2}), 35.3 (d, $^{2}J_{CP_0} = {}^{2}J_{CP_3} = 4$ Hz, CH_2SP_0, CH_2SP_3), 39.1 (d, $^{3}J_{CP'_3} = 8$ Hz, Me^{3}), 56.4 (d, $^{1}J_{CP'_3} = 78$ Hz, $CH_2P'_3$), 120.4 (s, $\underline{C}H_2{=}CH{-}CH_2{-}S{-}P_3$), 120.6 (s, $\underline{C}H_2{=}CH{-}CH_2{-}S{-}P_0$), 121.3 (br s, C_2^{2}), 121.4 (q, $^{1}J_{CF} = 321$ Hz, $\underline{C}F_3$), 121.5 (d, $^{3}J_{CP_3} = 4$ Hz, C_3^{2}), 121.8 (d, $^{3}J_{CP_0} = 4$ Hz, C_1^{2}), 121.9 (br s, C_0^{2}), 125.9 (dd, $^{1}J_{CP'_3} = 103$ Hz, $^{3}J_{CP_3} = 4$ Hz, C_3^{i}), 127.3 (s, C_2^{3}), 129.0 (br s, C_0^{3}, C_1^{3}), 129.5 (s, C_3^{3}), 129.7 (d, $^{2}J_{CP'_0} = {}^{2}J_{CP'_3} = 14$ Hz, C_0^{m}, C_3^{m}), 131.7 (d, $^{3}J_{CP'_0} = {}^{3}J_{CP'_3} = 11$ Hz, C_0^{o}, C_3^{o}), 131.8 (br s, CH=), 132.1 (br s, C_0^{4}, C_1^{4}), 133.3 (s, C_3^{4}), 133.5 (s, C_2^{4}), 133.9 (s, C_0^{p}, C_3^{p}), 134.4 (s, (CH=N)$_2$), 140.3 (m, (CH=N)$_0$, (CH=N)$_1$), 142.4 (d, $^{3}J_{CP_4} = 19$ Hz, (CH=N)$_3$), 150.2 (d, $^{2}J_{CP_2} = 7$ Hz, C_2^{1}), 150.7 (d, $^{2}J_{CP_3} = 10$ Hz, C_3^{1}), 151.5 (d, $^{2}J_{CP_0} = {}^{2}J_{CP_1} = 6$ Hz, C_0^{1}, C_1^{1}) ppm, ($(CH_2)^{2}$ and C_0^{i} not detected). $^{19}F\{^{1}H\}$ NMR (CD_3COCD_3): δ 2.61 (s, CF_3) ppm. Anal. Calcd for $C_{790}H_{794}N_{138}O_{84}P_{80}S_{80}Cl_{64}F_{54}$: C, 43.23; H, 3.65; N, 8.82. Found: C, 43.18; H, 3.60; N, 8.74.

7-[G_4]: 93% yield. $^{31}P\{^{1}H\}$ NMR (CD_3COCD_3): δ 18.8 (br d, $^{2}J_{P_0P'_0} = 12$ Hz, P_0), 19.6 (d, $^{2}J_{P_3P'_3} = 8$ Hz, P_3), 20.5 (d, $^{2}J_{P'_3P_3} = 8$ Hz, P'_3), 27.4 (br d, $^{2}J_{P'_0P_0} = 12$ Hz, P'_0), 61.8 (s, P_4), 62.1 (br s, P_1, P_2) ppm. ^{1}H NMR (CD_3COCD_3): δ 1.41 (m, 8 H, $(CH_2)^{2}$, $(CH_2)^{3}$), 2.91 (m, 4 H, $(CH_2)^{1}$), 2.99 (br s, 48 H, Me^{3}), 3.15 (br s, 18 H, ≡CH), 3.53 (br d, $^{3}J_{HP_1} = {}^{3}J_{HP_2} = {}^{3}J_{HP_4} = 14$ Hz, 132 H, Me^{1}, Me^{2}, Me^{4}), 4.15 (br d, $^{3}J_{HP_3} = 20$ Hz, 36 H, $CH_2{-}C{\equiv}$), 4.92 (br s, 32 H, $CH_2P'_3$), 6.87−8.04 (m, 480 H, C_6H_5, C_6H_4, CH=N) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): 21.0 (d, $^{2}J_{CP_0} = {}^{2}J_{CP_3} = 5$ Hz, CH_2SP_0, CH_2SP_3), 26.7 (br d, $^{1}J_{CP'_0} = 68$ Hz, $(CH_2)^{1}$), 32.0 (d, $^{2}J_{CP_4} = 12$ Hz, Me^{4}), 33.0 (br d, $^{2}J_{CP_1} = {}^{2}J_{CP_2} = 12$ Hz, Me^{1}, Me^{2}), 39.2 (d, $^{3}J_{CP'_3} = 9$ Hz, Me^{3}), 56.4 (d, $^{1}J_{CP'_3} = 79$ Hz, $CH_2P'_3$), 76.0 (s, ${\equiv}\underline{C}{-}CH_2$), 77.8 (d, $^{4}J_{CP_0} = {}^{4}J_{CP_3} = 5$ Hz, ≡CH), 121.4 (q, $^{1}J_{CF} = 318$ Hz, CF_3), 121.4 (br s, C_2^{2}), 121.7 (d, $^{3}J_{CP_3} = 5$ Hz, C_3^{2}), 121.9 (br s, C_0^{2}, C_1^{2}), 125.9 (dd, $^{1}J_{CP'_3} = 105$ Hz, $^{3}J_{CP_3} = 4$ Hz, C_3^{i}), 127.4 (s, C_2^{3}), 128.9 (br s, C_0^{3}, C_1^{3}), 129.5 (s, C_3^{3}), 129.8 (d, $^{2}J_{CP'_0} = {}^{2}J_{CP'_3} = 13$ Hz, C_0^{m}, C_3^{m}), 131.8 (d, $^{3}J_{CP'_0} = {}^{3}J_{CP'_3} = 11$ Hz, C_0^{o}, C_3^{o}), 132.3 (m, C_0^{4}, C_1^{4}), 133.4 (br s, C_2^{4}, C_3^{4}), 134.0 (s, C_0^{p}, C_3^{p}), 134.8 (s, (CH=N)$_2$), 140.4 (m, (CH=N)$_0$, (CH=N)$_1$), 142.4 (d, $^{3}J_{CP_4} = 19$ Hz, (CH=N)$_3$), 150.3 (d, $^{2}J_{CP_2} = 5$ Hz, C_2^{1}), 150.8 (d, $^{2}J_{CP_3} = 11$ Hz, C_3^{1}), 151.6 (d, $^{2}J_{CP_0} = {}^{2}J_{CP_1} = 7$ Hz, C_0^{1}, C_1^{1}) ppm, ((C_0^{i}, $(CH_2)^{2}$ and $(CH_2)^{3}$ not detected). $^{19}F\{^{1}H\}$ NMR (CD_3COCD_3): δ 2.50 (s, CF_3) ppm. Anal. Calcd for $C_{790}H_{758}N_{138}O_{84}P_{80}S_{80}Cl_{64}F_{54}$: C, 43.39; H, 3.48; N, 8.84. Found: C, 43.29; H, 3.38; N, 8.68.

9-[G_4]: 95% yield. $^{31}P\{^{1}H\}$ NMR (CD_3COCD_3): δ 19.7 (d, $^{2}J_{P'_3P_3} = 11.1$ Hz, P'_3), 22.4 (d, $^{2}J_{P_0P'_0} = 15.1$ Hz, P_0), 23.3 (d, $^{2}J_{P_3P'_3} = 11.1$ Hz, P_3), 27.6 (d, $^{2}J_{P'_0P_0} = 15.1$ Hz, P'_0), 61.8 (s, P_4), 62.1 (s, P_1), 62.2 (s, P_2). ^{1}H NMR (CD_3COCD_3): δ 1.41 (br s, 8 H, $(CH_2)^{2}$, $(CH_2)^{3}$), 2.70 (d, $^{3}J_{HP_0} = {}^{3}J_{HP_3} = 18$ Hz, 54 H, Me-S), 2.90 (br s, 4 H, $(CH_2)^{1}$), 3.09 (s, 48 H, Me^{3}), 3.65 (br d, $^{3}J_{HP_1} = {}^{3}J_{HP_2} = {}^{3}J_{HP_4} = 15$ Hz, 132 H, Me^{1}, Me^{2}, Me^{4}), 5.0 (br s, 32 H, $CH_2P'_3$), 7.00−8.16 (m, 800 H, C_6H_5, C_6H_4, CH=N) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): δ 12.7 (d, $^{2}J_{CP_0} = 5$ Hz, Me-S−P_0), 12.8 (d, $^{2}J_{CP_3} = 5$ Hz, Me-S−P_3), 21.3 (br s, $(CH_2)^{3}$), 26.7 (br d, $^{1}J_{CP'_0} = 70$ Hz, $(CH_2)^{1}$), 33.0 (br d, $^{2}J_{CP_1} = {}^{2}J_{CP_2} = {}^{2}J_{CP_4} = 11$ Hz, Me^{1}, Me^{2}, Me^{4}), 39.0 (d, $^{3}J_{CP'_3} = 8$ Hz, Me^{3}), 56.4 (d, $^{1}J_{CP'_3} = 78$ Hz, $CH_2P'_3$), 121.2 (br s, C_2^{2}), 121.3 (q, $^{1}J_{CF} = 321$ Hz, CF_3), 121.4 (d, $^{3}J_{CP_4} = 4$ Hz, C_4^{2}), 121.6 (d, $^{3}J_{CP_3} = 4$ Hz, C_3^{2}), 121.8 (d, $^{3}J_{CP_1} = 4$ Hz, C_1^{2}), 121.9 (br s, C_0^{2}), 125.3 (s, C_4^{4}), 125.8 (br d, $^{1}J_{CP'_3} = 103$ Hz, C_3^{i}), 127.5 (s, C_2^{3}), 129.0 (br s, C_0^{3}, C_1^{3}), 129.5 (s, C_3^{3}), 129.6 (s, C_4^{3}), 129.8 (d, $^{3}J_{CP'_0} = {}^{3}J_{CP'_3} = 14$ Hz, C_0^{m}, C_3^{m}), 131.6 (d, $^{2}J_{CP'_0} = {}^{2}J_{CP'_3} = 11$ Hz, C_0^{o}, C_3^{o}), 132.4 (br s, C_0^{4}, C_1^{4}), 133.3 (s, C_3^{4}), 133.5 (s, C_2^{4}), 133.9 (s, C_0^{p}, C_3^{p}), 134.6 (s, (CH=N)$_2$), 139.7 (d, $^{3}J_{CP_4} = 19$ Hz, (CH=N)$_3$), 140.3 (m, (CH=N)$_0$, (CH=N)$_1$), 150.2 (d, $^{2}J_{CP_2} = 7$ Hz, C_2^{1}), 150.8 (d, $^{2}J_{CP_3} = 10$ Hz, C_3^{1}), 151.0 (d, $^{2}J_{CP_4} = 8$ Hz, C_4^{1})), 151.4 (d, $^2J_{CP_0} = {}^2J_{CP_1} = 7$ Hz, C_0^1, C_1^1), ((CH_2)$_2$ and C_0^i not detected). $^{19}F\{^1H\}$ NMR (CD_3COCD_3): δ 2.60 (s, CF_3) ppm. Anal. Calcd for $C_{1138}H_{1078}N_{138}O_{178}P_{80}S_{80}F_{54}$: C, 53.38; H, 4.24; N, 7.55. Found: C, 53.21; H, 4.17; N, 7.48.

10-[G$_2$]: 98% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.0 (br s, P_0), 19.5 (d, $^2J_{P'_1P_1} = 9.3$ Hz, P'_1), 23.5 (d, $^2J_{P_1P'_1} = 9.3$ Hz, P_1), 61.2 (s, P_2). ^1H NMR ($CDCl_3$): δ 2.37 (d, $^3J_{HP_1} = 16.2$ Hz, 18 H, S-Me), 2.76 (s, 18 H, Me^1), 3.35 (d, $^3J_{HP_2} = 13$ Hz, 36 H, Me^2), 4.5 (br s, 12 H, CH_2), 6.80−7.75 (m, 270 H, C_6H_5, C_6H_4, HC=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.0 (d, $^2J_{CP_1} = 4$ Hz, SMe), 32.9 (d, $^2J_{CP_2} = 12$ Hz, Me^2), 39.3 (s, Me^1), 57.0 (d, $^1J_{CP'_1} = 72$ Hz, CH_2), 120.4 (s, C_0^2), 120.7 (q, $^1J_{CF} = 320$ Hz, CF_3), 120.7 (br s, C_1^2), 121.3 (d, $^3J_{CP_2} = 4$ Hz, C_2^2), 124.8 (br d, $^1J_{CP'_1} = 102$ Hz, C_1^i), 125.3 (s, C_2^4), 127.8 (s, C_0^3), 128.9 (s, C_1^3), 129.3 (s, C_2^3), 129.4 (d, $^3J_{CP'_1} = 13$ Hz, C_1^m), 131.5 (d, $^2J_{CP'_1} = 10$ Hz, C_1^o), 132.8 (s, C_0^4), 133.5 (s, C_1^4), 133.9 (s, C_1^p), 134.6 (s, (CH=N)$_0$), 138.5 (d, $^3J_{CP_2} = 14$ Hz, (HC=N)$_1$), 149.6 (d, $^2J_{CP_1} = 11$ Hz, C_1^1), 149.6 (s, C_0^1), 150.3 (d, $^2J_{CP_2} = 7$ Hz, C_2^1) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −2. 0 (s, CF_3) ppm. Anal. Calcd for $C_{378}H_{354}N_{45}O_{60}P_{27}S_{24}F_{18}$: C, 53.82; H, 4.23; N, 7.47. Found: C, 53.70; H, 4.19; N, 7.37.

10-[G$_3$]: 97% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.3 (br s, P_0), 19.8 (d, $^2J_{P'_1P_1} = 8$ Hz, P'_1), 24.0 (d, $^2J_{P_1P'_1} = 8$ Hz, P_1), 62.3 (s, P_2), 62.8 (s, P_3); ^1H NMR ($CDCl_3$): δ 2.36 (d, $^3J_{HP_1} = 16.2$ Hz, 18 H, S−Me), 2.76 (s, 18 H, Me^1), 3.30 (m, 108 H, Me^2, Me^3), 4.5 (br s, 12 H, CH_2), 6.80−7.75 (m, 510 H, C_6H_5, C_6H_4, HC=N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.5 (br s, SMe), 32.9 (d, $^2J_{CP_2} = {}^2J_{CP_3} = 13$ Hz, Me^2, Me^3), 39.4 (s, Me^1), 57.2 (d, $^1J_{CP'_1} = 73$ Hz, CH_2), 120.3 (s, C_0^2), 120.6 (q, $^1J_{CF} = 321$ Hz, CF_3), 120.7 (br s, C_1^2), 121.2 (d, $^3J_{CP_3} = 4$ Hz, C_3^2), 121.5 (d, $^3J_{CP_2} = 4$ Hz, C_2^2), 124.5 (br d, $^1J_{CP'_1} = 102$ Hz, C_1^i), 125.3 (s, C_3^4), 127.2 (s, C_0^3), 128.2 (s, C_2^3), 128.9 (s, C_1^3), 129.4 (s, C_3^3), 129.5 (d, $^3J_{CP'_1} = 13$ Hz, C_1^m), 131.4 (d, $^2J_{CP'_1} = 10$ Hz, C_1^o), 132.2 (s, C_2^4), 132.8 (s, C_0^4), 133.6 (s, C_1^4), 133.9 (s, C_1^p), 138.5 (d, $^3J_{CP_2} = {}^3J_{CP_3} = 14$ Hz, (HC=N)$_1$, (HC=N)$_2$), 149.6 (d, $^2J_{CP_1} = 11$ Hz, C_1^1), 149.6 (s, C_0^1), 150.4 (d, $^2J_{CP_3} = 7$ Hz, C_3^1), 151.1 (d, $^2J_{CP_2} = 6$ Hz, C_2^1) ((HC=N)$_0$ not detected). $^{19}F\{^1H\}$ NMR ($CDCl_3$): −1.96 (s, CF_3). Anal. Calcd for $C_{714}H_{666}N_{93}O_{108}P_{51}S_{48}F_{18}$: C, 54.49; H, 4.26; N, 8.28. Found: C, 54.18; H, 4.11; N, 8.11.

11-[G$_4$] (not isolated). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 8.7 (d, $^2J_{P'_3P_3} = 40.0$ Hz, P'_3), 14.2 (d, $^2J_{P'_0P_0} = 41.0$ Hz, P'_0), 62.1 (s, P_4), 62.5 (s, P_1), 62.6 (s, P_2), 144.1 (d, $^2J_{P_0P'_0} = 41.0$ Hz, P_0), 144.3 (d, $^2J_{P_3P'_3} = 40.0$ Hz, P_3) ppm.

12-[G$_2$]: (not isolated). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 8.0 (s, P_0), 8.6 (d, $^2J_{P'_1P_1} = 38.2$ Hz, P'_1), 61.6 (s, P_2), 144.2 (d, $^2J_{P_1P'_1} = 38.2$ Hz, P_1) ppm.

12-[G$_3$]: (not isolated). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 8.1 (br s, P_0), 8.7 (d, $^2J_{P'_1P_1} = 38$ Hz, P'_1), 62.2 (s, P_2,) 62.3 (s, P_3), 144.1 (d, $^2J_{P_1P'_1} = 38$ Hz, P_1) ppm.

15-[G$_2$]: 91% yield. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 7.4 (s, P_0), 17.4 (d, $^2J_{P'_1P_1} = 23$ Hz, P'_1), 27.0 (d, $^2J_{P_1P'_1} = 23$ Hz, P_1), 61.5 (s, P_2) ppm. ^1H NMR (CD_2Cl_2): δ 2.74 (d, $^2J_{HP_1} = 10.1$ Hz, 18 H, Me-P_1), 2.92 (br s, 18 H, Me^1), 3.35 (d, $^3J_{HP_2} = 10.3$ Hz, 36 H, Me^2), 4.80 (br s, 12 H, $CH_2P'_1$), 6.73−7.84 (m, 270 H, C_6H_4, C_6H_5, CH=N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 14.7 (d, $^1J_{CP_1} = 136$ Hz, Me-P_1), 33.8 (d, $^2J_{CP_2} = 12$ Hz, Me^2), 40.4 (s, Me^1), 58.3 (d, $^1J_{CP'_1} = 72$ Hz, $CH_2P'_1$), 121.4 (s, C_0^2), 121.9 (d, $^3J_{CP_1} = {}^3J_{CP_2} = 5$ Hz, C_1^2, C_2^2), 126.1 (s, C_2^4), 126.3 (br d, $^1J_{CP'_1} = 104$ Hz, C_1^i), 128.9 (s, C_0^3), 129.5 (s, C_1^3), 130.0 (d, $^3J_{CP'_1} = 14$ Hz, C_1^m), 130.3 (s, C_2^3), 132.3 (d, $^2J_{CP'_1} = 11$ Hz, C_1^o), 133.1 (s, C_0^4), 133.7 (s, C_1^p), 134.1 (s, C_2^4), 134.2 (s, C_1^4), 134.6 (s, (CH=N)$_0$), 139.0 (d, $^3J_{CP_2} = 13$ Hz, (CH=N)$_1$), 150.4 (d, $^2J_{CP_1} = 10$ Hz, C_1^1), 151.3 (d, $^2J_{CP_2} = 7$ Hz, C_2^1), 151.8 (d, $^1J_{CP_0} = 6$ Hz, C_0^1) ppm. Anal. Calcd for $C_{372}H_{354}N_{45}O_{42}P_{27}S_{12}I_6$: C, 55.09; H, 4.40; N, 7.72. Found: C, 54.89; H, 4.36; N, 7.61.

16-[G$_2$]: 91% yield. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 8.0 (s, P_0), 17.3 (d, $^2J_{P'_1P_1} = 17$ Hz, P'_1), 22.2 (d, $^2J_{P_1P'_1} = 17$ Hz, P_1), 61.4 (s, P_2) ppm. ^1H NMR (CD_3COCD_3): 2.99 (s, 18 H, Me^1), 3.41 (d, $^3J_{HP_2} = 10.4$ Hz, 36 H, Me^2), 3.65 (br m, 12 H, CH_2P_1), 4.95 (br s, 12 H, $CH_2P'_1$), 5.27 (br m, 6 H, H_B), 5.44 (br dd, $^3J_{H_CH_A} = 16$ Hz, $^4J_{H_CP} = 5$ Hz, 6 H, H_C), 5.86 (br m, 6 H, H_A), 6.99−8.00 (m, 270 H, C_6H_4, C_6H_5, CH=N) ppm. $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 33.0 (d, $^1J_{CP_0} = 140$ Hz, CH_2P_1), 33.1 (d, $^2J_{CP_2} = 13$ Hz, Me^2), 40.0 (s, Me^1), 56.4 (d, $^1J_{CP'_1} = 68$ Hz, $CH_2P'_1$), 120.6 (br s, C_0^2), 121.4 (d, $^3J_{CP_2} = 5$ Hz, C_2^2), 121.7 (br s, C_1^2), 123.4 (d, $^3J_{CP_1} = 17$ Hz, CH_2=), 125.0 (d, $^2J_{CP_1} = 12$ Hz, CH_A), 125.5 (s, C_2^4), 126.3 (br d, $^1J_{CP'_1} = 104$ Hz, C_1^i), 127.2 (s, C_0^3), 128.5 (s, C_1^3), 129.3 (d, $^3J_{CP'_1} = 11$ Hz, C_1^m), 129.8 (s, C_2^3), 131.2 (s, (CH=N)$_0$), 131.7 (d, $^2J_{CP'_1} = 11$ Hz, C_1^o), 132.4 (s, C_1^4), 133.8 (s, C_1^p, C_0^4), 140.0 (d, $^3J_{CP_2} = 14$ Hz, (CH=N)$_1$), 150.1 (d, $^2J_{CP_0} = 12$ Hz, C_0^1), 150.9 (d, $^2J_{CP_2} = 7$ Hz, C_2^1), 151.5 (d, $^2J_{CP_1} = 7$ Hz, C_1^1) ppm. Anal. Calcd for $C_{384}H_{366}N_{45}O_{42}P_{27}S_{12}I_6$: C, 55.80; H, 4.46; N, 7.63. Found: C, 55.69; H, 4.37; N, 7.52.

17: 88% yield. $^{31}P\{^1H\}$ NMR (THF): δ 15.5 (d, $^2J_{PP} = 32$ Hz, P'_0), 53.0 (d, $^2J_{PP} = 32$ Hz, P_0). ^1H NMR ($CDCl_3$): δ 2.20 (d, $^3J_{HP'_0} = 14$ Hz, 3 H, CH_3), 7.00−7.65 (m, 20 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.6 (d, $^2J_{CP'_0} = 67$ Hz, CH_3), 121.7 (d, $^3J_{CP_0} = 4$ Hz, C_0^2), 124.2 (s, C_0^4), 128.8 (d, $^3J_{CP'_0} = 13$ Hz, C_0^m), 129.1 (s, C_0^3), 130.6 (dd, $^1J_{CP'_0} = 108$ Hz, $^3J_{CP_0} = 5$ Hz, C_0^i), 131.1 (d, $^2J_{CP'_0} = 11$ Hz, C_0^o), 132.3 (d, $^4J_{CP'_0} = 3$ Hz, C_0^p), 152.1 (d, $^2J_{CP_0} = 8$ Hz, C_0^1). Anal. Calcd for $C_{25}H_{23}NO_2P_2S$: C, 64.79; H, 5.00; N, 3.02. Found: C, 64.98; H, 4.95; N, 2.97.

18: (not isolated). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 9.9 (d, $^2J_{PP} = 32$ Hz, P'_0), 143.9 (d, $^2J_{PP} = 32$ Hz, P_0).

19: 85% yield. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 27.3 (d, $^2J_{PP} = 20.3$ Hz, P_0 or P'_0), 28.9 (d, $^2J_{PP} = 20.3$ Hz, P'_0 or P_0). ^1H NMR (CD_3COCD_3): δ 2.57 (d, $^2J_{HP} = 13.4$ Hz, 3 H, CH_3), 3.87 (dddd, $^2J_{HP} = 20.1$ Hz, $^3J_{HH_A} = 7.3$ Hz, $^4J_{HH_B} \approx {}^4J_{HH_C} \approx 1.1$ Hz, 2 H, CH_2), 5.52 (dddt, $^3J_{H_BH_A} = 10.2$ Hz, $^4J_{H_BP} = 5.1$ Hz, $^2J_{H_BH_C} \approx {}^4J_{H_BCH_2} \approx 1.2$ Hz, 1 H, H_B), 5.64 (dddt, $^3J_{H_CH_A} = 16.8$ Hz, $^4J_{H_CP} = 6.1$ Hz, $^2J_{H_CH_B} \approx {}^4J_{H_CCH_2} \approx 1.3$ Hz, 1 H, H_C), 6.03 (dddt, $^3J_{H_AH_C} = 16.8$ Hz, $^3J_{H_AH_B} = 10.2$ Hz, $^3J_{H_ACH_2} \approx {}^3J_{H_AP} \approx 7.3$ Hz, 1 H, H_A), 7.20−7.90 (m, 20 H, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 15.8 (d, $^1J_{CP'_0} = 68$ Hz, CH_3), 33.2 (d, $^1J_{CP_0} = 134$ Hz, CH_2), 121.6 (d, $^3J_{CP_0} = 4$ Hz, C_0^2), 123.3 (d, $^3J_{CP_0} = 16$ Hz, CH_2=), 125.4 (d, $^2J_{CP_0} = 13$ Hz, CH_A), 126.9 (s, C_0^4), 128.2 (dd, $^1J_{CP'_0} = 108$ Hz, $^3J_{CP_0} = 4$ Hz, C_0^i), 129.7 (d, $^2J_{CP'_0} = 12$ Hz, C_0^m), 130.9 (s, C_0^3), 131.4 (d, $^3J_{CP'_0} = 12$ Hz, C_0^o), 133.7 (d, $^4J_{CP'_0} = 3$ Hz, C_0^p), 149.9 (d, $^2J_{CP_0} = 12$ Hz, C_0^1). Anal. Calcd for $C_{28}H_{28}NO_2P_2I$: C, 56.11; H, 4.71; N, 2.34. Found: C, 55.98; H, 4.63; N, 2.27.

20: 91% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.7 (d, $^2J_{PP} = 16$ Hz, P_0), 15.3 (d, $^2J_{PP} = 16$ Hz, P'_0). ^1H NMR ($CDCl_3$): δ 1.95 (d, $^3J_{HP} = 13.3$ Hz, 3H, CH_3), 6.80−7.80 (m, 24 H, C_6H_5, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.0 (d, $^1J_{CP'_0} = 69$ Hz, CH_3), 121.0 (d, $^3J_{CP_0} = 5$ Hz, C_0^2), 123.3 (d, $^3J_{CP_0} = 21$ Hz, C'^o), 124.2 (s, C_0^4), 126.3 (s, C'^m), 126.9 (s, C'^p), 128.7 (d, $^3J_{CP'_0} = 13.5$ Hz, C_0^m), 129.3 (s, C_0^3), 130.6 (dd, $^1J_{CP'_0} = 107$ Hz, $^3J_{CP_0} = 5$ Hz, C_0^i), 130.8 (d, $^2J_{CP'_0} = 10$ Hz, C_0^o), 132.3 (br s, C_0^p), 133.7 (s, C=S), 149.8 (br s, C'^i), 151.7 (d, $^2J_{CP_0} = 9$ Hz, C_0^1). Anal. Calcd for $C_{32}H_{27}N_3O_2P_2S$: C, 54.40; H, 3.85; N, 5.95. Found: C, 54.29; H, 3.80; N, 5.84.

21-[G$_4$]: 89% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −10.4 (d, $^2J_{P_3P'_3} = 31.1$ Hz, P3), −8.6 (d, $^2J_{P_0P'_0} = 30.5$ Hz, P_0) 17.5 (d, $^2J_{P'_0P_0} = 30.5$ Hz, P'_0), 18.2 (d, $^2J_{P'_3P_3} = 31.1$ Hz, P'_3), 62.3 (s, P_4), 62.8 (s, P1, P_2) ppm. ^1H NMR ($CDCl_3$): δ 2.71 (s, 48 H, Me^3), 3.29 (d, $^3J_{HP_1} = {}^3J_{HP_2} = {}^3J_{HP_4} = 8.9$ Hz, Me^1, Me^2, Me^4), 4.59 (m, 32 H, $CH_2P'_3$), 6.76−7.64 (m, 640 H, C_6H_4, C_6H_5, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 20.5 (br s, (CH_2)$_3$), 27.1 (d, $^1J_{CP'_0} = 73$ Hz, (CH_2)^1), 29.4 (d, $^2J_{CP'_0} = 17$ Hz, (CH_2)^2), 32.9 (br d, $^2J_{CP} = 12$ Hz, Me^1, Me^2, Me^4), 39.0 (d, $^3J_{CP'_3} = 6$ Hz, Me^3), 57.0 (d, $^1J_{CP'_3} = 75$ Hz, $CH_2P'_3$), 120.3 (d, $^3J_{CP_2} = 3$ Hz, C_2^2), 121.0 (br s, C_0^2, C_1^2), 121.1 (d, $^3J_{CP_4} = 4$ Hz, C_4^2), 121.2 (br s, C_3^2), 121.8 (br d, $^3J_{CP_3} = 20$ Hz, C'^o, C''^o), 125.3 (s, C_4^4), 126.8 (br s, C_2^3, C'^m, C''^m), 127.1 (s, C'^p, C''^p), 127.4 (dd, $^1J_{CP'_3} = 104$ Hz, $^3J_{CP_3} = 6$ Hz, C_3^i), 128.5 (s, C_1^3,C_3^3), 129.1 (d, $^3J_{CP'_0} = {}^3J_{CP'_3} = 13$ Hz, C_0^m, C_3^m), 129.5 (s, C_4^3), 131.0 (s, C_3^4), 131.2 (s, C_2^4), 131.7 (d, $^2J_{CP'_0} = {}^2J_{CP'_3} = 11$ Hz, C_0^o, C_3^o), 131.8 (s, C_0^p, C_3^p), 133.4 (s, (CH=N)$_2$), 133.5 (s, N=C=S), 137.8 (d, $^3J_{CP_4} = 13$ Hz, (CH=N)3), 139.0 (br d, (CH=N)$_1$), 149.6 (d, $^3J_{CP_3} = 9$ Hz, C_3^1), 149.8 (d, $^2J_{CP_2} = 7$ Hz, C_2^1), 150.5 (d, $^3J_{CP_4} = 7$ Hz, C_4^1), 151.1 (br s, C'^i, C''^i), 151.2 (d, $^3J_{CP_1} = 7$ Hz, C_1^1) ppm (C_1^4, C_0^1, C_0^3, C_0^i, (CH_2)^1, (CH_2)^2, (CH_2)^3, (CH=N)$_{0,1}$ not detected). IR (KBr): 2115 (ν_{NCS}) cm^{-1}. Anal. Calcd for $C_{1228}H_{1096}N_{174}O_{124}P_{80}S_{62}$: C, 59.61; H, 4.46; N, 9.85. Found: C, 59.30; H, 4.18; N, 9.58.

22-[G$_2$]: 94% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −9.4 (d, $^2J_{P_1P'_1} = 15.0$ Hz, P_1), 7.9 (s, P_0), 14.3 (d, $^2J_{P'_1P_1} = 15.0$ Hz, P'_1), 61.7 (s, P_2) ppm. ^1H NMR ($CDCl_3$): δ 2.66 (br s, 18 H, Me^1), 3.28 (d, $^3J_{HP_2} = 10.3$ Hz, 36 H, Me^2), 4.6 (br s, 12 H, CH_2), 6.75−7.51 (m, 294 H, C_6H_4, C_6H_5, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 33.8 (d, $^2J_{CP_2} =$

13 Hz, Me^2), 38.8 (s, Me^1), 57.5 (d, $^1J_{CP'_1} = 74$ Hz, CH_2), 120.4 (br s, C_0^2), 121.2 (d, $^3J_{CP_1} = {}^3J_{CP_2} = 4$ Hz, C_1^2, C_2^2), 122.8 (br d, C'^o), 125.2 (s, C_2^4), 126.4 (s, C_0^3, C'^m), 126.8 (dd, $^1J_{CP'_1} = 100$ Hz, $^3J_{CP_1} = 4$ Hz, C_1^i), 127.0 (s, C'^p), 127.9 (s, C_1^3), 128.4 (d, $^3J_{CP'_1} = 12$ Hz, C_1^m), 129.4 (s, C_2^3), 130.9 (m, C_1^4, $(CH{=}N)_0$), 131.9 (d, $^2J_{CP'_1} = 10$ Hz, C_1^o), 132.4 (s, C_1^p), 133.1 (s, C_0^4), 133.3 (s, N=C=S), 138.6 (d, $^3J_{CP_2} = 14$ Hz, $(CH{=}N)_1$), 149.6 (br s, C_0^1), 150.5 (d, $^2J_{CP_2} = 7$ Hz, C_2^1), 151.1 (br s, C'^i), 152.4 (br d, C_1^1) ppm. IR (KBr): 2116 (ν_{NCS}) cm^{-1}. Anal. Calcd for $C_{408}H_{360}N_{57}O_{42}P_{27}S_{18}$: C, 60.15; H, 4.45; N, 9.80. Found: C, 59.99; H, 4.32; N, 9.69.

22-[G$_3$]: 93% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −9.8 (d, $^2J_{P_1P'_1} = 14$ Hz, P_1), 7.9 (s, P_0), 14.0 (d, $^2J_{P'_1P_1} = 14$ Hz, P'_1), 61.7 (s, P_2, P_3) ppm. ^1H NMR ($CDCl_3$): δ 2.63 (br s, 18 H, Me^1), 3.30 (m, 108 H, Me^2, Me^3), 4.56 (br s, 12 H, CH_2), 6.88−7.68 (m, 336 H, C_6H_4, C_6H_5, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 32.8 (d, $^2J_{CP_2} = {}^2J_{CP_3} = 13$ Hz, Me^2, Me^3), 38.8 (s, Me^1), 120.6 (br d, $^3J_{CP_0} = 3$ Hz, C_0^2), 121.1 (d, $^3J_{CP_3} = 3$ Hz, C_3^2), 121.5 (m, C_1^2, C_2^2), 123.4 (d, $^3J_{CP_1} = 19$ Hz, C'^o), 125.2 (s, C_3^4), 126.2 (s, C'^m), 126.5 (s, C_0^3), 126.9 (s, C'^p), 128.0 (s, C_1^3, C_2^3), 128.4 (d, $^3J_{CP'_1} = 12$ Hz, C_1^m), 129.3 (s, C_3^3), 130.8 (br s, C_0^4, $(CH{=}N)_0$), 131.8 (d, $^2J_{CP'_1} = 11$ Hz, C_1^o), 132.1 (br s, C_2^4, C_1^p), 132.4 (s, C_1^4), 133.1 (s, N=C=S), 138.3 (d, $^3J_{CP_3} = 14$ Hz, $(CH{=}N)_2$), 139.1 (d, $^3J_{CP_2} = 14$ Hz, $(CH{=}N)_1$), 149.5 (br s, C_0^1), 150.3 (d, $^2J_{CP_3} = 7$ Hz, C_3^1), 151.0 (d, $^2J_{CP_2} = 6$ Hz, C_2^1), 151.8 (d, $^2J_{CP_1} = 7$ Hz, C_1^1) ppm (C_1^i, CH_2, C'^i not detected). IR (KBr): 2115 (ν_{NCS}) cm^{-1}. Anal. Calcd for $C_{744}H_{672}N_{105}O_{90}P_{51}S_{42}$: C, 57.84; H, 4.38; N, 9.52. Found: C, 57.99; H, 4.45; N, 9.40.

23-[G$_3$]: 91% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.5 (s, P_0), 9.4 (d, $^2J_{P_1P'_1} = 26$ Hz, P_1), 16.0 (d, $^2J_{P'_1P_1} = 26$ Hz, P'_1), 62.5 (s, P_2), 62.8 (s, P_3) ppm. ^1H NMR ($CDCl_3$): δ 1.30 (m, 12 H, C^bH_2), 2.80 (m, 42 H, C^aH_2, C^cH_2, Me^1), 3.29 (d, $^3J_{HP_2} = {}^3J_{HP_3} = 10$ Hz, 108 H, Me^2, Me^3), 4.83 (m, 12 H, $CH_2P'_1$), 6.80−7.68 (m, 510 H, C_6H_5, C_6H_4, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 24.8 (s, C^bH_2), 32.9 (d, $^2J_{CP_2} = {}^2J_{CP_3} = 13$ Hz, Me^2, Me^3), 38.9 (br s, C^cH_2, Me^1), 41.5 (br s, C^aH_2), 57.7 (dd, $^1J_{CP'_1} = 70$ Hz, $^3J_{CP_1} = 5$ Hz, $CH_2P'_1$), 120.5 (br s, C_0^2), 121.2 (d, $^3J_{CP_3} = 5$ Hz, C_3^2), 121.6 (s, C_1^2, C_2^2), 125.2 (s, C_3^4), 126.2 (br d, $^1J_{CP'_1} = 105$ Hz, C_1^i), 126.4 (s, C_0^3), 128.0 (s, C_1^3, C_2^3), 128.8 (d, $^3J_{CP'_1} = 12$ Hz, C_1^m), 129.3 (s, C_3^3), 129.8 (s, C_0^4), 130.5 (s, $(CH{=}N)_0$), 131.7 (d, $^2J_{CP'_1} = 10$ Hz, C_1^o), 132.0 (s, C_1^4), 132.1 (s, C_2^4), 132.9 (s, C_1^p), 138.4 (d, $^3J_{CP_3} = 14$ Hz, $(CH{=}N)_2$), 139.0 (d, $^3J_{CP_2} = 13$ Hz, $(CH{=}N)_1$), 149.4 (d, $^2J_{C_01P_0} = 7$ Hz, C_0^1), 150.4 (d, $^2J_{CP_3} = 7$ Hz, C_3^1), 151.1 (d, $^2J_{CP_1} = {}^2J_{CP_2} = 7$ Hz, C_1^1, C_2^1) ppm. Anal. Calcd for $C_{720}H_{696}N_{105}O_{90}P_{51}S_{36}$: C, 57.67; H, 4.68; N, 9.81. Found: C, 57.51; H, 4.52; N, 9.67.

24-[G$_3$]: 95% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −12.4 (dd, $^2J_{P_1P'_1} = 62$ Hz, $^2J_{P_1P''_1} = 21$ Hz, P_1), 8.0 (br s, P_0), 13.4 (d, $^2J_{P''_1P_1} = 21$ Hz, P″1), 44.7 (d, $^2J_{P'_1P_1} = 62$ Hz, P'_1), 62.6 (s, P_2), 62.7 (s, P3) ppm. ^1H NMR ($CDCl_3$): δ 2.71 (d, 18 H, Me^1), 3.30 (m, 108 H, Me^2, Me^3), 4.60 (br s, 12 H, CH_2), 6.80−7.70 (m, 558 H, C_6H_5, C_6H_4, HC=N), 9.73 (s, 12 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.9 (d, $^2J_{CP} = 13$ Hz, Me^2, Me^3), 39.0 (s, Me^1), 58.7 (d, $^1J_{CP'_1} = 78$ Hz, CH_2), 120.5 (s, C_0^2), 121.2 (d, $^3J_{CP_3} = 4$ Hz, C_3^2), 121.6 (br s, C_1^2, C_2^2, C''^o), 125.3 (s, C_3^4), 126.6 (s, C_0^3), 126.9 (br d, $^1J_{CP'_1} = 103$ Hz, C_1^i), 128.0 (s, C_1^3), 128.1 (s, C_2^3), 128.6 (d, $^3J_{CP'_1} = 12$ Hz, C_1^m), 129.4 (s, C_3^3), 130.9 (br s, C_1^4, $(HC{=}N)_0$, C''^m), 131.4 (s, C''^p), 132.1 (d, $^2J_{CP'_1} = 7$ Hz, C_1^o), 132.2 (s, C_2^4, C_1^p), 132.8 (s, C_0^4), 138.4 (d, $^3J_{CP_3} = 14$ Hz, $(HC{=}N)_2$), 138.9 (d, $^3J_{CP_2} = 13$ Hz, $(HC{=}N)_1$), 149.8 (s, C_0^1), 150.4 (d, $^2J_{CP_3} = 7$ Hz, C_3^1), 151.1 (d, $^2J_{CP_2} = 7$ Hz, C_2^1), 151.9 (d, $^2J_{CP_1} = 9$ Hz, C_1^1), 156.5 (d, $^2J_{CP''_1} = 9$ Hz, C''^i), 190.9 (s, CHO). IR (KBr): ($\nu_{C=O}$) cm^{-1}. Anal. Calcd for $C_{786}H_{708}N_{99}O_{114}P_{57}S_{42}$: C, 57.29; H, 4.33; N, 8.42. Found: C, 57.11; H, 4.28; N, 8.27.

Preparation of 25-[G$_3$]. To a solution of dendrimer **24-G$_3$** (0.300 g; 0.018 mmol) in THF (10 mL) was added 12 equiv of 1-amino-3-azidopropane (0.021 g, 0.218 mmol). The solution was stirred overnight at room temperature, and then evaporated to dryness. The resulting powder is washed with THF/pentane (1/5) to yield **25-G$_3$** as a white powder.

25-[G$_3$]: 96% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −12.7 (dd, $^2J_{P_1P'_1} = 22.0$ Hz, $^2J_{P_1P''_1} = 61.0$ Hz, P_1), 8.1 (br s, P_0), 13.4 (d, $^2J_{P'_1P_1} = 22.0$ Hz, P'_1), 45.5 (d, $^2J_{P''_1P_1} = 61.0$ Hz, P''_1), 62.7 (s, P_2, P_3) ppm. ^1H NMR ($CDCl_3$): δ 1.85 (m, 24 H, C^bH_2), 2.60−2.84 (m, 42 H, Me^1, C^cH_2), 3.28 (m, 132 H, C^aH_2, Me^2, Me^3), 4.66 (br s, 12 H, $CH_2P'_1$), 7.19−7.64 (m, 558 H, C_6H_4, C_6H_5, CH=N−N), 8.10 (s, 12 H, CH=N−C) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.9 (s, C^bH_2), 32.8 (d, $^2J_{CP_2} = {}^2J_{CP_3} = 13$ Hz, Me^2, Me^3), 38.9 (s, Me^1), 48.9 (s, C^aH_2), 57.6 (br d, $^1J_{CP'_1} = 74$ Hz, $CH_2P'_1$), 57.7 (br s, C^cH_2), 120.5 (s, C_0^2), 121.2 (br s, C_3^2), 121.6 (br s, C_1^2, C_2^2, C''^o), 125.2 (s, C_3^4), 126.4 (s, C_0^3), 126.9 (br d, $^1J_{CP'_1} = 103$ Hz, C_1^i), 128.0 (s, C_1^3), 128.1 (s, C_2^3), 128.5 (d, $^3J_{CP'_1} = 12$ Hz, C_1^m), 128.9 (s, C''^m), 129.3 (s, C_3^3), 130.8 (s, C_1^4), 131.1 (br s, $(HC{=}N)_0$), 131.9 (d, $^2J_{CP'_1} = 14$ Hz, C_1^o), 132.1 (br s, C_2^4, C_1^p), 132.6 (s, C_0^4), 138.3 (d, $^3J_{CP_3} = 14$ Hz, $(HC{=}N)_2$), 139.1 (d, $^3J_{CP_2} = 13$ Hz, $(HC{=}N)_1$), 149.7 (br s, C_0^1), 150.4 (d, $^2J_{CP_3} = 7$ Hz, C_3^1), 151.1 (d, $^2J_{CP_2} = 7$ Hz, C_2^1), 152.1 (d, $^2J_{CP_1} = 9$ Hz, C_1^1), 153.8 (d, $^2J_{CP''_1} = 10$ Hz, C''^i), 160.7 (s, $\underline{C}$H=N−C). IR (KBr): 2095 (ν_{N3}) cm^{-1}. Anal. Calcd for $C_{822}H_{780}N_{147}O_{102}P_{57}S_{42}$: C, 56.54; H, 4.50; N, 11.9. Found: C, 56.38; H, 4.33; N, 11.67.

Preparation of 26-[G$_3$]. To a solution of dendrimer **24-G$_3$** (0.350 g; 0.021 mmol) in THF (10 mL) was added 12 equiv (0.072 g, 0.240 mmol) of 4′-amino[15]crown-5. The solution was refluxed for 1 week, and then evaporated to dryness. The resulting powder was washed with THF/pentane (1/5) to yield **26-G$_3$** as a pale yellow powder.

26-[G$_3$]: 93% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −12.6 (dd, $^2J_{P_1P'_1} = 20.0$ Hz, $^2J_{P_1P''_1} = 60.0$ Hz, P_1), 8.3 (s, P_0), 13.6 (d, $^2J_{P'_1P_1} = 20.0$ Hz, P'_1), 46.0 (d, $^2J_{P''_1P_1} = 60.0$ Hz, P''_1), 62.7 (s, P_2, P_3) ppm. ^1H NMR ($CDCl_3$): δ 2.65 (s, 18 H, Me^1), 3.278 (m, 108 H, Me^2, Me^3), 3.60−4.10 (m, 192 H, CH_2O), 4.63 (br s, 12 H, $CH_2P'_1$), 6.10−6.80 (m, 36 H, C_6H_3), 7.10−7.70 (m, 558 H, C_6H_4, C_6H_5, CH=N−N), 8.10 (br s, 12 H, CH=N−C) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.8 (d, $^2J_{CP_2} = {}^2J_{CP_3} = 13$ Hz, Me^2, Me^3), 38.9 (br s, Me^1), 68.1−70.3 (m, CH_2O), 107.2 (s, $\underline{C}_6\underline{H}_3$), 112.5 (s, $\underline{C}_6\underline{H}_3$), 114.0 (s, C_6H_3), 120.5 (br s, C_0^2), 121.2 (br s, $\overline{C}_3^2$), 121.6 (br s, $\overline{C}_1^2$, C_2^2, C''^o), 125.2 (s, C_3^4), 126.4 (br s, C_0^3), 127.8 (br s, C_1^3), 128.0 (s, C_2^3), 128.5 (d, $^3J_{CP'_1} = 13$ Hz, C_1^m), 128.7 (s, C''^m), 129.3 (s, C_3^3), 130.6 (s, C_1^4), 131.2 (br s, $(HC{=}N)_0$), 132.0 (br s, C_1^o), 132.1 (br s, C_2^4, C_1^p), 133.4 (s, C_0^4), 138.3 (d, $^3J_{CP_3} = 13$ Hz, $(HC{=}N)_2$), 138.9 (br d, $^3J_{CP_2} = 12$ Hz, (HC=N)1), 145.0 (s, C_6H_3), 147.6 (s, C_6H_3), 149.1 (s, C_6H_3), 149.5 (br s, C_0^1), 150.3 (d, $^2J_{CP_3} = 7$ Hz, C_3^1), 151.0 (d, $^2J_{CP_2} = 7$ Hz, C_2^1), 152.0 (br s, C_1^1), 152.6 (br s, C''^i), 156.9 (s, $\underline{C}$H=N−C). ($CH_2P'_1$, C_1^i not detected). Anal. Calcd for $C_{954}H_{936}N_{111}O_{162}P_{57}S_{42}$: C, 58.28; H, 4.80; N, 7.91. Found: C, 56.08; H, 4.61; N, 7.76.

X-ray Structure Determination for Compounds 5-[G$_1$] [$C_{64}H_{70}N_{10}O_4S_6P_8Cl_8$][$CF_3SO_3$]$_2$, 6($CH_2Cl_2$) and 8-[G$_1$] [$C_{68}H_{70}N_{10}O_4S_6P_8Cl_8$][$CF_3SO_3$]$_2$, 2($CH_2Cl_2$), 4($CH_3OH$). Data were collected on a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems cooler device for both compounds. The crystal-to-detector distance was 80 mm. Crystal decay was monitored by measuring 200 reflections by image. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections, any important fluctuations of the intensity were observed over the course of the data collection.

For **5-[G$_1$]** and **8-[G$_1$]** the structures were solved by direct methods (SIR92)[19] and refined by least-squares procedures on F_{obs}. All hydrogen atoms were located on a difference Fourier map, but they were introduced in calculation in idealized positions (d(C−H)= 0.96 Å), their atomic coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the carbon atoms to which they were connected. All non hydrogen atoms were anisotropically refined excepted the C atoms of the allene of **8-[G$_1$]** and the molecules of methanol. For **5-[G$_1$]**, the molecules of the triflate anions and the C atoms of the dichloromethane were isotropically refined.

The models were easily located for both structures, excepted concerning the allene chain for **8-[G$_1$]**. In fact, around this hydrocarbon chain, the electron density seems highly disordered, a best model to fit this electron density was to consider the last C atom of the allene chain C(6) distributed on two sites with a ratio (60/40). Some solvents (CH_2Cl_2 for compound **5-[G$_1$]**, CH_2Cl_2 and CH_3OH for compound **8-[G$_1$]**) were located on difference Fourier maps. The electron density around these molecules is strongly disordered and appears as a diffuse spread. Finally the differences Fourier synthesis still show some residual electron

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density in these regions which could not be fitted to any model. Least-squares refinement were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. A weighting scheme was used in the last refinement cycles where weights are calculated from the following expression: $w = [\text{weight}][1 - (\Delta(F)/6\sigma(F)]^2$.[20] Models reached convergence with Rw $= [\sum w(|F_o| - |F_c|)^2/\sum(|F_o|)^2]^{1/2}$ and Rw $= [\sum w(|F_o| - ||F_c||)^2/\sum(|F_o|)^2]^{1/2}$ R (Rw) were 0.095 (0.097) with 3789 reflections used [$I >$ 3s(I)] and 555 parameters refined for **5-[G$_1$]**, and 0.083 (0.093) with 4115 reflections used [$I >$ 2.5s(I)] and 606 parameters refined for **8-[G$_1$]**. Further details of data collection and refinement are given in Supporting Information. The calculation were performed with a CRYSTALS programs[21] running on a PC. The drawing of the molecules was realized with the aid of CAMERON.[22] The atomic scattering factors were taken from the *International Tables for X-ray Crystallography*.[23]

Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ UK, on quoting the full journal citation.

Experimental section concerning the synthesis of dendrimers and spectroscopic data of 1-[G1], **1-[G$'_1$]**, **1-[G$_2$]**, **1-[G$'_2$]**, **1-[G$''_2$]**, **1-[G$'''_2$]**, **1-[G$'_3$]**, **2-[G$_1$]**, **2-[G$_2$]**, **3-[G$''_0$]**, **3-[G$'''_0$]**, **3-[G$'_1$]**, **3-[G$'_2$]**, **3-[G$_3$]**, **5-[G$_1$]**, **6-[G$_1$]**, **7-[G$_1$]**, **8-[G$_1$]**, **9-[G$_1$]**, **9-[G$_2$]**, **11-[G$_1$]**, **12-[G$_2$]**, **13-[G$_2$]**, **14-[G$_2$]**, and **21-[G$_1$]** (35 pages). See any current masthead page for ordering information and Web access instructions.

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Supporting Information Available: Experimental procedures and results as well as tables of crystal data, fractional atomic coordinates, isotropic and anisotropic thermal parameters, interatomic distances, and bond angles (35 pages). See any current masthead page for ordering information and Web access instructions.

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