Michael-Type Addition of Amines to the Vinyl Core of Dendrons − Application to the Synthesis of Multidendritic Systems

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Michael-type additions of functionalized amines to CH_2=CH–P=N–P=S linkages located at the core of phosphorus-containing dendrons allowed for the grafting of functions suitable to join these dendrons together or to various dendritic molecules. This reactivity led to original multidendritic systems incorporating different types of subunits.

Introduction

Tailored approaches to dendritic architectures incorporating different subunits with various constitutions or topologies appear to be among the most promising fields of research in dendrimer synthesis.[1] An interesting way of obtaining such dendritic assemblies consists in using dendrons[2] as subunits, taking advantage of the presence of one reactive function located at the core level, in addition to the numerous other functions located on the surface. The nature of this unique function is crucial when a divergent process is used, since it must not react during the synthesis of the dendron, but must be easily activated later. In the course of our studies concerning phosphorus-containing dendrimers,[3] we have demonstrated that the P=N−P=S linkages[4] exhibit a versatile reactivity, including alkylation[5] and complexation[6] properties induced by the polarity of this linkage ($P^+-N=P-S^-$). We reasoned that such a polarity could also lead to the use of this linkage as an activating group of alkenes in Michael-type[7] additions that could be used to introduce various new functions at the core level, suitable to graft the dendron to various dendritic molecules. Taking into account the large number of functionalized primary and secondary amines easily available, we decided to focus our work on the use of such compounds in Michael-type additions to CH_2=CH−P=N−P=S linkages. The subsequent reactions of the functions introduced in this way ought to lead to original multidendritic systems, which would be difficult or impossible to synthesize by other methods.

Results and Discussion

The activated vinyl group is obtained by using a Staudinger reaction between diphenylvinylphosphane and the azide **1** (Scheme 1). This reaction gives compound **2a-G′$_0$**, possessing a P=N−P=S linkage conjugated with the vinyl group, and two aldehyde groups. The dendron is grown starting from the aldehyde groups. The alternative use of $H_2NNMeP(S)Cl_2$ and 4-hydroxybenzaldehyde sodium salt leads to the dendron **2a-G$_n$** (n = 1−3). The grafting of diverse phenol salts (**b**: phenol, **c**: *p*-cyanophenol, **d**: *p*-diphenylphosphanylphenol, **e**: *m*-dimethylaminophenol) at the last step gives dendrons coated with various functional groups (Figure 1). The growing of the dendron was stopped at the third generation, in order to be able to easily detect all the changes induced by the reactions we intended to perform at the core level. Every step of the synthesis of dendrons is easily monitored by ^{31}P, ^{1}H, and ^{13}C NMR, and IR spectroscopy. Only the signal corresponding to *C*H−(P=N−P=S) is undetectable in ^{13}C NMR, owing to the coupling with both phosphorus atoms and to the overlap with other peaks. The purity of the dendrons is also checked by size exclusion chromatography, which gives a narrower signal than the narrow-distribution polystyrene standards with polydispersity M_w/M_n = 1.03.

In order to check the feasibility of the Michael-type addition of amines, our first attempts consisted of the reaction of functionalized monoamines, either primary amines such as propargylamine and tyramine or secondary amines such as diallylamine and thiomorpholine with dendrons **2-G′$_3$** (Scheme 2). In all cases, the reactions were first carried out at room temperature, with excess amine, and monitored by ^{31}P NMR. If no reaction occurred or if the reaction rate was very slow, the reaction mixture was heated and amount of amine was further increased. In fact, it appeared to be difficult to predict the conditions to use, and no clear trend could be inferred from the nature and the structure of the amine, as was already observed in the reaction of amines with vinylphosphoryl derivatives.[8] These reactions led to the grafting of the alkyne, phenol, alkene or thioether group at the level of the core. In all cases, the addition was unambiguously monitored by examination of the signals in the ^{31}P NMR corresponding to the P=N−P=S linkage. The doublet corresponding to the PPh_2 group was deshielded from approximately δ = 10−12 for **2-G′$_3$** to approximately δ = 17−18 for **3b-G′$_3$**, **4e-G′$_3$**, **5b-G′$_3$**, **6c-G′$_3$**, and a slight

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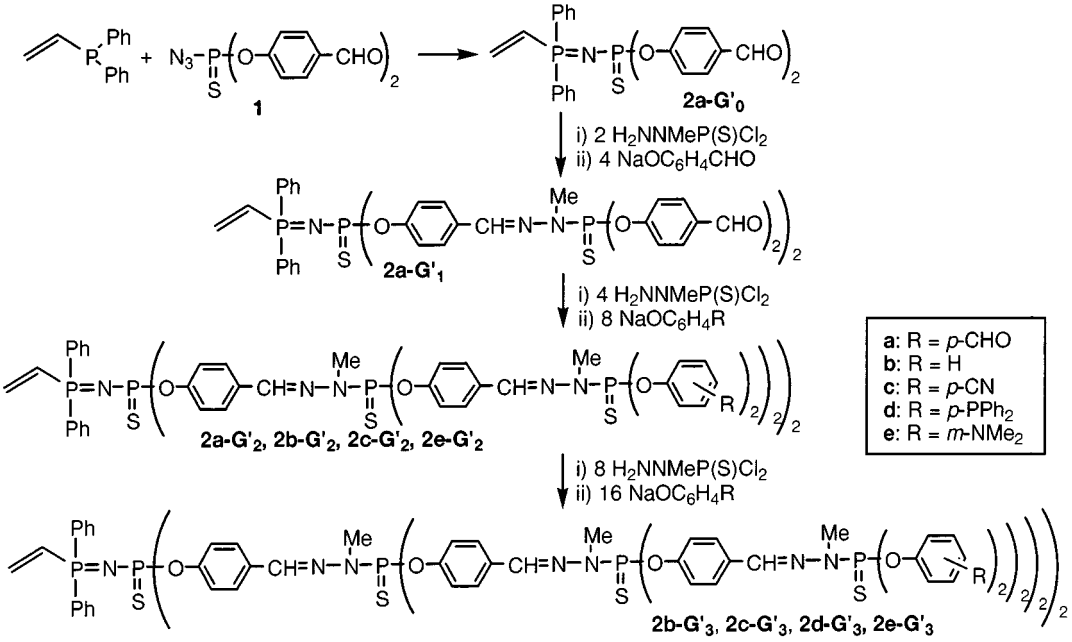


Scheme 1. Synthesis of dendrons

shielding of the signal of the P=S group ($\Delta\delta$ ca 1 ppm) was observed. In the case of tyramine, only the amino group reacted, as shown by the deshielding of the signal corresponding to the $C_6H_5CH_2CH_2N$ group in ^{13}C NMR from $\delta = 43.7$ for tyramine to $\delta = 50.7$ for the dendron **4e-G′$_3$**. This fact is not surprising, since it has been shown that the addition of alcohols must be catalyzed by BuLi or NaOH.[9]

The use of diamino reagents gave less clear results. In fact, two cases must be distinguished: either the diamine possesses two analogous amino groups or the diamine possesses two different amino groups (one primary and one secondary). Both cases were considered with second and third generation dendrons (Scheme 3). In the former case, the use of a very large excess of diamine (several hundred equivalents) should allow for the prevention of the coupling of two dendrons. This was evidenced by ^1H and also by ^{13}C NMR spectroscopy, which shows a loss of symmetry of the initially symmetric diamine. For instance the reaction of *trans*-diaminocyclohexane with **2e-G′$_2$** led to the appearance of one singlet for the *C*H-NH group (δ $^{13}C = 55.1$) and of one singlet for the *C*H-NH_2 group (δ $^{13}C = 63.5$) of **7e-G′$_2$**. Analogous behavior was observed for the reaction of ethylenediamine with **2b-G′$_3$** which led to **9b-G′$_3$** characterized by the appearance of 4 signals assigned to the $H_2NCH_2CH_2NHCH_2CH_2P$ linkage in ^{13}C NMR.

In the case of the presence of two different amino groups, the main point is that one function must be much more reactive than the other one. We have chosen to use methylhydrazine as a special type of unsymmetrical diamine. Excess methylhydrazine (30 equiv.) were treated with dendrons **2c-G′$_2$**, **2b-G′$_3$**, and **2e-G′$_3$** at room temperature (Scheme 3). The reaction proceeded rapidly, leading to a single product in all cases, i.e. dendrons **8c-G′$_2$**, **8b-G′$_3$**, and **8e-G′$_3$**, respectively. At this step, it was difficult to ascertain from NMR spectroscopic data whether the (Me)N−H or the NH_2 group of methylhydrazine had reacted; however, it has been already noted that the more substituted nitrogen reacts preferentially in the Michael addition of hydrazines.[10] Furthermore, the reactivity of these dendrons **8** with aldehydes demonstrates that the former addition occurred only with the (Me)NH group (see later).

With several dendrons functionalized at the core level in hand, we decided to use them as building blocks for the synthesis of more complex molecular architectures. In a first attempt, we tried to graft together two identical dendrons. Schiff condensations between two equivalents of the dendron **8e-G′$_3$** and the dialdehyde $N_3P(S)(OC_6H_4CHO)_2$ led to the bis(dendron) **10e-[G′$_3$]$_2$** (Scheme 4). The condensation led to the shielding of the singlet corresponding to the CH_3-NCH_2 group in ^{13}C NMR from $\delta = 50.4$ for **8e-G′$_3$** to $\delta = 37.7$ for **10e-[G′$_3$]$_2$**, and the appearance of a singlet at $\delta = 134.9$, corresponding to the formation of the $CH{=}N-N(Me)CH_2CH_2$ linkages. Such a reaction demonstrated that the addition of methylhydrazine to dendron **2e-G′$_3$** occurred with the (Me)NH group. The presence of an azido group at the core allows for the consideration of the bis(dendron) **10e-[G′$_3$]$_2$** as another building block for the synthesis of more complex dendritic structures, as will be evidenced later.

In a second step, we tried to synthesize unsymmetrical dendrimers, grafting two different dendrons by their core (Scheme 5, Figure 1). The first attempt involved the second-generation dendrons **2b-G′$_2$** and **7e-G′$_2$** (100% excess). The Michael type addition occurs with the primary amino group of **7e-G′$_2$**, leading to compound **11-G′$_2$-G′$_2$**, as evidenced by the increased symmetry of the core detected by ^{13}C NMR. Only one singlet for the carbons of the cyclohexane ring α to nitrogen was observed at $\delta = 55$. However, compound **11-G′$_2$-G′$_2$** as a whole is unsymmetrical, owing to the presence of two different end groups, phenoxy and

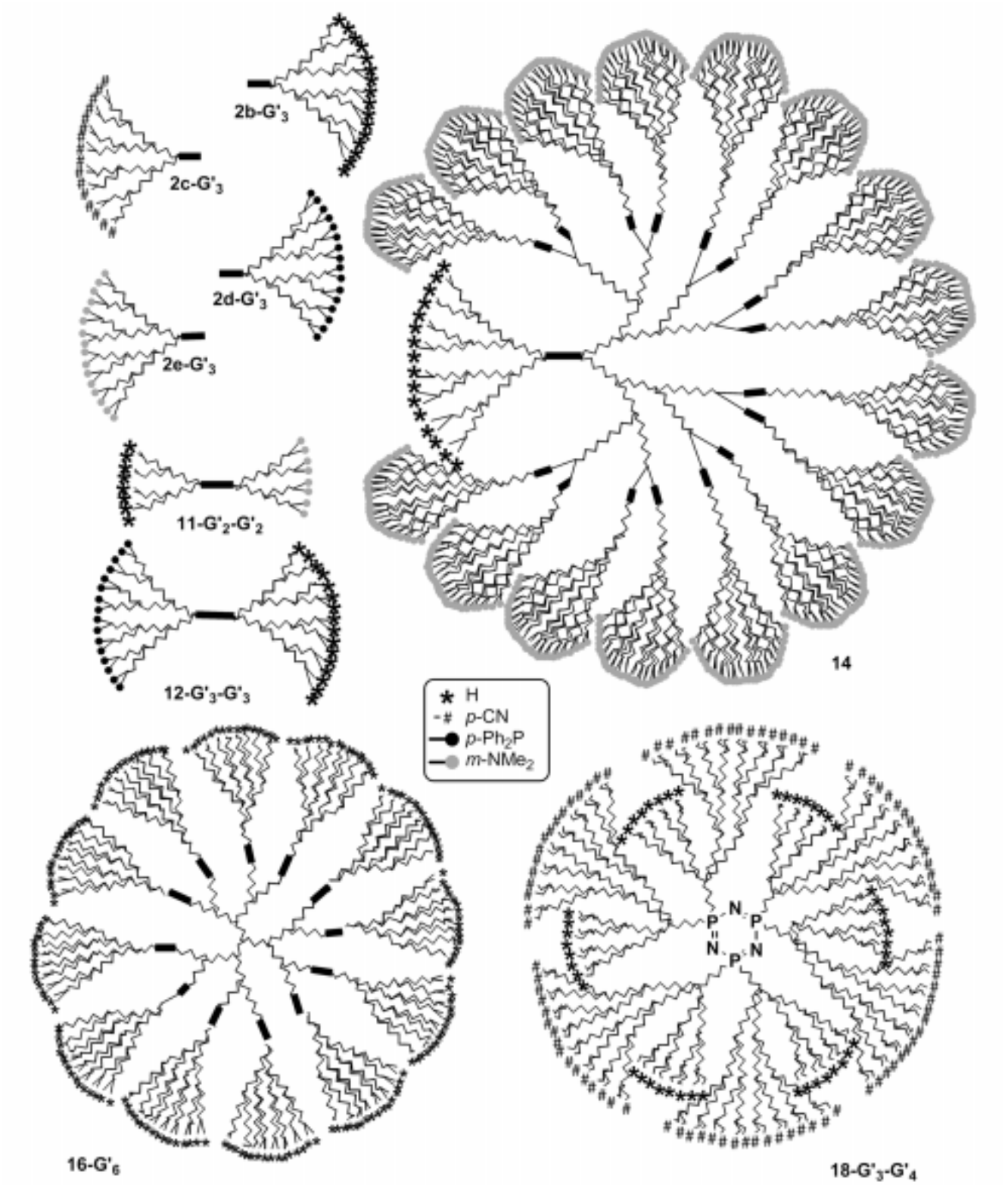
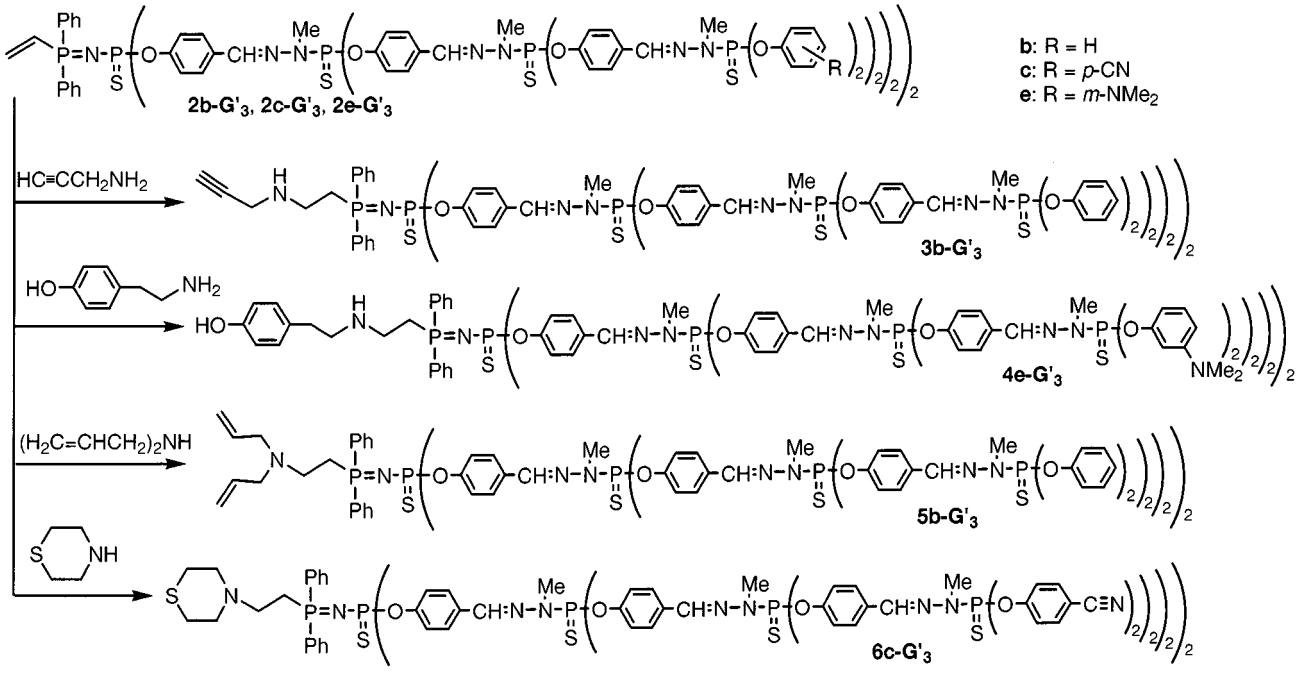


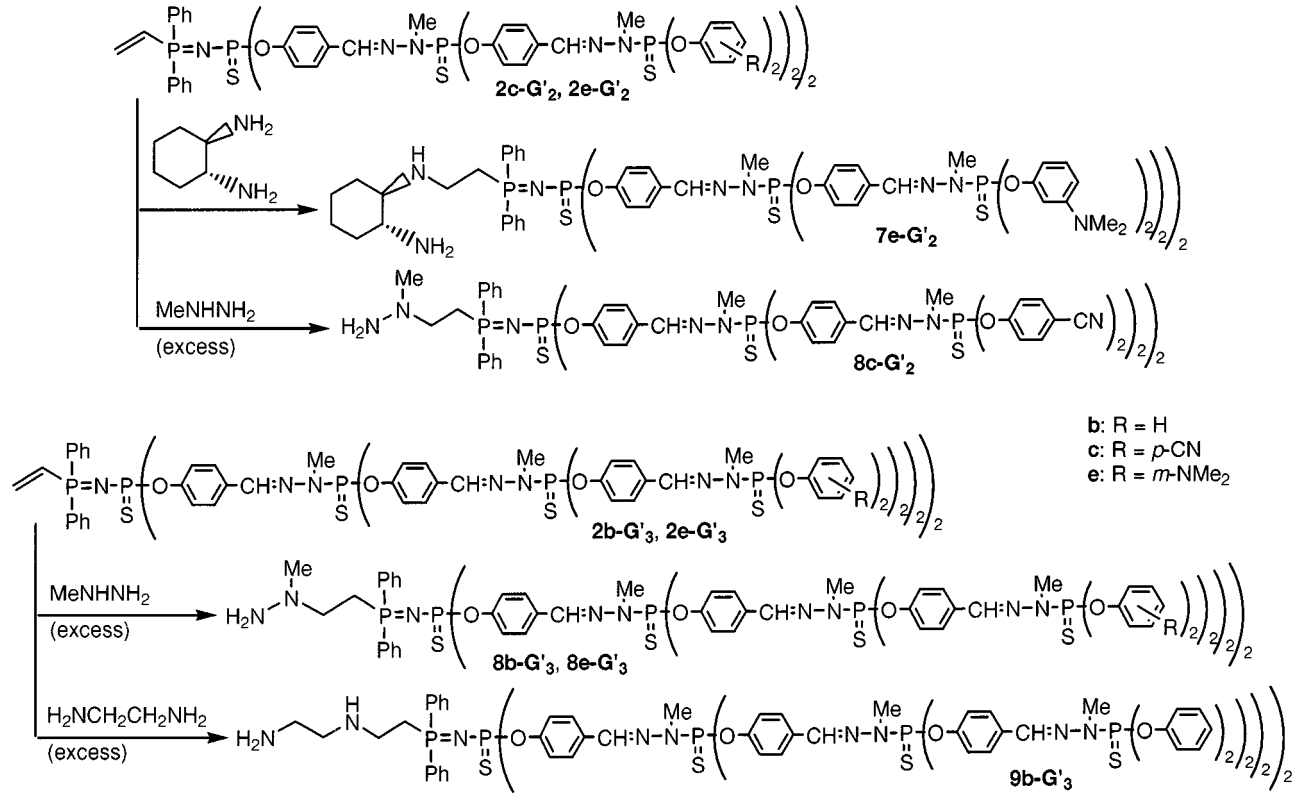
Figure 1. Schematic drawing of dendrons and multidendritic systems

amino phenoxy. The two N−H functions remaining at the core, could result in an interesting reactivity, leading to the grafting of a third or even a fourth arm. However, our first attempts in this field failed up to now.

Our second attempt to graft together two different dendrons consisted of reacting two third-generation dendrons **2d-G′3** and **9b-G′3** (100% excess), leading to compound **12-G′3-G′3** (Scheme 6, Figure 1). We tried to purify and separate compound **12-G′3-G′3** from the excess **9b-G′3** by size exclusion chromatography. The process allowed for the elimination of **9b-G′3**, but resulted in the total oxidation of the diphenylphosphanyl groups of **12-G′3-G′3**, leading to



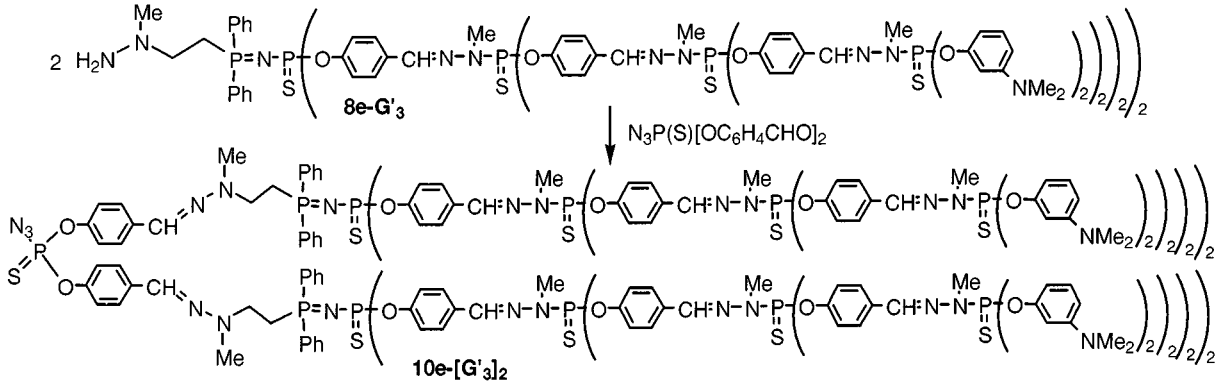
Scheme 2. Reactivity of the core of dendrons with various monoamines



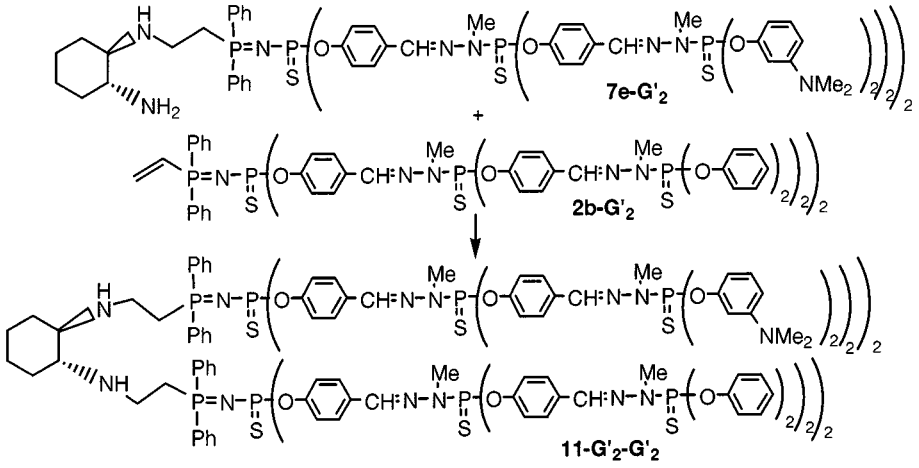
Scheme 3. Reactivity of the core of dendrons with various diamines

13-G′3-G′3 which was isolated and characterized. The Michael addition with the primary amino group was again demonstrated by ^{13}C NMR, which showed that the $PCH_2CH_2NHCH_2CH_2NHCH_2CH_2P$ linkage is totally symmetric (only 3 signals for the CH_2 groups). However, here again the molecule as a whole is not symmetric, owing to the presence of phenoxy groups as end groups on one side and phosphane oxide groups on the other.

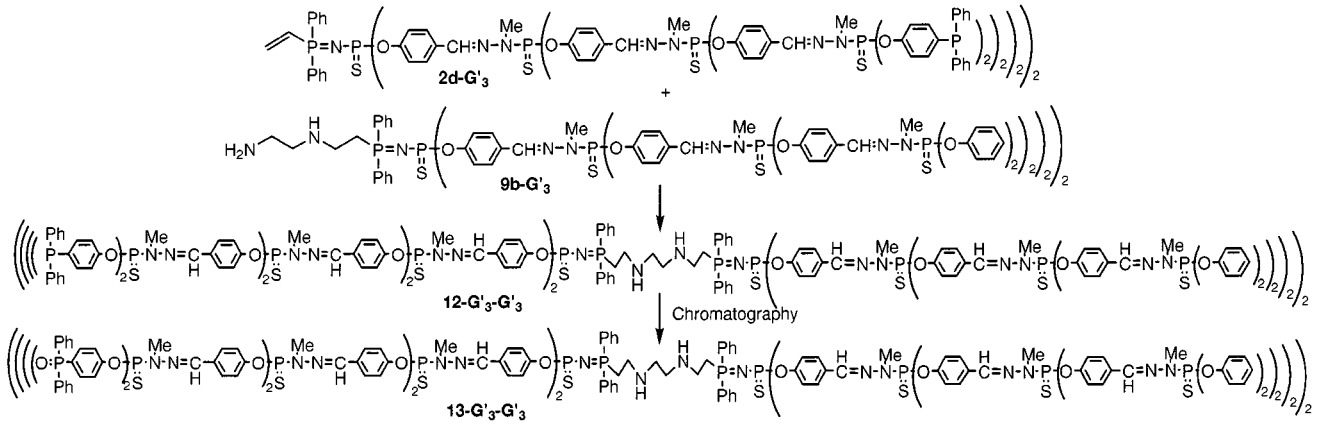
The oxidation observed during workup prevented the use of **13-G′3-G′3** as a precursor for more complex macromolecules. However, the fact that we could not isolate compound **12-G′3-G′3** did not prevent its use as starting mat-



Scheme 4. Synthesis of a bis(dendron) with a single type of end group

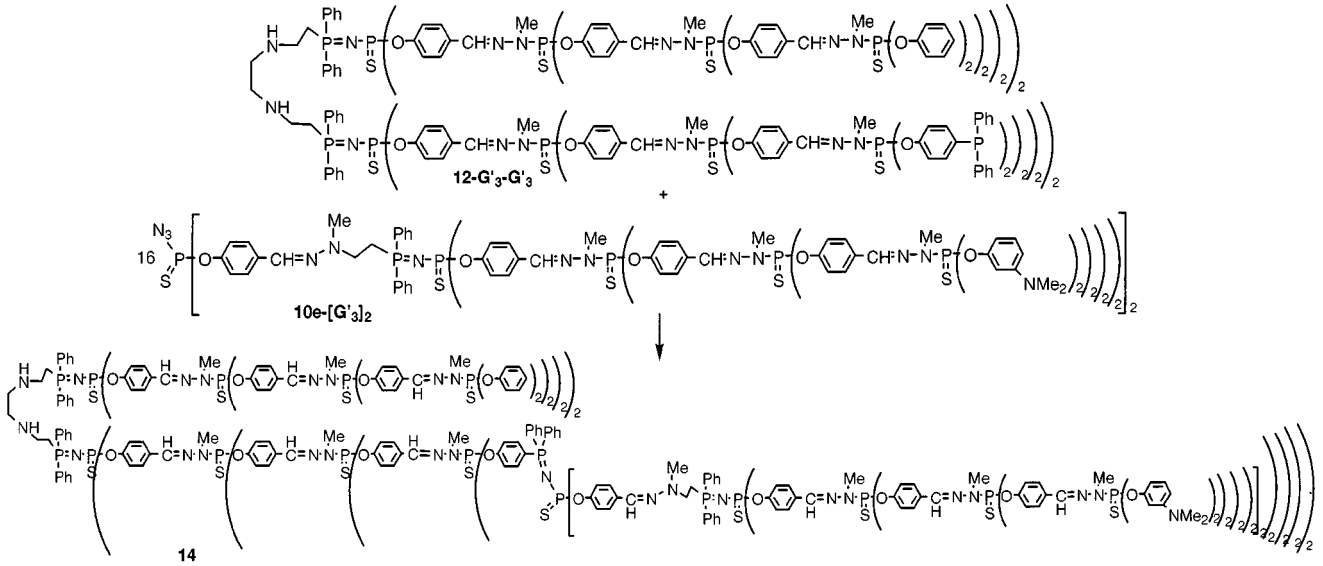


Scheme 5. Synthesis of a second-generation dendrimer composed of two dendrons having different end groups



Scheme 6. Synthesis of a third-generation dendrimer composed of two dendrons having different end groups

erial, provided that the reagent used to react with it cannot also react with the excess **9b-G′$_3$**. We thus treated crude **12-G′$_3$-G′$_3$** with an excess of the azido dendron **10e-[G′$_3$]$_2$** (Scheme 7, Figure 1). The Staudinger reaction led to the formation of compound **14**, incorporating sixteen new $C_6H_4Ph_2P{=}N{-}P{=}S$ linkages (δ ^{31}P = 13.0 for P=N) different from the $CH_2Ph_2P{=}N{-}P{=}S$ linkages already present in **12-G′$_3$-G′$_3$** and **10e-[G′$_3$]$_2$** (δ ^{31}P = 17.7 for P=N). The formation of these linkages was also characterized in the ^{13}C NMR spectrum by the appearance of one doublet at δ = 134.3 ($^2J_{CP}$ = 12 Hz) corresponding to the carbon *ortho* to phosphorus in the C_6H_4 part, different from the



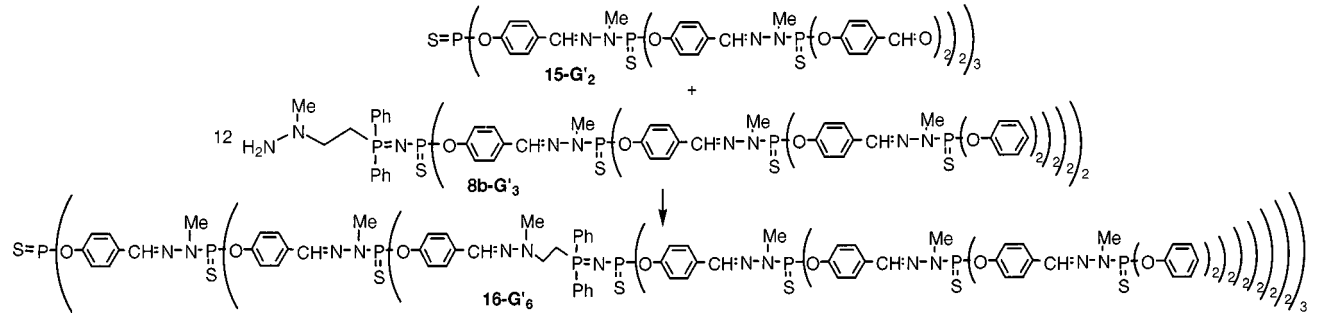
Scheme 7. Grafting of dendrons on half of the surface of a dendrimer

doublet corresponding to the same carbon in the initial phosphane ($\delta = 135$, $^2J_{CP} = 20.5$ Hz) or in the oxide **13-G′$_3$-G′$_3$** ($\delta = 133.7$, $^2J_{CP} = 10.9$ Hz).

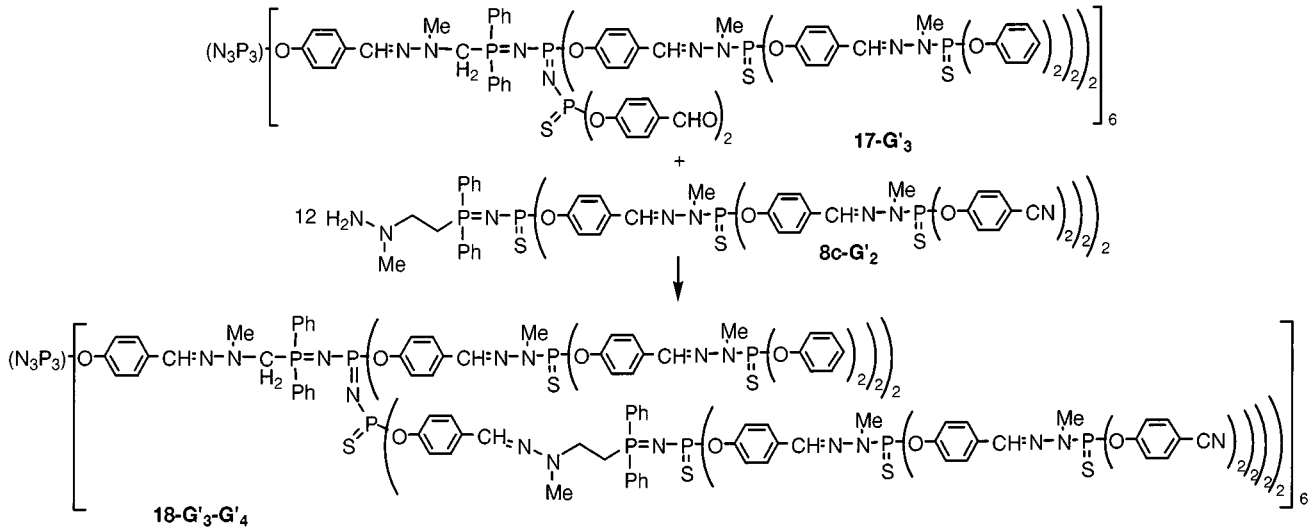
Another way of using dendrons as building blocks consists in reacting them with the functions located on the surface of dendrimers. We carried out this type of experiment with the second-generation dendrimer **15-G′$_2$** and an excess of dendron **8b-G′$_3$** (Scheme 8, Figure 1). The reaction was monitored by the disappearance of the signal corresponding to the CHO end groups of dendrimer **15-G′$_2$** in the ^{1}H NMR and IR spectra. The reaction was slow and went to completion only after 18 days, but we decided to wait another two days before working up the reaction, in order to maximize the chance of substituting all the end groups. This reaction thus led to the formation of the sixth generation dendrimer **16-G′$_6$** from a second generation dendrimer in a single step. An analogous reaction carried out with the third generation dendrimer **15-G′$_3$** (24 CHO end groups) did not go to completion, even after 40 days: a weak signal corresponding to CHO groups was still distinguishable in the ^{1}H NMR spectrum, with its integration corresponding to approximately 1/24 of the CHO functions remaining unchanged. Thus, steric hindrance renders **15-G′$_3$** reluctant to the incorporation of 24 dendrons, which would have led directly to synthesis of a seventh generation dendrimer. However, it must be noted that we have already obtained seventh- and higher-generation dendrimers using a different strategy.[3b][3e] It is thus clear that it is easier to incorporate a large number of small molecules than a small number of large molecules.

In order to demonstrate the versatility of the use of dendrons as building blocks, we finally tried to graft them to the internal layers of a dendrimer. The experiment was carried out with the second-generation dendron **8c-G′$_2$** and the dendrimer **17-G′$_3$** possessing 12 internal aldehyde groups (Scheme 9, Figure 1). The condensation was relatively slow. The reaction required 10 days to go to completion and was monitored by ^{1}H NMR spectroscopy. However, it must be emphasized that this very complex multidendritic species **18-G′$_3$-G′$_4$** was obtained in a single step starting from **17-G′$_3$**, whereas the formation of a similar type of compound required at least 6 steps, using a divergent growth from the aldehyde groups of **17-G′$_3$**.[5a]

All the multidendritic systems reported in this paper have been characterized by multi-nucleus NMR and IR spectroscopy. All attempts to use the MALDI-TOF technique to detect structure defects failed up to now, since the laser light used by this technique (337 nm) induces the cleavage of a number of hydrazino bonds, owing to the very broad UV-absorption at 210−360 nm of all these dendritic species.[11]



Scheme 8. Grafting of dendrons on the surface of a dendrimer



Scheme 9. Grafting of dendrons inside a dendrimer

However, the narrow signals obtained in all cases by size exclusion chromatography confirmed the high purity of these dendritic species. Furthermore, a plot of the SEC elution time versus the logarithm of the molecular weight of these compounds gave a straight line (Figure 2), a tendency already reported for other dendritic species.[2a]

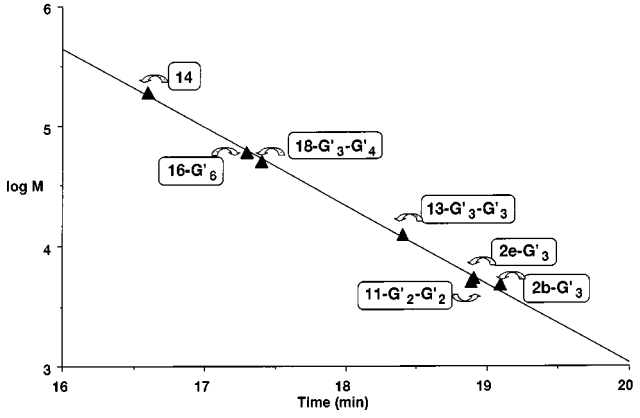


Figure 2. Plot of elution time of Size Exclusion Chromatography versus Log(Molecular Weight) of dendrons and multidendritic species

Conclusion

We have demonstrated in this paper that the P=N−P=S linkage is a good activating group of alkenes, which facilitates the Michael-type addition of various functionalized amines. The subsequent reaction of the function introduced in this way at the core of dendrons allowed for the synthesis of several original dendritic architectures, through core−core, core−surface and core−internal layer couplings. These dendritic architectures incorporate various subunits having different constitutions and topologies, for instance two types of functional groups located in definite areas on the surface of the macromolecule. The functional groups reported in this paper (phenoxy, *m*-dimethylaminophenoxy, *p*-diphenylphosphanylphenoxy, *p*-cyanophenoxy) constitute only examples, which could easily be extended to other substituents in order to bring about specific properties. It must also be emphasized that all these multidendritic species include several P=N−P=S linkages which could be used later to afford even more complex compounds, since we have shown that these linkages react cleanly and quantitatively with electrophiles.[5]

Experimental Section

General: All manipulations were carried out with standard high-vacuum and dry-argon techniques. − ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, or AMX 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^{1}H 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. The numbering scheme used for NMR is depicted in Figure 3 and Figure 4. Compounds **1**,[12] HOC_6H_4*p*-PPh_2,[13] **15-G′$_2$**,[3a−3e] and **17-G′$_3$**[5a] were prepared according to published procedures.

Preparative size exclusion chromatography was performed using Bio-Beads S-X1 beads (operating range 600−14000 g·mol^{-1}) from Bio-Rad company, with THF as eluent. SEC analytical data were obtained at 37 °C using a Waters 410 differential refractometer, three 5μm Waters Styragel® HR columns (300 × 8 mm) connected in series in order of decreasing pore size (10000 Å, 1000 Å, 100 Å) and THF as eluent with a nominal flow of 1.2 mL/min.

Synthesis of 2a-G′$_0$: To a solution of diphenylvinylphosphane (2.000 g, 9.434 mmol) in CH_2Cl_2 (10 mL) was added at 0°C one equivalent of the azide **1** (3.276 g, 9.434 mmol). Ten minutes after the end of the addition, the mixture was warmed to room temperature and stirred for 3 h. The solvent was then removed under vacuum. The product was washed with a THF/pentane mixture (1:5) to give a pale yellow powder (3.61 g, 72%).

2a-G′$_0$: ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 10.6 (d, $^{2}J_{PP}$ = 31.3 Hz, P′$_0$), 50.9 (d, $^{2}J_{PP}$ = 31.3 Hz, P$_0$). − ^{1}H NMR ($CDCl_3$): δ = 6.1 (ddd, $^{3}J_{HP}$ = 24.3 Hz, $^{3}J_{HHa}$ = 18.2 Hz, $^{2}J_{HH}$ = 1.0 Hz, 1 H, H$_c$), 6.4

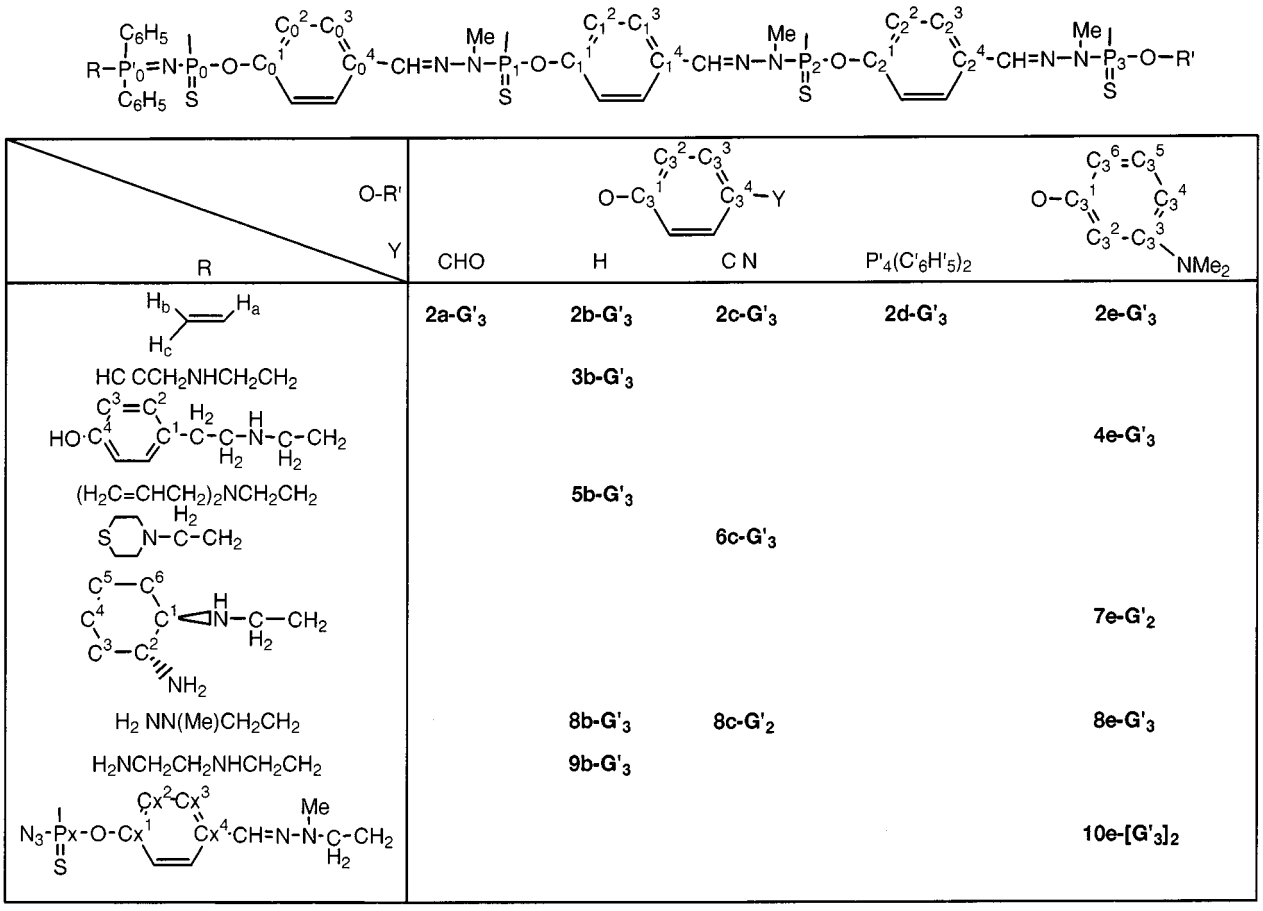


Figure 3. Numbering scheme used in NMR for dendrons

(ddd, $^3J_{HP}$ = 58.5 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.0 Hz, 1 H, H_b), 6.8 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.2 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.2 Hz, 1 H, H_a), 7.2−7.8 (m, 18 H, CH_{arom}), 9.9 (s, 2 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 121.9 (d, $^3J_{CP}$ = 5.6 Hz, C_0^2), 127.2 (dd, $^1J_{CP}$ = 97.2 Hz, $^3J_{CP}$ = 2.4 Hz, *i*-C_6H_5), 128.7 (d, $^3J_{CP}$ = 13.1 Hz, *m*-C_6H_5), 129.8 (dd, $^1J_{CP}$ = 135.9 Hz, $^3J_{CP}$ = 4.7 Hz, CH_a=), 131.1 (s, C_0^3), 131.9 (d, $^2J_{CP}$ = 11.3 Hz, *o*-C_6H_5), 132.5 (s, C_0^4), 132.7 (d, $^4J_{CP}$ = 2.6 Hz, *p*-C_6H_5), 136.9 (s, CH_2=), 156.6 (d, $^2J_{CP}$ = 8.5 Hz, C_0^1), 190.9 (s, CHO). − IR (KBr): 1702 ($\nu_{C=O}$) cm^{-1}. − $C_{28}H_{23}NO_4P_2S$ (531.5): calcd. C 63.27, H 4.36, N 2.63; found C 63.12, H 4.38, N 2.57.

General Procedure for the Synthesis of 2a-G_n (n = 1−3): To a solution of **2a-G′$_{n-1}$** (typically 2.00 g) in THF was added a small excess of dichloromethylhydrazinothiophosphane as a solution in chloroform. The mixture was stirred at room temperature for 12 h. After evaporation of the solvents, the product was washed several times with a THF/pentane mixture (1:5) to give **2a-G_n (n = 1−3)** as white powders.

General Procedure for the Synthesis of 2a-e-G′$_n$ (n = 1−3): To a solution of **2a-G_n** (typically 2.00 g) in THF (typically 20 mL) was added a small excess of sodium salt $NaOC_6H_4R$ (**a**: R = *p*-CHO; **b**: R = H; **c**: R = *p*-CN; **d**: R = *p*-PPh_2; **e**: R = *m*-NMe_2). The resulting mixture was stirred at room temperature for 12 h. The solution was first centrifuged, then evaporated under vacuum. The product was washed several times with a THF/pentane mixture (1:5) to give a white powder for **2a-d-G′$_n$** or a brown powder for **2e-G′$_n$**.

2a-G_1: (2.83 g, 88%). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.8 (d, $^2J_{PP}$ = 32.2 Hz, P'_0), 52.7 (d, $^2J_{PP}$ = 32.2 Hz, P_0), 63.5 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 3.4 (d, $^3J_{HP}$ = 14.1 Hz, 6 H, P_1-N-CH_3), 6.1 (ddd, $^3J_{HP}$ = 24.2 Hz, $^3J_{HHa}$ = 18.3 Hz, $^2J_{HH}$ = 1.0 Hz, 1 H, H_c), 6.4 (ddd, $^3J_{HP}$ = 46.0 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.0 Hz, 1 H, H_b), 6.8 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.3 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.0, Hz 1 H, H_a), 7.2−7.7 (m, 20 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.8 (d, $^2J_{CP}$ = 13.1 Hz, P_1-N-CH_3), 122.0 (d, $^3J_{CP}$ = 4.3 Hz, C_0^2), 128.0 (dd, $^1J_{CP}$ = 97.2 Hz, $^3J_{CP}$ = 4.5 Hz, *i*-C_6H_5), 128.4 (s, C_0^3), 128.8 (d, $^3J_{CP}$ = 13.6 Hz, *m*-C_6H_5), 130.2 (s, C_0^4), 130.4 (dd, $^1J_{CP}$ = 135.9 Hz, $^3J_{CP}$ = 4.7 Hz, CH_a=), 132.1 (d, $^2J_{CP}$ = 11.0 Hz, *o*-C_6H_5), 132.7 (s, *p*-C_6H_5), 136.9 (s, CH_2=), 141.4 (d, $^3J_{CP}$ = 18.2 Hz, C_0^4-*C*H=N), 153.6 (d, $^2J_{CP}$ = 9.7 Hz, C_0^1). − $C_{30}H_{29}Cl_4N_5O_2P_4S_3$ (853.5): calcd. C 42.21, H 3.42, N 8.20; found C 42.10, H 3.39, N 8.14.

2a-G′$_1$: (2.66 g, 95%). − $^{31}P\{^1H\}$ NMR (THF): δ = 9.8 (d, $^2J_{PP}$ = 31.5 Hz, P'_0), 52.2 (d, $^2J_{PP}$ = 31.5 Hz, P_0), 60.3 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 3.4 (d, $^3J_{HP}$ = 11.1 Hz, 6 H, P_1-N-CH_3), 6.1 (ddd, $^3J_{HP}$ = 24.2 Hz, $^3J_{HHa}$ = 18.2 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H_c), 6.4 (ddd, $^3J_{HP}$ = 45.9 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H_b), 6.8 (dddd, $^2J_{HP}$ = 25.3 Hz, $^3J_{HHc}$ = 18.2 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.1 Hz, 1 H, H_a), 7.2−7.9 (m, 36 H, CH_{arom}, CH=N), 9.9 (s, 4 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.8 (d, $^2J_{CP}$ = 13.0 Hz, P_1-N-CH_3), 121.9 (d, $^3J_{CP}$ = 5.2 Hz, C_0^2, C_1^2), 127.8 (dd, $^1J_{CP}$ = 91.2 Hz, $^3J_{CP}$ = 4.5 Hz, *i*-C_6H_5), 127.9 (s, C_0^3), 128.6 (d, $^3J_{CP}$ = 13.0 Hz, *m*-C_6H_5), 130.4 (s, C_0^4), 131.3 (s, C_1^3), 132.0 (d, $^2J_{CP}$ = 10.8 Hz, *o*-C_6H_5), 132.6 (d, $^4J_{CP}$ = 2.3 Hz, *p*-C_6H_5), 133.4

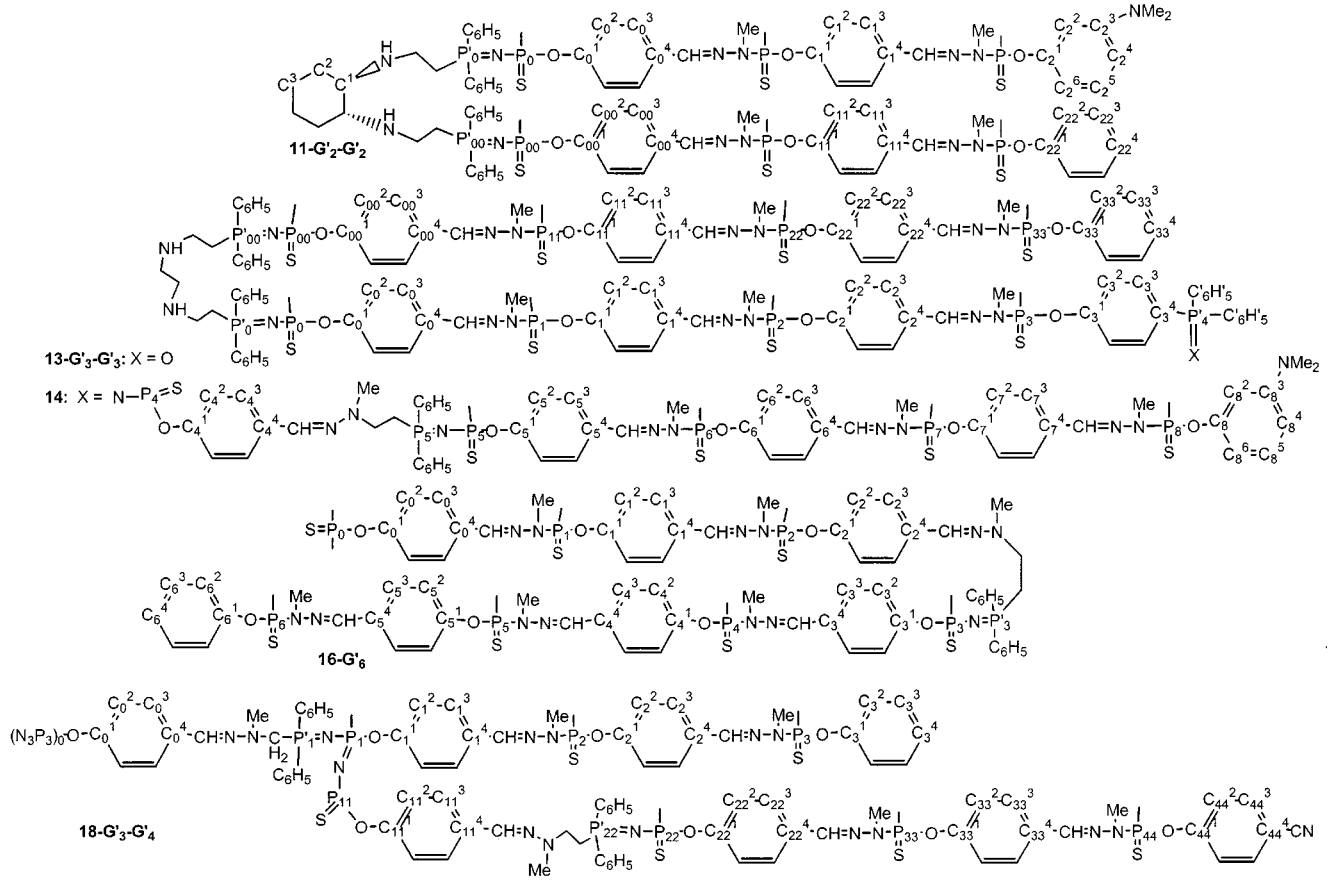


Figure 4. Numbering scheme used in NMR for multidendritic species

(s, C_1^4), 136.7 (s, CH_2=), 140.1 (d, $^3J_{CP}$ = 13.7 Hz, C_0^4-*C*H=N), 153.1 (d, $^2J_{CP}$ = 10.4 Hz, C_0^1), 155.0 (d, $^2J_{CP}$ = 7.0 Hz, C_1^1). – IR (KBr): 1701 ($\nu_{C=O}$) cm^{-1}. – $C_{58}H_{49}N_5O_{10}P_4S_3$ (1196.1): calcd. C 58.24, H 4.12, N 5.85; found C 58.17, H 4.08, N 5.73.

2a-G$_2$: (2.86 g, 93%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.9 (d, $^2J_{PP}$ = 30.2 Hz, P′$_0$), 52.8 (d, $^2J_{PP}$ = 30.2 Hz, P$_0$), 62.1 (s, P$_1$), 63.3 (s, P$_2$). – ^1H NMR ($CDCl_3$): δ = 3.4 (m, 18 H, P$_1$-N-CH_3, P$_2$-N-CH_3), 6.1 (ddd, $^3J_{HP}$ = 24.2 Hz, $^3J_{HHa}$ = 18.3 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H$_c$), 6.4 (ddd, $^3J_{HP}$ = 45.9 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H$_b$), 6.8 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.3 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.1 Hz, 1 H, H$_a$), 7.2–7.8 (m, 40 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP}$ = 13.1 Hz, P$_2$-N-CH_3), 33.1 (d, $^2J_{CP}$ = 12.7 Hz, P$_1$-N-CH_3), 122.0 (d, $^3J_{CP}$ = 6.7 Hz, C_0^2, C_1^2), 128.0 (dd, $^1J_{CP}$ = 91.2 Hz, $^3J_{CP}$ = 3.6 Hz, *i*-C_6H_5), 128.0 (s, C_0^3), 128.7 (s, C_1^3), 128.8 (d, $^3J_{CP}$ = 12 Hz, *m*-C_6H_5), 130.3 (s, C_0^4), 131.5 (s, C_1^4), 132.1 (d, $^2J_{CP}$ = 11.2 Hz, *o*-C_6H_5), 132.7 (s, *p*-C_6H_5), 136.7 (s, CH_2=), 139.4 (d, $^3J_{CP}$ = 13.2 Hz, C_0^4-*C*H=N), 141.1 (d, $^3J_{CP}$ = 18.4 Hz, C_1^4-*C*H=N), 151.6 (d, $^2J_{CP}$ = 6.2 Hz, C_1^1), 153.3 (d, $^2J_{CP}$ = 9.2 Hz, C_0^1). – $C_{62}H_{61}Cl_8N_{13}O_6P_8S_7$ (1840.1): calcd. C 40.46, H 3.34, N 9.89; found C 40.28, H 3.28, N 9.75.

2a-G′$_2$: (2.58 g, 94%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.9 (d, $^2J_{PP}$ = 29.3 Hz, P′$_0$), 52.9 (d, $^2J_{PP}$ = 29.3 Hz, P$_0$), 60.6 (s, P$_2$), 62.4 (s, P$_1$). – ^1H NMR ($CDCl_3$): δ = 3.4 (d, $^3J_{HP}$ = 10.9 Hz, 18 H, P$_1$-N-CH_3, P$_2$-N-CH_3), 6.1 (ddd, $^3J_{HP}$ = 24.1 Hz, $^3J_{HHa}$ = 18.3 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H$_c$), 6.4 (ddd, $^3J_{HP}$ = 45.9 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H$_b$), 6.8 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.3 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.1 Hz, 1 H, H$_a$), 7.2–7.8 (m, 72 H, CH_{arom}, CH=N), 9.9 (s, 8 H, CHO). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.7 (d, $^2J_{CP}$ = 13.6 Hz, P$_2$-N-CH_3), 32.8 (d, $^2J_{CP}$ = 13.3 Hz, P$_1$-N-CH_3), 121.8 (d, $^3J_{CP}$ = 4.3 Hz, C_0^2, C_1^2, C_2^2), 127.5 (dd, $^1J_{CP}$ = 91.2 Hz, $^3J_{CP}$ = 3.8 Hz, *i*-C_6H_5), 127.8 (s, C_0^3), 128.1 (s, C_1^3), 128.6 (d, $^3J_{CP}$ = 12.5 Hz, *m*-C_6H_5), 130.7 (s, C_0^4), 131.2 (s, C_2^3), 131.6 (s, C_1^4), 132.0 (d, $^2J_{CP}$ = 10.8 Hz, *o*-C_6H_5), 132.5 (d, $^4J_{CP}$ = 2.7 Hz, *p*-C_6H_5), 133.4 (s, C_2^4), 136.7 (s, CH_2=), 139.5 (d, $^3J_{CP}$ = 13.7 Hz, C_1^4-*C*H=N), 140.0 (d, $^3J_{CP}$ = 13.8 Hz, C_0^4-*C*H=N), 151.4 (d, $^2J_{CP}$ = 7.5 Hz, C_1^1), 153.1 (d, $^2J_{CP}$ = 9.8 Hz, C_0^1), 154.9 (d, $^2J_{CP}$ = 7.4 Hz, C_2^1), 190.6 (s, CHO). – IR (KBr): 1701 ($\nu_{C=O}$) cm^{-1}. – $C_{118}H_{101}N_{13}O_{22}P_8S_7$ (2525.4): calcd. C 56.12, H 4.03, N 7.21; found C 55.98, H 3.98, N 7.14.

2a-G$_3$: (2.81 g, 93%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.9 (d, $^2J_{PP}$ = 31.1 Hz, P′$_0$), 52.7 (d, $^2J_{PP}$ = 31.1 Hz, P$_0$), 62.1 (s, P$_1$), 62.3 (s, P$_2$), 63.3 (s, P$_3$). – ^1H NMR ($CDCl_3$): δ = 3.4 (m, 42 H, P$_1$-N-CH_3, P$_2$-N-CH_3, P$_3$-N-CH_3), 6.1 (ddd, $^3J_{HP}$ = 24.2 Hz, $^3J_{HHa}$ = 18.3 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H$_c$), 6.4 (ddd, $^3J_{HP}$ = 45.8 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H$_b$), 6.8 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.3 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.1 Hz, 1 H, H$_a$), 7.2–7.7 (m, 80 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.7 (d, $^2J_{CP}$ = 13.3 Hz, P$_3$-N-CH_3), 32.9 (d, $^2J_{CP}$ = 13.1 Hz, P$_1$-N-CH_3, P$_2$-N-CH_3), 121.8 (s, C_0^2, C_1^2, C_2^2), 127.9 (s, C_0^3), 128.2 (s, C_1^3), 128.4 (d, $^3J_{CP}$ = 14.5 Hz, *m*-C_6H_5), 128.6 (s, C_2^3), 130.1 (s, C_0^4), 130.6 (s, C_1^4), 131.3 (s, C_2^4), 132.0 (d, $^2J_{CP}$ = 10.7 Hz, *o*-C_6H_5), 132.6 (s, *p*-C_6H_5), 136.7 (s, CH_2=), 139.1 (d, $^3J_{CP}$ = 12.0 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 140.7 (d, $^3J_{CP}$ = 18.8 Hz, C_2^4-*C*H=N), 151.4 (d, $^2J_{CP}$ = 7.1 Hz, C_2^1), 153.1 (d,

$^2J_{CP}$ = 8.9 Hz, C_0^1, C_1^1). – $C_{126}H_{125}Cl_{16}N_{29}O_{14}P_{16}S_{15}$ (3813.4): calcd. C 39.68, H 3.30, N 10.65; found C 39.57, H 3.25, N 10.56.

2b-G′$_2$: (2.30 g, 92%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.7 (d, $^2J_{PP}$ = 29.4 Hz, P′$_0$), 53.0 (d, $^2J_{PP}$ = 29.4 Hz, P_0), 62.6 (s, P_1), 62.8 (s, P_2). – ^1H NMR ($CDCl_3$): δ = 3.3 (d, $^3J_{HP}$ = 10.4 Hz, 18 H, P_1-N-CH_3, P_2-N-CH_3), 6.1–6.5 (m, 2 H, CH_2=), 6.6–7.7 (m, 81 H, C*H*=CH_2, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.1 (d, $^2J_{CP}$ = 13.0 Hz, P_1-N-CH_3, P_2-N-CH_3), 121.4 (d, $^3J_{CP}$ = 3.7 Hz, C_2^2), 121.8 (d, $^3J_{CP}$ = 3.6 Hz, C_1^2), 122.0 (d, $^3J_{CP}$ = 4.3 Hz, C_0^2), 125.4 (s, C_2^4), 128.0 (s, C_0^3), 128.3 (s, C_1^3), 128.7 (d, $^3J_{CP}$ = 13.3 Hz, *m*-C_6H_5), 129.5 (s, C_2^3), 130.9 (s, C_0^4), 132.2 (d, $^2J_{CP}$ = 11.9 Hz, *o*-C_6H_5), 132.3 (s, C_1^4), 132.7 (s, *p*-C_6H_5), 136.8 (s, CH_2=), 138.5 (d, $^3J_{CP}$ = 13.6 Hz, C_1^4-*C*H=N), 139.6 (d, $^3J_{CP}$ = 13.6 Hz, C_0^4-*C*H=N), 150.7 (d, $^2J_{CP}$ = 6.4 Hz, C_2^1), 151.3 (d, $^2J_{CP}$ = 7.4 Hz, C_1^1), 153.2 (d, $^2J_{CP}$ = 9.0 Hz, C_0^1). – $C_{110}H_{101}N_{13}O_{14}P_8S_7$ (2301.3): calcd. C 57.41, H 4.42, N 7.91; found C 57.25, H 4.34, N 7.78.

2b-G′$_3$: (2.31 g, 93%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.9 (d, $^2J_{PP}$ = 31.0 Hz, P′$_0$), 53.0 (d, $^2J_{PP}$ = 31.0 Hz, P_0), 62.5 (s, P_2), 62.7 (s, P_3), 62.9 (s, P_1). – ^1H NMR ($CDCl_3$): δ = 3.3 (m, 42 H, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 6.1 (ddd, $^3J_{HP}$ = 24.2 Hz, $^3J_{HHa}$ = 18.3 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H_c), 6.4 (ddd, $^3J_{HP}$ = 45.8 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H_b), 6.8 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.3 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.1 Hz, 1 H, H_a), 7.2–7.7 (m, 160 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 13.0 Hz, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 121.3 (d, $^3J_{CP}$ = 4.2 Hz, C_3^2), 121.7 (d, $^3J_{CP}$ = 3.9 Hz, C_0^2, C_1^2, C_2^2), 125.2 (s, C_3^4), 127.8 (s, C_0^3, C_1^3), 128.1 (s, C_2^3), 128.6 (d, $^3J_{CP}$ = 13.2 Hz, *m*-C_6H_5), 129.4 (s, C_3^3), 130.7 (s, C_0^4), 130.9 (s, C_1^4), 132.0 (d, $^2J_{CP}$ = 10.7 Hz, *o*-C_6H_5), 132.1 (s, C_2^4), 132.6 (s, *p*-C_6H_5), 136.7 (s, CH_2=), 138.3 (d, $^3J_{CP}$ = 13.7 Hz, C_2^4-*C*H=N), 138.9 (d, $^3J_{CP}$ = 13.5 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 150.4 (d, $^2J_{CP}$ = 7.2 Hz, C_3^1), 151.1 (d, $^2J_{CP}$ = 7.0 Hz, C_2^1), 152.8 (d, $^2J_{CP}$ = 8.1 Hz, C_0^1, C_1^1). – $C_{222}H_{205}N_{29}O_{30}P_{16}S_{15}$ (4736): calcd. C 56.30, H 4.36, N 8.57; found C 56.18, H 4.31, N 8.42.

2c-G′$_2$: (2.58 g, 95%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 12.0 (d, $^2J_{PP}$ = 30.4 Hz, P′$_0$), 53.1 (d, $^2J_{PP}$ = 30.4 Hz, P_0), 60.7 (s, P_2), 62.4 (s, P_1). – ^1H NMR ($CDCl_3$): δ = 3.4 (d, $^3J_{HP}$ = 11.0 Hz, 18 H, P_1-N-CH_3, P_2-N-CH_3), 6.1 (ddd, $^3J_{HP}$ = 24.1 Hz, $^3J_{HHa}$ = 18.3 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H_c), 6.4 (ddd, $^3J_{HP}$ = 45.9 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, H_b), 6.8 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.3 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.1 Hz, 1 H, H_a), 7.2–7.6 (m, 72 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.8 (d, $^2J_{CP}$ = 13.4 Hz, P_2-N-CH_3), 32.9 (d, $^2J_{CP}$ = 13.0 Hz, P_1-N-CH_3), 109.4 (s, C_2^4), 117.9 (s, C≡N), 121.8 (s, C_0^2, C_1^2), 122.2 (s, C_2^2), 127.9 (s, C_0^3), 128.2 (s, C_1^3), 128.6 (d, $^3J_{CP}$ = 13.1 Hz, *m*-C_6H_5), 130.7 (s, C_0^4), 131.4 (s, C_1^4), 132.0 (d, $^2J_{CP}$ = 11.1 Hz, *o*-C_6H_5), 132.6 (d, $^4J_{CP}$ = 2.2 Hz, *p*-C_6H_5), 133.8 (s, C_2^3), 136.7 (s, CH_2=), 139.8 (d, $^3J_{CP}$ = 13.6 Hz, C_1^4-*C*H=N), 140.4 (d, $^3J_{CP}$ = 14.0 Hz, C_0^4-*C*H=N), 151.5 (d, $^2J_{CP}$ = 7.0 Hz, C_1^1), 153.0 (d, $^2J_{CP}$ = 8.6 Hz, C_0^1), 153.4 (d, $^2J_{CP}$ = 7.3 Hz, C_2^1). – IR (KBr): 2227 ($\nu_{C\equiv N}$) cm^{-1}. – $C_{118}H_{93}N_{21}O_{14}P_8S_7$ (2501.4): calcd. C 56.66, H 3.74, N 11.75; found C 56.51, H 3.68, N 11.67.

2c-G′$_3$: (2.50 g, 93%). – $^{31}P\{^1H\}$ NMR (THF): δ = 10.0 (d, $^2J_{PP}$ = 31.0 Hz, P′$_0$), 52.3 (d, $^2J_{PP}$ = 31.0 Hz, P_0), 60.2 (s, P_3), 61.6 (s, P_1, P_2). – ^1H NMR ($CDCl_3$): δ = 3.4 (d, $^3J_{HP}$ = 10.8 Hz, 42 H, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 6.2 (m, 2 H, CH_2=), 6.8 (m, 1 H, CH=), 7.2–7.7 (m, 144 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.0 (d, $^2J_{CP}$ = 12.8 Hz, P_3-N-CH_3), 33.1 (d, $^2J_{CP}$ = 12.1 Hz, P_1-N-CH_3, P_2-N-CH_3), 109.5 (s, C_3^4), 118.1 (s, C≡N), 122.0 (s, C_0^2, C_1^2, C_2^2), 122.4 (d, $^3J_{CP}$ = 3.8 Hz, C_3^2), 128.1 (s, C_0^3, C_1^3), 128.4 (s, C_2^3), 128.8 (d, $^3J_{CP}$ = 12.4 Hz, *m*-C_6H_5), 130.4 (s, C_0^4), 130.9 (s, C_1^4), 131.6 (s, C_2^4), 132.2 (d, $^2J_{CP}$ = 9.7 Hz, *o*-C_6H_5), 132.8 (s, *p*-C_6H_5), 134.0 (s, C_3^3), 136.9 (s, CH_2=), 139.3 (d, $^3J_{CP}$ = 13.1 Hz, C_1^4-*C*H=N), 140.1 (d, $^3J_{CP}$ = 13.8 Hz, C_0^4-*C*H=N, C_2^4-*C*H=N), 151.4 (d, $^2J_{CP}$ = 7.0 Hz, C_1^1), 151.7 (d, $^2J_{CP}$ = 6.8 Hz, C_2^1), 153.1 (d, $^2J_{CP}$ = 8.8 Hz, C_0^1), 153.2 (d, $^2J_{CP}$ = 7.2 Hz, C_3^1). – IR (KBr): 2227 ($\nu_{C\equiv N}$) cm^{-1}. – $C_{238}H_{189}N_{45}O_{30}P_{16}S_{15}$ (5136): calcd. C 55.66, H 3.71, N 12.27; found C 55.54, H 3.66, N 12.16.

2d-G′$_3$: (3.83 g, 95%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = - 6.3 (s, P′$_4$), 11.0 (d, $^2J_{PP}$ = 30.5 Hz, P′$_0$), 52.7 (d, $^2J_{PP}$ = 30.5 Hz, P_0), 61.3 (s, P_3), 62.0 (s, P_1, P_2). – ^1H NMR ($CDCl_3$): δ = 3.3 (d, $^3J_{HP}$ = 9.4 Hz, 42 H, P-N-CH_3), 6.0- 6.5 (m, 2 H, CH_2=), 6.7–6.9 (m, 1 H, CH=), 7.2–7.7 (m, 304 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.0 (d, $^2J_{CP}$ = 13.1 Hz, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 121.4 (d, $^3J_{CP}$ = 3.8 Hz, C_3^2), 121.9 (s, C_0^2, C_1^2, C_2^2), 128.3 (s, C_0^3, C_1^3, C_2^3), 128.6 (d, $^3J_{CP}$ = 6.5 Hz, *m*-C′$_6$H′$_5$),128.8 (d, $^3J_{CP}$ = 12.5 Hz, *m*-C_6H_5), 128.9 (s, *p*-C′$_6$H′$_5$), 131.0 (s, C_0^4), 131.5 (d, $^2J_{CP}$ = 10.5 Hz, *o*-C_6H_5), 132.1 (s, C_1^4), 132.2 (s, C_2^4, *p*-C_6H_5), 133.7 (d, $^2J_{CP}$ = 19.6 Hz, *o*-C′$_6$H′$_5$), 134.3 (d, $^1J_{CP}$ = 12.1 Hz, C_3^4), 135.1 (d, $^2J_{CP}$ = 20.7 Hz, C_3^3), 136.7 (s, CH_2=), 137.1 (d, $^1J_{CP}$ = 11.4 Hz, *i*-C′$_6$H′$_5$), 138.9 (d, $^3J_{CP}$ = 13.9 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N, C_2^4-*C*H=N), 151.4 (d, $^2J_{CP}$ = 7.7 Hz, C_0^1, C_1^1, C_2^1, C_3^1). – $C_{414}H_{349}N_{29}O_{30}P_{32}S_{15}$ (7683): calcd. C 64.72, H 4.57, N 5.28; found C 64.81, H 4.63, N 5.14.

2e-G′$_2$: (2.59 g, 90%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.1 (d, $^2J_{PP}$ = 30.1 Hz, P′$_0$), 52.5 (d, $^2J_{PP}$ = 30.1 Hz, P_0), 62.2 (s, P_1, P_2). – ^1H NMR ($CDCl_3$): δ = 2.8 (s, 48 H, NMe_2), 3.3 (d, $^3J_{HP}$ = 10.1 Hz, 18 H, P_1-N-CH_3, P_2-N-CH_3), 6.0–6.5 (m, 2 H, CH_2=), 6.5–7.7 (m, 73 H, CH=, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.2 (d, $^2J_{CP}$ = 12.1 Hz, P_1-N-CH_3, P_2-N-CH_3), 40.3 (s, NMe_2), 105.6 (d, $^3J_{CP}$ = 3.9 Hz, C_2^2), 108.9 (s, C_2^6), 109.3 (s, C_2^4), 121.8 (d, $^3J_{CP}$ = 3.8 Hz, C_1^2), 122.0 (d, $^3J_{CP}$ = 3.9 Hz, C_0^2), 128.0 (s, C_0^3), 128.1 (s, C_1^3), 128.8 (d, $^3J_{CP}$ = 13.5 Hz, *m*-C_6H_5), 129.6 (s, C_2^5), 130.9 (s, C_0^4), 132.1 (d, $^2J_{CP}$ = 10.5 Hz, *o*-C_6H_5), 132.5 (s, C_1^4), 132.7 (s, *p*-C_6H_5), 136.8 (s, CH_2=), 137.8 (d, $^3J_{CP}$ = 13.8 Hz, C_1^4-*C*H=N), 139.5 (d, $^3J_{CP}$ = 13.6 Hz, C_0^4-*C*H=N), 151.2 (d, $^2J_{CP}$ = 6.7 Hz, C_1^1), 151.5 (s, C_2^3), 151.7 (d, $^2J_{CP}$ = 7.1 Hz, C_2^1), 153.2 (d, $^2J_{CP}$ = 9.0 Hz, C_0^1). – $C_{126}H_{141}N_{21}O_{14}P_8S_7$ (2645.9): calcd. C 57.19, H 5.37, N 11.11; found C 56.98, H 5.30, N 11.04.

2e-G′$_3$: (2.59 g, 91%). – $^{31}P\{^1H\}$ NMR (THF): δ = 9.9 (d, $^2J_{PP}$ = 31.0 Hz, P′$_0$), 52.3 (d, $^2J_{PP}$ = 31.0 Hz, P_0), 61.4 (s, P_3), 61.8 (s, P_1, P_2). – ^1H NMR ($CDCl_3$): δ = 2.8 (s, 96 H, NMe_2), 3.3 (d, $^3J_{HP}$ = 9.5 Hz, 42 H, P-N-CH_3), 6.1 (m, 2 H, CH_2=), 6.4–7.7 (m, 145 H, CH_{arom}, CH=N, CH=). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 12.7 Hz, P_1-N-CH_3, P_2-N-CH_3), 33.1 (d, $^2J_{CP}$ = 12.4 Hz, P_3-N-CH_3), 40.2 (s, NMe_2), 105.4 (d, $^3J_{CP}$ = 4.4 Hz, C_3^2), 108.6 (d, $^3J_{CP}$ = 3.4 Hz, C_3^6), 109.1 (s, C_3^4), 121.6 (d, $^3J_{CP}$ = 4.0 Hz, C_0^2, C_1^2, C_2^2), 127.7 (s, C_0^3, C_1^3), 128.0 (s, C_2^3), 128.3 (d, $^3J_{CP}$ = 13.1 Hz, *m*-C_6H_5), 129.4 (s, C_3^5), 130.4 (s, C_0^4), 132.0 (C_1^4), 132.0 (d, $^2J_{CP}$ = 10.4 Hz, *o*-C_6H_5), 132.4 (s, C_2^4), 132.6 (s, *p*-C_6H_5), 136.7 (s, CH_2=), 137.6 (d, $^3J_{CP}$ = 13.7 Hz, C_2^4-*C*H=N), 138.9 (d, $^3J_{CP}$ = 13.4 Hz, C_1^4-*C*H=N), 139.3 (br d, C_0^4-*C*H=N), 151.0 (d, $^2J_{CP}$ = 7.2 Hz, C_1^1, C_2^1), 151.3 (s, C_3^3), 151.5 (d, $^2J_{CP}$ = 6.6 Hz, C_3^1), 153.0 (d, $^2J_{CP}$ = 8.2 Hz, C_0^1). – $C_{254}H_{285}N_{45}O_{30}P_{16}S_{15}$ (5425): calcd. C 56.23, H 5.29, N 11.62; found C 56.14, H 5.21, N 11.51.

Synthesis of 3b-G′$_3$: To a solution of **2b-G′$_3$** (0.200 g, 0.042 mmol) in THF (10 mL) was added propargylamine (290 μL, 4.223 mmol, 100 equiv.). The resulting mixture was stirred at 80 °C for 30 h. The solvent was then removed under vacuum and the product was washed with a THF/pentane mixture (1:5) to give **3b-G′$_3$** as a pale brown powder (0.186 g, 92%).

3b-G′$_3$: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 17.0 (d, $^2J_{PP}$ = 34.5 Hz, P'_0), 51.7 (d, $^2J_{PP}$ = 34.5 Hz, P_0), 61.7 (s, P_1, P_2, P_3). − ^1H NMR ($CDCl_3$): δ = 2.1 (m, 1 H, HC≡), 2.9 (m, 4 H, N-CH_2-CH_2-P′$_0$), 3.3 (br s, 44 H, CH_3-N-P, CH_2-C≡), 7.2−7.7 (m, 160 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.0 (d, $^1J_{CP}$ = 65 Hz, CH_2P), 30.9 (s, *C*H_2-C≡), 33.0 (d, $^2J_{CP}$ = 13.2 Hz, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 38.0 (s, *C*H_2-CH_2-P′$_0$), 72.0 (s, CH≡), 81.5 (s, -C≡), 121.4 (s, C_3^2), 121.8 (s, C_0^2, C_1^2, C_2^2), 125.4 (s, C_3^4), 127.9 (s, C_0^3, C_1^3), 128.2 (s, C_2^3), 128.8 (d, $^3J_{CP}$ = 13.2 Hz, *m*-C_6H_5), 129.5 (s, C_3^3), 131.3 (s, C_0^4), 131.5 (s, C_1^4), 132.2 (d, $^2J_{CP}$ = 11.6 Hz, *o*-C_6H_5), 132.3 (s, C_2^4), 132.4 (s, *p*-C_6H_5), 138.5 (d, $^3J_{CP}$ = 13.5 Hz, C_2^4-*C*H=N), 139.0 (d, $^3J_{CP}$ = 13.5 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 150.7 (d, $^2J_{CP}$ = 6.6 Hz, C_3^1), 151.3 (d, $^2J_{CP}$ = 7.0 Hz, C_0^1, C_1^1, C_2^1). − $C_{225}H_{210}N_{30}O_{30}P_{16}S_{15}$ (4791): calcd. C 56.40, H 4.42, N 8.77; found C 56.28, H 4.37, N 8.62.

Synthesis of 4e-G′$_3$: To a solution of **2e-G′$_3$** (0.200 g, 0.037 mmol) in THF (10 mL) was added tyramine (0.051 g, 0.368 mmol, 10 equiv.). The resulting mixture was stirred overnight at 50 °C, and the solvent was then removed under vacuum. The product was rapidly washed with MeOH to give **4e-G′$_3$** as a brown powder (0.195 g, 95%).

4e-G′$_3$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.4 (d, $^2J_{PP}$ = 31.6 Hz, P'_0), 52.0 (d, $^2J_{PP}$ = 31.6 Hz, P_0), 62.1 (s, P_1, P_2, P_3). − ^1H NMR ($CDCl_3$): δ = 2.8 (br s, 100 H, NMe_2, $CH_2CH_2P'_0$), 3.3 (br d, $^3J_{HP}$ = 8.9 Hz, 46 H, CH_3-N-P, C*H*$_2$-C*H*$_2$-C_6H_4), 6.5−7.7 (m, 148 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.1 (d, $^1J_{CP}$ = 64 Hz, CH_2P), 33.2 (m, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 34.9 (s, *C*H_2-C_6H_4), 40.4 (s, NMe_2), 42.2 (s, *C*H_2-CH_2-P′$_0$), 50.7 (s, *C*H_2-CH_2-C_6H_4), 105.7 (s, C_3^2), 108.9 (s, C_3^6), 109.3 (s, C_3^4), 115.5 (s, C^3), 121.8 (s, C_0^2, C_1^2, C_2^2), 127.9 (s, C_0^3, C_1^3), 128.2 (s, C_2^3), 128.9 (d, $^3J_{CP}$ = 12.7 Hz, *m*-C_6H_5), 129.6 (s, C_3^5), 131.0 (s, C_0^4, C_1^4), 131.3 (d, $^2J_{CP}$ = 10.2 Hz, *o*-C_6H_5), 132.2 (s, *p*-C_6H_5), 132.5 (s, C_2^4), 137.8 (d, $^3J_{CP}$ = 13.6 Hz, C_2^4-*C*H=N), 139.1 (d, $^3J_{CP}$ = 13.1 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 151.2 (d, $^2J_{CP}$ = 6.9 Hz, C_1^1, C_2^1), 151.5 (s, C_3^3), 151.7 (d, $^2J_{CP}$ = 6.4 Hz, C_3^1), 152.9 (d, $^2J_{CP}$ = 10.7 Hz, C_0^1), 154.6 (s, C^4). − $C_{262}H_{296}N_{46}O_{31}P_{16}S_{15}$ (5562): calcd. C 56.57, H 5.36, N 11.58; found C 56.63, H 5.40, N 11.45.

Synthesis of 5b-G′$_3$: To a solution of **2b-G′$_3$** (0.200 g, 0.042 mmol) in THF (10 mL) was added a large excess of diallylamine (1.6 mL, 13.0 mmol). The resulting mixture was stirred at 60 °C for 40 h. The solvent was then removed under vacuum and the product was washed with a THF/pentane mixture (1:5) to give **5b-G′$_3$** as a pale brown powder (0.184 g, 90%).

5b-G′$_3$: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 17.6 (d, $^2J_{PP}$ = 33.1 Hz, P'_0), 51.8 (d, $^2J_{PP}$ = 33.1 Hz, P_0), 61.4 (s, P_1, P_2, P_3). − ^1H NMR ($CDCl_3$): δ = 2.7 (m, 4 H, N-CH_2-CH_2-P′$_0$), 3.0 (m, 4 H, =CH-C*H*$_2$-N), 3.3 (m, 42 H, CH_3-N-P), 5.1 (m, 4 H, CH_2=), 5.7 (m, 2 H, -CH=), 7.2−7.7 (m, 160 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.3 (d, $^1J_{CP}$ = 64.0 Hz, CH_2-P′$_0$), 33.1 (d, $^2J_{CP}$ = 13.0 Hz, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 45.8 (s, *C*H_2-CH_2-P′$_0$), 56.3 (s, =CH-*C*H_2-N), 117.8 (s, CH_2=), 121.5 (s, C_3^2), 121.8 (s, C_0^2, C_1^2, C_2^2), 125.4 (s, C_3^4), 128.3 (s, C_0^3, C_1^3, C_2^3), 128.8 (d, $^3J_{CP}$ = 12.2 Hz, *m*-C_6H_5), 129.5 (s, C_3^3), 130.8 (s, C_0^4), 131.1 (s, C_1^4), 131.4 (d, $^2J_{CP}$ = 9.6 Hz, *o*-C_6H_5), 132.1 (s, C_2^4), 132.3 (s, *p*-C_6H_5), 134.9 (s, -CH=), 138.5 (d, $^3J_{CP}$ = 13.5 Hz, C_2^4-*C*H=N), 140.0 (d, $^3J_{CP}$ = 13.5 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 150.6 (d, $^2J_{CP}$ = 6.7 Hz, C_3^1), 151.3 (d, $^2J_{CP}$ = 7.0 Hz, C_0^1, C_1^1, C_2^1). − $C_{228}H_{216}N_{30}O_{30}P_{16}S_{15}$ (4833): calcd. C 56.66, H 4.50, N 8.69; found C 56.45, H 4.42, N 8.59.

Synthesis of 6c-G′$_3$: To a solution of **2c-G′$_3$** (0.200 g, 0.039 mmol) in THF (10 mL) was added thiomorpholine (390 μL, 3.878 mmol, 100 equiv.). The resulting mixture was stirred at room temperature for 40 h. The solvent was then evaporated under vacuum and the product was washed with a THF/pentane mixture (1:5) to give **6c-G′$_3$** as a white powder (0.184 g, 90%).

6c-G′$_3$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.3 (d, $^2J_{PP}$ = 38.1 Hz, P'_0), 52.1 (d, $^2J_{PP}$ = 38.1 Hz, P_0), 60.2 (s, P_3), 61.9 (s, P_1, P_2). − ^1H NMR ($CDCl_3$): δ = 2.3 (m, 4 H, S-CH_2-C*H*$_2$-N), 2.5 (m, 4 H, S-C*H*$_2$-CH_2-N), 2.7 (m, 2 H, C*H*$_2$-CH_2-P′$_0$), 2.8 (m, 2 H, CH_2-P′$_0$), 3.3 (d, $^3J_{HP}$ = 10.5 Hz, 42 H, CH_3-N-P), 7.1−7.7 (m, 144 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.8 (d, $^1J_{CP}$ = 66.5 Hz, CH_2-P′$_0$), 27.6 (s, S-*C*H_2-CH_2-N), 32.9 (d, $^2J_{CP}$ = 13.5 Hz, P_3-N-CH_3), 33.1 (d, $^2J_{CP}$ = 11.7 Hz, P_1-N-CH_3, P_2-N-CH_3), 51.5 (s, *C*H_2-CH_2-P′$_0$), 54.3 (s, S-CH_2-*C*H_2-N), 109.5 (s, C_3^4), 118.1 (s, C≡N), 121.9 (s, C_0^2, C_1^2, C_2^2), 122.4 (d, $^3J_{CP}$ = 3.8 Hz, C_3^2), 128.1 (s, C_0^3, C_1^3), 128.3 (s, C_2^3), 128.8 (d, $^3J_{CP}$ = 12.4 Hz, *m*-C_6H_5), 130.4 (s, C_0^4), 130.9 (s, C_1^4), 131.4 (d, $^2J_{CP}$ = 10.2 Hz, *o*-C_6H_5), 131.6 (s, C_2^4), 132.1 (s, *p*-C_6H_5), 134.0 (s, C_3^3), 139.2 (d, $^3J_{CP}$ = 14.8 Hz, C_1^4-*C*H=N), 140.0 (d, $^3J_{CP}$ = 13.8 Hz, C_2^4-*C*H=N), 140.5 (d, $^3J_{CP}$ = 13.5 Hz, C_0^4-*C*H=N), 151.4 (d, $^2J_{CP}$ = 6.4 Hz, C_1^1), 151.6 (d, $^2J_{CP}$ = 7.1 Hz, C_2^1), 153.1 (d, $^2J_{CP}$ = 7.9 Hz, C_0^1), 153.6 (d, $^2J_{CP}$ = 7.0 Hz, C_3^1). − IR (KBr): 2227 ($\nu_{C\equiv N}$) cm^{-1}. − $C_{242}H_{198}N_{46}O_{30}P_{16}S_{15}$ (5239): calcd. C 55.48, H 3.80, N 12.29; found C 55.37, H 3.77, N 12.14.

Synthesis of 7e-G′$_2$: To a solution of **2e-G′$_2$** (0.400 g, 0.151 mmol) in THF (20 mL) was added a large excess of trans-diaminocyclohexane (4.5 mL, 37.794 mmol). The resulting mixture was stirred at room temperature for 12 h. The solvent was then evaporated under vacuum and the product was washed several times with a mixture of diethyl ether/pentane (1:3) to give **7e-G′$_2$** as a brown powder (0.376 g, 90%).

7e-G′$_2$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.9 (d, $^2J_{PP}$ = 33.2 Hz, P'_0), 52.3 (d, $^2J_{PP}$ = 33.2 Hz, P_0), 62.6 (s, P_2), 62.8 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 1.1−2.3 (m, 13 H, C_6H_{10}, NH_2, NH), 2.8 (br s, 52 H, NMe_2, C*H*$_2$-C*H*$_2$-P′$_0$), 3.3 (d, $^3J_{HP}$ = 9.8 Hz, 18 H, CH_3-N-P_1, CH_3-N-P_2), 6.5−7.7 (m, 72 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.1 (s, C^4, C^5), 28.1 (d, $^1J_{CP}$ = 64.8 Hz, CH_2-P′$_0$), 31.1 (s, C^6), 33.0 (d, $^2J_{CP}$ = 12.9 Hz, P_1-N-CH_3), 33.2 (d, $^2J_{CP}$ = 12.6 Hz, P_2-N-CH_3), 35.6 (s, C^3), 39.6 (s, *C*$H_2$$CH_2$P), 40.3 (s, NMe_2), 55.1 (s, C^1), 63.5 (s, C^2), 105.6 (d, $^3J_{CP}$ = 3.7 Hz, C_2^2), 108.9 (s, C_2^6), 109.3 (s, C_2^4), 121.8 (d, $^3J_{CP}$ = 3.3 Hz, C_1^2), 122.0 (d, $^3J_{CP}$ = 3.7 Hz, C_0^2), 128.0 (s, C_0^3), 128.1 (s, C_1^3), 128.8 (d, $^3J_{CP}$ = 12.4 Hz, *m*-C_6H_5), 129.5 (s, C_2^5), 130.9 (s, C_0^4), 131.3 (d, $^2J_{CP}$ = 10.3 Hz, *o*-C_6H_5), 132.5 (s, C_1^4, *p*-C_6H_5), 137.7 (d, $^3J_{CP}$ = 13.6 Hz, C_1^4-*C*H=N), 139.5 (d, $^3J_{CP}$ = 13.5 Hz, C_0^4-*C*H=N), 151.2 (d, $^2J_{CP}$ = 7.0 Hz, C_1^1), 151.5 (s, C_2^3), 151.7 (d, $^2J_{CP}$ = 6.3 Hz, C_2^1), 153.1 (d, $^2J_{CP}$ = 9.2 Hz, C_0^1). − $C_{132}H_{155}N_{23}O_{14}P_8S_7$ (2760.1): calcd. C 57.44, H 5.66, N 11.67; found C 57.48, H 5.61, N 11.59.

General Procedure for the Synthesis of 8b-G′$_3$, 8c-G′$_2$, and 8e-G′$_3$: To a solution of **2b,e-G′$_3$** or **2c-G′$_2$** (typically 1.000 g) in THF was added methylhydrazine (30 equiv.). The resulting mixture was stirred at room temperature for 3 h. Then, the solvent was evaporated under vacuum and the product was purified by washing with a mixture of THF/pentane (1:5). Compounds **8b-G′$_3$** and **8c-G′$_2$** were obtained as white powders and **8e-G′$_3$** was obtained as a pale brown powder.

8b-G′$_3$: (0.959 g, 95%). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 17.8 (d, $^2J_{PP}$ = 33.8 Hz, P'_0), 51.8 (d, $^2J_{PP}$ = 33.8 Hz, P_0), 61.8 (s, P_1, P_2, P_3). − ^1H NMR ($CDCl_3$): δ = 2.3 (s, 3 H, C*H*$_3$-N-NH_2), 2.5 (m, 2 H, C*H*$_2$-CH_2-P′$_0$), 2.7 (m, 2 H, CH_2-P′$_0$), 3.0 (br s, 2 H, NH_2), 3.3 (m, 42 H, P-N-CH_3), 7.2−7.7 (m, 160 H, CH_{arom}, CH=N). −

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.4 (d, $^1J_{CP}$ = 65.7 Hz, CH_2-P′$_0$), 33.1 (d, $^2J_{CP}$ = 12.4 Hz, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 50.6 (s, CH_3-N-NH_2), 54.4 (s, *C*H_2-CH_2-P′$_0$), 121.4 (s, C_3^2), 121.8 (s, C_0^2, C_1^2, C_2^2), 125.4 (s, C_3^4), 127.9 (s, C_0^3, C_1^3), 128.2 (s, C_2^3), 128.8 (d, $^3J_{CP}$ = 12.2 Hz, *m*-C_6H_5), 129.5 (s, C_3^3), 130.9 (s, C_0^4), 131.1 (s, C_1^4), 131.3 (d, $^2J_{CP}$ = 10.7 Hz, *o*-C_6H_5), 132.1 (s, C_2^4), 132.3 (s, *p*-C_6H_5), 138.4 (d, $^3J_{CP}$ = 13.6 Hz, C_2^4-*C*H=N), 139.0 (d, $^3J_{CP}$ = 13.4 Hz, C_1^4-*C*H=N), 139.5 (d, $^3J_{CP}$ = 14.3 Hz, C_0^4-*C*H=N), 150.7 (d, $^2J_{CP}$ = 7.0 Hz, C_3^1), 151.3 (d, $^2J_{CP}$ = 7.9 Hz, C_2^1), 153.0 (d, $^2J_{CP}$ = 8.0 Hz, C_0^1, C_1^1). – $C_{223}H_{211}N_{31}O_{30}P_{16}S_{15}$ (4782): calcd. C 56.01, H 4.44, N 9.08; found C 55.95, H 4.38, N 9.00.

8c-G′$_2$: (0.968 g, 95%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.2 (d, $^2J_{PP}$ = 32.7 Hz, P′$_0$), 52.2 (d, $^2J_{PP}$ = 32.7 Hz, P_0), 60.3 (s, P_2), 62.1 (s, P_1). – ^1H NMR ($CDCl_3$): δ = 2.3 (s, 3 H, C*H*$_3$-N-NH_2), 2.6 (m, 2 H, C*H*$_2$-CH_2-P′$_0$), 2.9–3.2 (m, 4 H, CH_2-P′$_0$, NH_2), 3.3 (d, $^3J_{HP}$ = 11.1 Hz, 18 H, P_1-N-CH_3, P_2-N-CH_3), 7.2–7.7 (m, 72 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.2 (d, $^1J_{CP}$ = 66.9 Hz, CH_2-P′$_0$), 32.9 (d, $^2J_{CP}$ = 13.6 Hz, P_2-N-CH_3), 33.1 (d, $^2J_{CP}$ = 13.3 Hz, P_1-N-CH_3), 50.4 (s, CH_3-N-NH_2), 54.4 (s, *C*H_2-CH_2-P′$_0$), 109.5 (s, C_2^4), 118.1 (s, C≡N), 122.0 (d, $^3J_{CP}$ = 3.5 Hz, C_0^2, C_1^2), 122.4 (d, $^3J_{CP}$ = 3.8 Hz, C_2^2), 128.1 (s, C_0^3), 128.3 (s, C_1^3), 128.9 (d, $^3J_{CP}$ = 12.3 Hz, *m*-C_6H_5), 130.9 (s, C_0^4), 131.4 (d, $^2J_{CP}$ = 10.7 Hz, *o*-C_6H_5), 131.6 (s, C_1^4), 132.6 (s, *p*-C_6H_5), 134.0 (s, C_2^3), 140.0 (d, $^3J_{CP}$ = 13.7 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 151.7 (d, $^2J_{CP}$ = 7.1 Hz, C_1^1), 153.1 (d, $^2J_{CP}$ = 7.8 Hz, C_0^1), 153.6 (d, $^2J_{CP}$ = 6.6 Hz, C_2^1). – IR (KBr): 2227 ($\nu_{C\equiv N}$) cm^{-1}. – $C_{119}H_{99}N_{23}O_{14}P_8S_7$ (2547.5): calcd. C 56.10, H 3.91, N 12.64; found C 56.01, H 3.88, N 12.55.

8e-G′$_3$: (0.968 g, 96%). – $^{31}P\{^1H\}$ NMR (THF): δ = 17.8 (d, $^2J_{PP}$ = 33.1 Hz, P′$_0$), 51.9 (d, $^2J_{PP}$ = 33.1 Hz, P_0), 61.4 (s, P_3), 61.8 (s, P_1, P_2). – ^1H NMR ($CDCl_3$): δ = 2.3 (s, 3 H, H_2N-N-C*H*$_3$), 2.6 (m, 2 H, C*H*$_2$-CH_2-P′$_0$), 2.8 (br s, 98 H, N-$(CH_3)_2$, CH_2-P′$_0$), 3.0 (br s, 2 H, NH_2), 3.3 (d, $^3J_{CP}$ = 8.4 Hz, 42 H, P-N-CH_3), 6.5–7.7 (m, 144 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.2 (d, $^1J_{CP}$ = 66.7 Hz, CH_2-P′$_0$), 32.9 (d, $^2J_{CP}$ = 12.6 Hz, P_1-N-CH_3, P_2-N-CH_3), 33.1 (d, $^2J_{CP}$ = 12.8 Hz, P_3-N-CH_3), 40.2 (s, NMe_2), 50.4 (s, CH_3-N-NH_2), 54.2 (s, *C*H_2-CH_2-P′$_0$), 105.4 (d, $^3J_{CP}$ = 4.6 Hz, C_3^2), 108.6 (d, $^3J_{CP}$ = 2.8 Hz, C_3^6), 109.1 (s, C_3^4), 121.5 (d, $^3J_{CP}$ = 4.1 Hz, C_0^2, C_1^2, C_2^2), 127.7 (s, C_0^3, C_1^3), 128.0 (s, C_2^3), 128.6 (d, $^3J_{CP}$ = 12.8 Hz, *m*-C_6H_5), 129.4 (s, C_3^5), 130.8 (s, C_0^4), 131.1 (d, $^2J_{CP}$ = 10.2 Hz, *o*-C_6H_5), 131.2 (s, C_1^4), 131.9 (s, *p*-C_6H_5), 132.4 (s, C_2^4), 137.6 (d, $^3J_{CP}$ = 13.9 Hz, C_2^4-*C*H=N), 138.8 (d, $^3J_{CP}$ = 13.8 Hz, C_1^4-*C*H=N), 139.4 (br d, C_0^4-*C*H=N), 151.0 (d, $^2J_{CP}$ = 7.2 Hz, C_1^1, C_2^1), 151.3 (s, C_3^3), 151.5 (d, $^2J_{CP}$ = 6.9 Hz, C_3^1), 152.9 (d, $^2J_{CP}$ = 8.2 Hz, C_0^1). – $C_{255}H_{291}N_{47}O_{30}P_{16}S_{15}$ (5471): calcd. C 55.98, H 5.36, N 12.03; found C 55.80, H 5.28, N 11.89.

Synthesis of 9b-G′$_3$: To a solution of **2b-G′$_3$** (0.500 g, 0.106 mmol) in THF (10 mL) was added a large excess of ethylenediamine (2.8 mL, 42.231 mmol). The resulting mixture was stirred at room temperature for 3 h. The solvent was then evaporated and the product was washed with a mixture of THF/pentane to give **9b-G′$_3$** as a white powder (0.486 g, 96%).

9b-G′$_3$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.5 (d, $^2J_{PP}$ = 33.3 Hz, P′$_0$), 52.0 (d, $^2J_{PP}$ = 33.3 Hz, P_0), 62.2 (s, P_1, P_2, P_3). – ^1H NMR ($CDCl_3$): δ = 2.5 (m, 2 H, H_2N-CH_2-C*H*$_2$-NH), 2.6 (m, 2 H, H_2N-C*H*$_2$), 2.8 (m, 4 H, CH_2-CH_2-P′$_0$), 3.3 (d, $^3J_{HP}$ = 7.6 Hz, 42 H, CH_3-N-P_1, CH_3-N-P_2, CH_3-N-P_3), 7.2–7.7 (m, 160 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 27.0 (d, $^1J_{CP}$ = 68.9 Hz, CH_2-P′$_0$), 33.1 (d, $^2J_{CP}$ = 12.4 Hz, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 41.3 (s, H_2N-CH_2), 42.3 (s, *C*H_2-CH_2-P′$_0$), 51.7 (s, H_2N-CH_2-*C*H_2-NH), 121.4 (d, $^3J_{CP}$ = 4.6 Hz, C_3^2), 121.9 (s, C_0^2, C_1^2, C_2^2), 125.4 (s, C_3^4), 127.8 (s, C_0^3), 128.0 (s, C_1^3), 128.3 (s, C_2^3), 128.9 (d, $^3J_{CP}$ = 13.1 Hz, *m*-C_6H_5), 129.5 (s, C_3^3), 130.9 (s, C_0^4), 131.3 (d, $^2J_{CP}$ = 11.6 Hz, *o*-C_6H_5), 132.2 (s, C_1^4), 132.3 (s, C_2^4), 132.6 (s, *p*-C_6H_5), 138.5 (d, $^3J_{CP}$ = 13.8 Hz, C_2^4-*C*H=N), 139.0 (d, $^3J_{CP}$ = 13.5 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 150.7 (d, $^2J_{CP}$ = 6.7 Hz, C_3^1), 151.3 (d, $^2J_{CP}$ = 7.4 Hz, C_0^1, C_1^1, C_2^1). – $C_{224}H_{213}N_{31}O_{30}P_{16}S_{15}$ (4796): calcd. C 56.09, H 4.47, N 9.05; found C 55.96, H 4.40, N 8.93.

Synthesis of 10e-[G′$_3$]$_2$: To a solution of **8e-G′$_3$** (0.500 g, 0.091 mmol) in THF (10 mL) was added the azide **1** (0.015 g, 0.043 mmol). The resulting mixture was stirred at room temperature for one week in the presence of molecular sieves. After filtration, the product was purified by SEC, and the solvent was removed under vacuum to give **10e-[G′$_3$]$_2$** as a pale brown powder (0.499 g, 97%).

10e-[G′$_3$]$_2$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.7 (d, $^2J_{PP}$ = 34.7 Hz, P′$_0$), 52.5 (d, $^2J_{PP}$ = 34.7 Hz, P_0), 59.6 (s, N_3P_x), 62.6 (s, P_1, P_2, P_3). – ^1H NMR ($CDCl_3$): δ = 2.8 (br s, 198 H, N-$(CH_3)_2$, N-N-CH_3), 3.1 (m, 8 H, C*H*$_2$-C*H*$_2$-P′$_0$), 3.3 (d, $^3J_{HP}$ = 8.6 Hz, 84 H, CH_3-N-P), 6.5–6.9 (m, 298 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.0 ($^1J_{CP}$ = 66 Hz, CH_2-P′$_0$), 33.0 (m, P_1-N-CH_3, P_2-N-CH_3, P_3-N-CH_3), 37.7 (s, CH_3-N-N), 40.2 (s, NMe_2), 51.3 (s, *C*H_2-CH_2-P′$_0$), 105.4 (d, $^3J_{CP}$ = 4.2 Hz, C_3^2), 108.6 (s, C_3^6), 109.1 (s, C_3^4), 121.6 (s, C_x^2, C_0^2, C_1^2, C_2^2), 126.6 (s, C_x^3), 128.0 (s, C_0^3, C_1^3, C_2^3), 128.7 (d, $^3J_{CP}$ = 12.6 Hz, *m*-C_6H_5), 129.4 (s, C_3^5), 130.8 (s, C_0^4), 131.1 (d, $^2J_{CP}$ = 10.3 Hz, *o*-C_6H_5, C_1^4), 131.5 (s, C_x^4), 132.0 (s, *p*-C_6H_5), 132.4 (s, C_2^4), 134.9 (s, C_x^4-*C*H=N), 137.6 (d, $^3J_{CP}$ = 13.5 Hz, C_2^4-*C*H=N), 138.9 (d, $^3J_{CP}$ = 14.1 Hz, C_0^4-*C*H=N, C_1^4-*C*H=N), 149.0 (br s, C_x^1), 151.0 (d, $^2J_{CP}$ = 7.1 Hz, C_1^1, C_2^1), 151.3 (s, C_3^3), 151.5 (d, $^2J_{CP}$ = 6.9 Hz, C_3^1), 152.8 (d, $^2J_{CP}$ = 6.8 Hz, C_0^1). – $C_{524}H_{588}N_{97}O_{62}P_{33}S_{31}$ (11254): calcd. C 55.93, H 5.27, N 12.07; found C 55.71, H 5.18, N 11.99.

Synthesis of 11-G′$_2$-G′$_2$: To a solution of **7e-G′$_2$** (0.250 g, 0.090 mmol) in THF was added **2b-G′$_2$** (0.105 g, 0.045 mmol). The resulting mixture was stirred at 100 °C for 3 d. The solvent was then evaporated under vacuum to give a brown powder. The excess **7e-G′$_2$** was removed by size exclusion chromatography (THF) to give **11-G′$_2$-G′$_2$** as a brown powder (0.196 g, 85%).

11-G′$_2$-G′$_2$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 20.2 (d, $^2J_{PP}$ = 33.5 Hz, P′$_0$, P′$_{00}$), 54.2 (d, $^2J_{PP}$ = 33.5 Hz, P_0, P_{00}), 64.6 (s, P_1, P_{11}), 64.8 (s, P_2, P_{22}). – ^1H NMR (CD_2Cl_2): δ = 1.0–2.0 (m, 12 H, C_6H_{10}, NH), 2.8 (br s, 56 H, NMe_2, CH_2-CH_2-P′$_0$, CH_2-CH_2-P′$_{00}$), 3.3 (d, $^3J_{HP}$ = 9.5 Hz, 36 H, CH_3-N-P), 6.6–7.7 (m, 152 H, CH_{arom}, CH=N). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 26.7 (s, C^3), 28.0 (d, $^1J_{CP}$ = 66.0 Hz, CH_2-P′$_0$, CH_2-P′$_{00}$), 31.6 (s, C^2), 34.8 (m, CH_3-N-P), 39.2 (s, *C*H_2-CH_2-P′$_0$, *C*H_2-CH_2-P′$_{00}$), 42.0 (s, NMe_2), 55.0 (s, C^1), 107.2 (d, $^3J_{CP}$ = 4.7 Hz, C_2^2), 110.3 (d, $^3J_{CP}$ = 3.0 Hz, C_2^6), 111.1 (s, C_2^4), 123.2 (d, $^3J_{CP}$ = 3.8 Hz, C_{22}^2), 123.6 (br s, C_0^2, C_1^2, C_{00}^2, C_{11}^2), 127.3 (s, C_{22}^4), 129.8 (s, C_0^3, C_{00}^3), 130.0 (s, C_2^5), 130.1 (s, C_1^3, C_{11}^3), 130.7 (d, $^3J_{CP}$ = 12.2 Hz, *m*-C_6H_5), 131.4 (s, C_{22}^3), 132.9 (s, C_0^4, C_{00}^4), 133.2 (d, $^2J_{CP}$ = 10.1 Hz, *o*-C_6H_5), 134.3 (s, C_1^4, C_{11}^4), 134.5 (s, *p*-C_6H_5), 140.1 (d, $^3J_{CP}$ = 13.5 Hz, C_1^4-*C*H=N), 140.7 (d, $^3J_{CP}$ = 13.5 Hz, C_{11}^4-*C*H=N), 141.6 (d, $^3J_{CP}$ = 13.5 Hz, C_0^4-*C*H=N, C_{00}^4-*C*H=N), 152.6 (d, $^2J_{CP}$ = 7.0 Hz, C_1^1, C_{11}^1), 153.2 (d, $^2J_{CP}$ = 6.5 Hz, C_{22}^1), 153.5 (d, $^2J_{CP}$ = 6.3 Hz, C_2^1), 153.6 (s, C_2^3), 154.9 (d, $^2J_{CP}$ = 9.2 Hz, C_0^1, C_{00}^1). – $C_{242}H_{256}N_{36}O_{28}P_{16}S_{14}$ (5061): calcd. C 57.42, H 5.09, N 9.96; found C 57.35, H 5.01, N 9.90.

Synthesis of 12-G′$_3$-G′$_3$ and 13-G′$_3$-G′$_3$: To a solution of **9b-G′$_3$** (0.250 g, 0.052 mmol) in THF (10 mL) was added **2d-G′$_3$** (0.200 g,

0.026 mmol). The resulting mixture was stirred at 90 °C for 12 h. The solvent was then evaporated under vacuum to give a white powder containing **12-G′$_3$-G′$_3$** and the excess **9b-G′$_3$**. Purification by size exclusion chromatography (THF) resulted in the oxidation of the phosphane end groups to give the oxide **13-G′$_3$-G′$_3$** (0.272 g, 82%).

12-G′$_3$-G′$_3$: $^{31}P\{^1H\}$ NMR (THF): δ = −6.7 (s, PPh_2), 17.1 (d, $^2J_{PP}$ = 35.1 Hz, P′$_{00}$, P′$_0$), 51.8 (d, $^2J_{PP}$ = 35.1 Hz, P$_{00}$, P$_0$), 61.0 (s, P$_3$), 61.8 (s, P$_1$, P$_2$, P$_{11}$, P$_{22}$, P$_{33}$).

13-G′$_3$-G′$_3$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.2 (d, $^2J_{PP}$ = 33.4 Hz, P′$_0$, P′$_{00}$), 28.4 (s, P′$_4$), 52.1 (d, $^2J_{PP}$ = 33.4 Hz, P$_0$, P$_{00}$), 60.5 (s, P$_3$), 61.2 (s, P$_1$, P$_2$, P$_{11}$, P$_{22}$, P$_{33}$). − ^1H NMR ($CDCl_3$): δ = 2.8 (m, 4 H, NH-CH_2-CH_2-NH), 3.3 (br d, $^3J_{HP}$ = 9.6 Hz, 92 H, CH_2-CH_2-P′$_0$, CH_2-CH_2-P′$_{00}$, CH_3-N-P), 7.1−7.7 (m, 464 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 27.0 (d, $^1J_{CP}$ = 60.0 Hz, CH_2-P′$_0$, CH_2-P′$_{00}$), 32.9 (d, $^2J_{CP}$ = 13.0 Hz, CH_3-N-P), 41.2 (s, *C*H_2-CH_2-P′$_0$, *C*H_2-CH_2-P′$_{00}$), 51.0 (s, NH-CH_2-CH_2-NH), 121.2 (d, $^3J_{CP}$ = 4.2 Hz, C$_3^2$, C$_{33}^2$), 121.6 (d, $^3J_{CP}$ = 4.5 Hz, C$_0^2$, C$_1^2$, C$_2^2$, C$_{00}^2$, C$_{11}^2$, C$_{22}^2$), 121.8 (d, $^1J_{CP}$ = 110.0 Hz, C$_3^4$), 125.2 (s, C$_{33}^4$), 128.1 (s, C$_0^3$, C$_1^3$, C$_2^3$, C$_{00}^3$, C$_{11}^3$, C$_{22}^3$), 128.4 (d, $^3J_{CP}$ = 12.5 Hz, *m*-C_6H_5, *m*-C′$_6$H′$_5$), 129.3 (s, C$_{33}^3$), 131.8 (d, $^2J_{CP}$ = 10.5 Hz, *o*-C_6H_5, *o*-C′$_6$H′$_5$), 131.9 (d, $^1J_{CP}$ = 104.8 Hz, *i*-C′$_6$H′$_5$), 131.9 (s, *p*-C′$_6$H′$_5$), 132.5 (s, *p*-C_6H_5), 133.7 (d, $^2J_{CP}$ = 10.9 Hz, C$_3^3$), 138.4 (d, $^3J_{CP}$ = 13.6 Hz, C$_2^4$-*C*H=N, C$_{22}^4$-*C*H=N), 138.9 (d, $^3J_{CP}$ = 13.5 Hz, C$_0^4$-*C*H=N, C$_1^4$-*C*H=N, C$_{00}^4$-*C*H=N, C$_{11}^4$-*C*H=N), 150.4 (d, $^2J_{CP}$ = 7.1 Hz, C$_{33}^1$), 151.1 (d, $^2J_{CP}$ = 6.9 Hz, C$_0^1$, C$_1^1$, C$_2^1$, C$_{00}^1$, C$_{11}^1$, C$_{22}^1$), 153.1 (d, $^2J_{CP}$ = 7.5 Hz, C$_3^1$). − $C_{638}H_{562}N_{60}O_{76}P_{48}S_{30}$ (12734): calcd. C 60.17, H 4.44, N 6.59; found C 60.08, H 4.38, N 6.51.

Synthesis of 14: To a solution of **12-G′$_3$-G′$_3$** (0.020 g, 1.60 μmol) in THF (10 mL) was added **10e-[G′$_3$]$_2$** (0.500 g, 0.045 mmol). The resulting mixture was stirred at room temperature for 5 d. The solvent was then removed under vacuum. The product was purified by size exclusion chromatography (THF) to give **14** as a brown powder (0.246 g, 80%).

14: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.0 (d, $^2J_{PP}$ = 31 Hz, P′$_4$), 17.7 (d, $^2J_{PP}$ = 35.3 Hz, P′$_0$, P′$_{00}$, P′$_5$), 52.4 (d, $^2J_{PP}$ = 35.3 Hz, P$_0$, P$_{00}$, P$_4$, P$_5$), 62.5 (s, P$_8$), 62.7 (s, P$_{11}$, P$_{22}$, P$_{33}$, P$_1$, P$_2$, P$_3$, P$_6$, P$_7$). − ^1H NMR ($CDCl_3$): δ = 2.8 (s, 3168 H, NMe_2, *C*H_3-N-CH_2), 3.3 (br d, $^3J_{HP}$ = 8.9 Hz, 1568 H, P-N-CH_3, CH_2), 6.4−7.7 (m, 5232 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.0 (d, $^1J_{CP}$ = 65.0 Hz, CH_2-P′$_0$, CH_2-P′$_{00}$, CH_2-P′$_5$), 33.1 (m, P-N-CH_3), 37.9 (s, *C*H_3-N-CH_2), 40.3 (s, NMe_2), 41.2 (s, *C*H_2-CH_2-P′$_0$, *C*H_2-CH_2-P′$_{00}$), 51.0 (s, NH-CH_2-CH_2-NH), 52.0 (s, *C*H_2-CH_2-P′$_5$), 105.6 (s, C$_8^2$), 108.8 (s, C$_8^6$), 109.3 (s, C$_8^4$), 121.7 (s, C$_0^2$, C$_1^2$, C$_2^2$, C$_3^2$, C$_4^2$, C$_5^2$, C$_6^2$, C$_7^2$, C$_{00}^2$, C$_{11}^2$, C$_{22}^2$, C$_{33}^2$, C$_3^4$), 125.4 (s, C$_{33}^4$), 128.2 (s, C$_0^3$, C$_1^3$, C$_2^3$, C$_4^3$, C$_5^3$, C$_6^3$, C$_7^3$, C$_{00}^3$, C$_{11}^3$, C$_{22}^3$), 128.8 (d, $^3J_{CP}$ = 12.3 Hz, *m*-C_6H_5, *m*-C′$_6$H′$_5$), 129.6 (s, C$_{33}^3$, C$_8^5$), 131.3 (d, $^2J_{CP}$ = 10.4 Hz, *o*-C_6H_5, *o*-C′$_6$H′$_5$), 132.1 (s, C$_0^4$, C$_1^4$, C$_2^4$, C$_4^4$, C$_5^4$, C$_6^4$, C$_7^4$, C$_{00}^4$, C$_{11}^4$, C$_{22}^4$), 132.5 (s, C$_4^4$-*C*H=N, *p*-C_6H_5, *p*-C′$_6$H′$_5$), 134.3 (d, $^2J_{CP}$ = 12.0 Hz, C$_3^3$), 137.8 (d, $^3J_{CP}$ = 13.3 Hz, C$_7^4$-*C*H=N), 139.0 (d, $^3J_{CP}$ = 11.9 Hz, CH=N), 151.1 (d, $^2J_{CP}$ = 6.3 Hz, C$_0^1$, C$_1^1$, C$_2^1$, C$_3^1$, C$_4^1$, C$_5^1$, C$_6^1$, C$_7^1$, C$_{00}^1$, C$_{11}^1$, C$_{22}^1$, C$_{33}^1$), 151.5 (s, C$_8^3$), 151.7 (d, $^2J_{CP}$ = 6.3 Hz, C$_8^1$). − $C_{9022}H_{9970}N_{1580}O_{1052}P_{576}S_{526}$ (192080): calcd. C 56.41, H 5.23, N 11.52; found C 56.29, H 5.17, N 11.40.

Synthesis of 16-G′$_6$: To a solution of **15-G′$_2$** (0.050 g, 0.015 mmol) in THF (10 mL) was added **8b-G′$_2$** (1.050 g, 0.219 mmol). The resulting mixture was stirred at room temperature for 20 d in the presence of molecular sieves. After filtration, the solvent was evaporated under vacuum. The excess **8b-G′$_3$** was removed by size exclusion chromatography (THF) to afford **16-G′$_6$** as a white powder (0.798 g, 90%).

16-G′$_6$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.3 (d, $^2J_{PP}$ = 33.3 Hz, P′$_3$), 52.0 (d, $^2J_{PP}$ = 33.3 Hz, P$_3$), 62.2 (s, P$_1$, P$_2$, P$_4$, P$_5$, P$_6$). − ^1H NMR ($CDCl_3$): δ = 2.7 (br s, 36 H, CH_2-N-C*H*$_3$), 3.3 (br d, $^3J_{HP}$ = 9.3 Hz, 579 H, CH_3-N-P, C*H*$_2$-C*H*$_2$-P′$_3$), 7.2−7.7 (m, 2025 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 26.0 (d, $^1J_{CP}$ = 66.0 Hz, CH_2-P′$_3$), 33.1 (d, $^2J_{CP}$ = 13.3 Hz, CH_3-N-P), 37.9 (s, *C*H_3-N-CH_2), 53.5 (s, *C*H_2-CH_2-P′$_3$), 121.4 (d, $^3J_{CP}$ = 4.0 Hz, C$_6^2$), 121.9 (s, C$_0^2$, C$_1^2$, C$_2^2$, C$_3^2$, C$_4^2$, C$_5^2$), 125.4 (s, C$_6^4$), 128.3 (s, C$_0^3$, C$_1^3$, C$_2^3$, C$_3^3$, C$_4^3$, C$_5^3$), 128.9 (d, $^3J_{CP}$ = 13.0 Hz, *m*-C_6H_5), 129.6 (s, C$_6^3$), 131.3 (d, $^2J_{CP}$ = 11.1 Hz, *o*-C_6H_5), 132.3 (s, C$_0^4$, C$_1^4$, C$_2^4$, C$_3^4$, C$_4^4$, C$_5^4$), 138.5 (d, $^3J_{CP}$ = 13.8 Hz, C$_5^4$-*C*H=N), 139.0 (d, $^3J_{CP}$ = 13.0 Hz, CH=N), 150.7 (d, $^2J_{CP}$ = 7.4 Hz, C$_6^1$), 151.3 (d, $^2J_{CP}$ = 6.7 Hz, C$_0^1$, C$_1^1$, C$_2^1$, C$_3^1$, C$_4^1$, C$_5^1$). − $C_{2832}H_{2640}N_{390}O_{381}P_{202}S_{190}$ (60583): calcd. C 56.14, H 4.39, N 9.01; found C 56.01, H 4.30, N 8.96.

Synthesis of 18-G′$_3$-G′$_4$: To a solution of **17-G′$_3$** (0.100 g, 6.069 μmol) in THF (10 mL) was added **8c-G′$_2$** (0.371 g, 0.146 mmol). The resulting mixture was stirred at room temperature for 10 d in the presence of molecular sieves. After filtration, the solvent was evaporated under vacuum. The excess **8c-G′$_2$** was removed by size exclusion chromatography (THF) to afford **18-G′$_3$-G′$_4$** as a white powder (0.242 g, 80%).

18-G′$_3$-G′$_4$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −13.0 (dd, $^2J_{PP}$ = 21.1 Hz, $^2J_{PP}$ = 51.1 Hz, P$_1$), 7.8 (s, P$_0$), 13.2 (d, $^2J_{PP}$ = 21.1 Hz, P′$_1$), 17.6 (d, $^2J_{PP}$ = 32.8 Hz, P′$_{22}$), 45.8 (d, $^2J_{PP}$ = 51.1 Hz, P$_{11}$), 52.0 (d, $^2J_{PP}$ = 32.8 Hz, P$_{22}$), 60.2 (s, P$_{44}$), 62.1 (s, P$_2$, P$_3$, P$_{33}$). − ^1H NMR ($CDCl_3$): δ = 2.6 (br s, 54 H, C*H*$_3$-N-CH_2), 3.3 (d, $^3J_{HP}$ = 10.5 Hz, 372 H, CH_3-N-P, C*H*$_2$-C*H*$_2$-P′$_{22}$), 4.6 (br s, 12 H, CH_2-P′$_1$), 7.1−7.6 (m, 1434 H, CH_{arom}, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.4 (d, $^1J_{CP}$ = 60.9 Hz, CH_2-P′$_{22}$), 37.8 (s, *C*H_3-N-CH_2-CH_2-P′$_{22}$), 39.0 (s, *C*H_3-N-CH_2-P′$_1$), 51.6 (s, *C*H_2-CH_2-P′$_{22}$), 109.5 (s, C$_{44}^4$), 118.1 (s, C≡N), 121.4 (s, C$_3^2$), 121.8 (s, C$_0^2$, C$_1^2$, C$_2^2$, C$_{11}^2$), 122.0 (s, C$_{22}^2$, C$_{33}^2$), 122.4 (d, $^3J_{CP}$ = 3.4 Hz, C$_{44}^2$), 125.4 (s, C$_3^4$), 126.4 (s, C$_0^3$), 128.1 (s, C$_1^3$, C$_2^3$, C$_{11}^3$, C$_{22}^3$), 128.4 (s, C$_{33}^3$), 128.9 (d, $^3J_{CP}$ = 12.8 Hz, *m*-C_6H_5), 129.5 (s, C$_3^3$), 131.0 (s, C$_1^4$, C$_{11}^4$, C$_{22}^4$, C$_0^4$-*C*H=N, C$_{11}^4$-*C*H=N), 131.3 (d, $^2J_{CP}$ = 9.8 Hz, *o*-C_6H_5), 131.6 (s, C$_{33}^4$), 132.3 (s, C$_2^4$), 132.6 (s, C$_0^4$, *p*-C_6H_5), 134.0 (s, C$_{44}^3$), 138.6 (d, $^3J_{CP}$ = 14.1 Hz, C$_1^4$-*C*H=N, C$_2^4$-*C*H=N), 140.1 (d, $^3J_{CP}$ = 13.4 Hz, C$_{22}^4$-*C*H=N, C$_{33}^4$-*C*H=N), 149.8 (br s, C$_0^1$), 150.6 (d, $^2J_{CP}$ = 6.4 Hz, C$_3^1$), 151.2 (d, $^2J_{CP}$ = 6.5 Hz, C$_2^1$), 151.7 (d, $^2J_{CP}$ = 6.2 Hz, C$_{33}^1$), 152.3 (d, $^2J_{CP}$ = 7.6 Hz, C$_1^1$), 153.1 (d, $^2J_{CP}$ = 8.4 Hz, C$_{11}^1$, C$_{22}^1$), 153.6 (d, $^2J_{CP}$ = 6.8 Hz, C$_{44}^1$). − IR (KBr): 2227 ($\nu_{C\equiv N}$) cm^{-1}. − $C_{2214}H_{1872}N_{375}O_{270}P_{153}S_{126}$ (49831): calcd. C 56.78, H 4.02, N 11.21; found C 56.60, H 3.95, N 11.07.

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