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Dendrimers with *N*,*N*-Disubstituted Hydrazines as End Groups, Useful Precursors for the Synthesis of Water-Soluble Dendrimers Capped with Carbohydrate, Carboxylic or Boronic Acid Derivatives

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Abstract—The first synthesis of dendrimers possessing *N*,*N*-disubstituted hydrazines as end groups allows us to carry out a versatile reactivity. Carbohydrate, carboxylic acid and boronic acid derivatives have been linked to the surface of the dendrimer in a very simple fashion, using the Schiff condensation. The stability of the resulting functionalized dendrimers has been checked: those linked to carboxylic acid derivatives are stable more than 7 months in water, demonstrating the high stability of both the hydrazone bonds and the whole skeleton of the dendrimer.

Introduction

One of the main features of the highly branched monodisperse polymers called dendrimers[1] is the presence of many functions easily accessible and reactive since they are located on the surface of these macromolecules. A large variety of end groups have already been grafted on dendrimers, bringing new properties, such as solubility, complexation ability, catalysis, liquid crystal behavior. One of the functions most frequently encountered at each generation on the surface of dendrimers is certainly the primary amino group which can be found for instance on polyamine dendrimers[2] and polyamidoamine dendrimers.[3] These primary amino groups gave birth to a versatile reactivity, but are difficult to use to react with aldehydes or ketones, due to the sensitivity toward hydrolysis of most of the imine bonds formed by the Schiff condensation. This unstability is really disappointing because the Schiff condensation could allow the grafting of numerous interesting functional groups in a very simple fashion, using easily available functionalized aldehydes or ketones. However, it is well known that *N*,*N*-disubstituted hydrazines also undergo the Schiff condensation, leading to hydrazone derivatives which are much less sensitive toward hydrolysis than imines. Thus, the synthesis of dendrimers possessing *N*,*N*-disubstituted hydrazine derivatives as end groups at each generation during the reiterative process, which has never been described before now, appears as an interesting challenge.

Results and Discussion

We decided to use phosphorhydrazides as *N*,*N*-disubstituted hydrazines for two reasons: first, a phosphorus atom in β position enhances the stability of the C═N hydrazone bond,[4] and, second, the presence of phosphorus allows us to monitor the reactions by ^{31}P NMR, which has been demonstrated to be an extraordinarily useful tool to characterize dendrimers.[5] In first attempts, we tried to react methylhydrazine directly on the $P(S)Cl_2$ end groups of phosphorus-containing dendrimers such as compound **1** ($(S)P[OC_6H_4CH{=}N{-}NMeP(S)Cl_2]_3$).[5] Several experiments carried out by varying the temperature, the solvent and the concentration of reagents always resulted in the formation of the expected $(S)P[OC_6H_4CH{=}N{-}NMeP(S)(NMeNH_2)_2]_3$ derivative as the major component of a mixture of compounds, presumably due to the occurrence of the reaction on both sides of some methylhydrazine molecules. However, we never succeeded in isolating the expected compound in a yield compatible with the extension of this process to higher generations.

Thus, we tried to use an indirect way to graft phosphorhydrazides on the surface of dendrimers, starting again from **1** as a model compound to test the feasability of the synthesis. We have previously reported that the Staudinger reaction of phosphorus azides with alkyldiphenylphosphines led to the quantitative formation of P═N–P═S

Keywords: dendrimers; hydrazines; hydrazones; Schiff condensation; carbohydrates; carboxylic acids; boronic acids.

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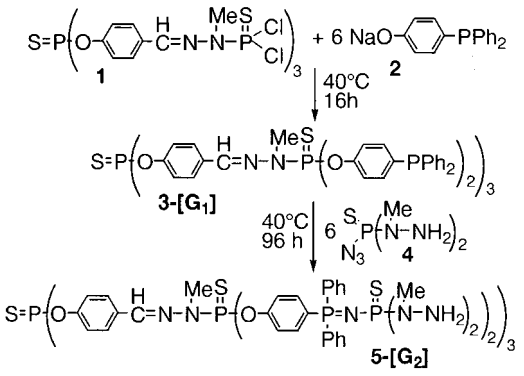
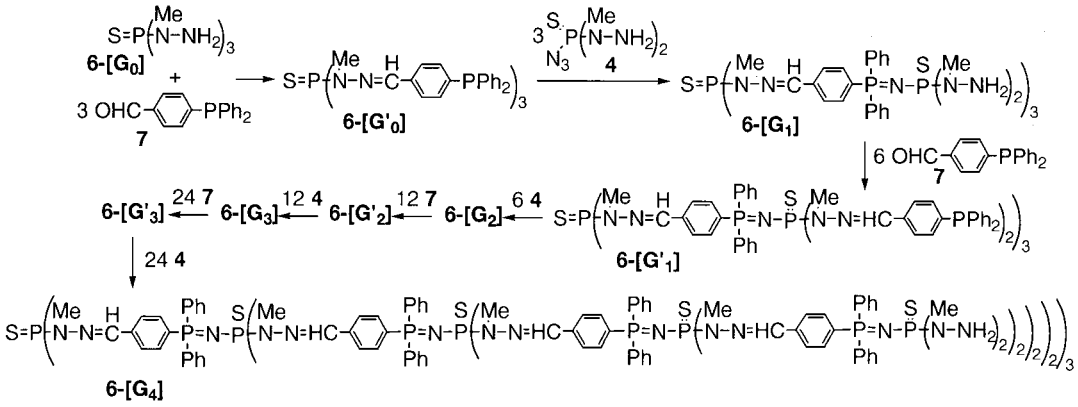


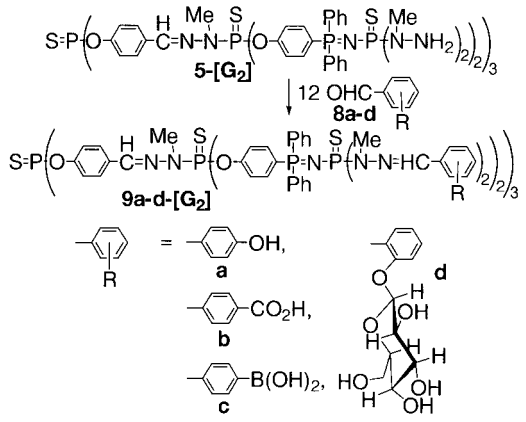
Scheme 1. Synthesis of the second generation dendrimer having 12 *N*,*N*-disubstituted hydrazines as end groups.

linkages, very useful for the synthesis of special multidendritic compounds.[6] The phosphorus azide bearing two methylhydrazino groups $N_3P(S)(NMeNH_2)_2$ **4**[7] could be used to obtain dendrimers capped by hydrazino groups, provided phosphino groups could be first grafted on the surface. However, this azide is not very reactive, and in previous attempts to react it with alkyldiphenylphosphino derivatives, we could not avoid a partial oxidation of the phosphino groups by residual oxygen. Therefore, we needed to graft to the dendrimer, phosphino groups almost insensitive to oxygen, that is to say triphenylphosphino derivatives. The synthetic pathway used is described in Scheme 1. Diphenylphosphinophenoxy sodium salt **2**[8] reacts first with dendrimer **1** to yield compound **3-[G$_1$]**, then the Staudinger reaction with $N_3P(S)(NMeNH_2)_2$ **4** affords dendrimer **5-[G$_2$]**, possessing 12 methylhydrazine derivatives as end groups. Both reactions are relatively slow, as indicated by monitoring using ^{31}P NMR. The substitution reaction induces the shielding of the signal corresponding to the NP(S) group from 61.9 ppm for **1** to 60.9 ppm for **3-[G$_1$]**, and the appearance of a new singlet at $\delta=-6.6$ ppm, corresponding to the PPh_2 groups. The Staudinger reaction induces the disappearance of the latter singlet and the appearance of two doublets at $\delta=11.9$ ppm (Ph_2P═N) and $\delta=70.9$ (N–P═S) with $^2J_{PP}=17.8$ Hz for the P═N–P═S linkages of **5-[G$_2$]**.

This synthetic pathway could be applied to graft hydrazine derivatives to the surface of higher generation dendrimers constituted of (S)POC$_6$H$_4$CH═NNMeP linkages;[5] however, it is also interesting to use the hydrazide **4** as intrinsic building block for the synthesis of a new family of dendrimers. Such a procedure would give hydrazide derivatives as end groups at each generation. The second partner necessary to built a dendrimer must have a phosphino group and an aldehyde group in order to react with the azido and the hydrazido moieties of **4**, respectively. Thus, (4-formylphenyl)(diphenyl)phosphine **7**[9] appears as the most suitable compound for this purpose. The first step of the synthesis of the dendrimer is the condensation of OHCC$_6$H$_4$PPh$_2$ **7** with the trihydrazide (S)P(NMeNH$_2$)$_3$ **6-[G$_0$]** to yield **6-[G′$_0$]**. The second step is the Staudinger reaction of **6-[G′$_0$]** with 3 equiv. of the azide **4** to give the first generation **6-[G$_1$]**, possessing 6 *N*,*N*-disubstituted hydrazine derivatives (Scheme 2). Both steps are easily monitored by ^{31}P NMR: the condensation reaction induces the shielding of the signal corresponding to the P═S group from $\delta=85$ ppm for **6-[G$_0$]** to $\delta=73.7$ ppm for **6-[G′$_0$]**; the Staudinger reaction induces the disappearance of the signal corresponding to the tricoordinated phosphorus atoms of **6-[G′$_0$]** ($\delta=-5.7$ ppm) on behalf of the appearance of two doublets at $\delta=13.0$ and 71.3 ppm ($^2J_{PP}=17.0$ Hz), corresponding to the *P*═N–*P*═S linkage, respectively. Dendrimer **6-[G$_n$]** is built by repeating both steps: the condensation with compound **7** and the Staudinger reaction with compound **4**. Each step is again monitored by ^{31}P NMR, which indicates the shielding of the doublet corresponding to the most external P═S groups from $\delta=71.3$ ppm to ca 56 ppm for the **6-[G$_n$]→6-[G′$_n$]** transformation, and the appearance of a new system of two doublets ($\delta=13.1$ and 71.3 ppm, $^2J_{PP}$ ca 16 Hz) for the **6-[G′$_n$]→6-[G$_{n+1}$]** transformation. Each step is also characterized by ^{1}H and ^{13}C NMR, as well as IR spectroscopy which confirms the disappearance of the CHO group (ν ca 1700 cm^{-1}) and the azido groups (ν ca 2150 cm^{-1}). The repetition of both steps has been carried out to obtain the fourth generation dendrimer **6-[G$_4$]**, possessing 48 *N*,*N*-disubstituted hydrazines on the surface and 45 P═N–P═S linkages within the inner shells. We stopped the synthesis at this step, because a side and unidentified reaction occurred during each Staudinger reaction. We were able to purify the dendrimer from this side product which corresponds to less than 5%, but the purification became more and more difficult as the number of generations increased,



Scheme 2. Synthesis of dendrimers having *N*,*N*-disubstituted hydrazines as end groups at each generation, up to the fourth generation (48 hydrazine end groups).



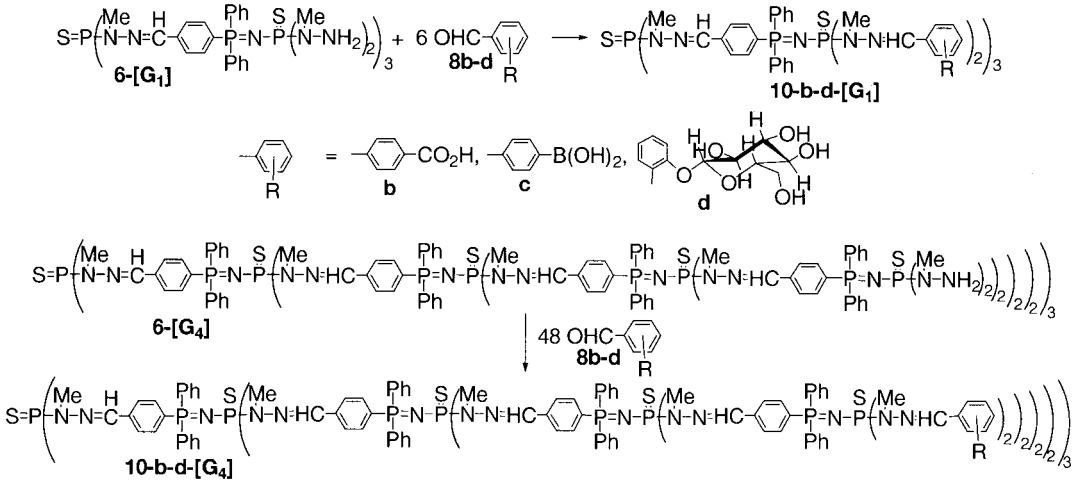
Scheme 3. Reactivity of the second generation dendrimer having 12 *N,N*-disubstituted hydrazines as end groups with various functionalized benzaldehydes.

hampering the access to high generations in a reasonable yield.

The obtaining of two types of dendrimers capped with hydrazide end groups allows us to study their reactivity toward functionalized aldehydes, and particularly toward benzaldehydes linked to various groups possessing labile hydrogen such as alcohol, carboxylic acid, boronic acid, or carbohydrate. First attempts were carried out with dendrimer **5-[G$_2$]** and 12 equiv. of benzaldehydes **8a–d**, leading to the functionalized dendrimers **9a–d-[G$_2$]** in nearly quantitative yields (Scheme 3). In all cases, the condensation induced the shielding of the signal corresponding to the most external phosphorus atoms from δ=70.9 ppm for **5-[G$_2$]** to ca 56 ppm for **9a–d-[G$_2$]** in ^{31}P NMR. An analogous phenomenon is observed for the most external methyl groups from δ=39.2 ppm for **5-[G$_2$]** to ca 33 ppm for **9a–d-[G$_2$]** in ^{13}C NMR. Unexpectedly, the ^{13}C NMR spectrum of compound **9d-[G$_2$]** displays two doublets (in a 1:1 ratio) for the most external CH_3 groups at 32.63 and 32.68 ppm and two doublets (1:1) for the most external CH=N groups.

The same type of reaction has been carried out with dendrimers **6-[G$_n$]** (n=1, 4) and 6 or 48 equiv., respectively, of functionalized benzaldehydes **8b–d**, leading to dendrimers **10-b–d-[G$_n$]** (n=1, 4) (Scheme 4). Such reactions lead to the grafting of up to 48 carboxylic acid, boronic acid and glucose (helicin) derivatives as external functions of phosphorus-containing dendrimers. The phenomenon of shielding already reported between compounds **5** and **9a–d** in ^{31}P and ^{13}C NMR is also observed here for the most external P–N–Me groups from δ=71.3 ppm for **6-[G$_n$]** to ca 60.8 ppm for **10-b–d-[G$_n$]** (^{31}P NMR) and from ca 39.5 ppm for **6-[G$_n$]** to ca 33 ppm for **10-b–d-[G$_n$]** (^{13}C NMR). In this case also, the ^{13}C NMR spectra of compounds **10d-[G$_1$]** and **10d-[G$_4$]** appear abnormal, with the presence of two doublets for the most external CH_3 groups. Furthermore, the same phenomenon is observed in ^{1}H NMR, with the appearance of two doublets (1:1 ratio) for the same CH_3 groups of **10d-[G$_1$]**. The most plausible explanation for this phenomenon is the formation of both *cis* and *trans* isomers of the hydrazone bonds. However, X-ray diffraction studies of compounds including P–N(Me)–N=CHR linkages have demonstrated in all cases (about 20 examples) except one that the hydrazone has a *trans* configuration. The only exception comes from a phosphorus-containing macrocycle formed by two P–(N(Me)–N=CHR)$_2$ linkages, each of them constituted of one *trans* and one *cis* hydrazone bond.[10] Thus, one can postulate that the ability of helicine to form hydrogen bonds forces half of the outer hydrazone linkages of dendrimers **9d-[G$_2$]**, **10d-[G$_1$]**, and **10d-[G$_1$]** to adopt a *cis* configuration.

In order to check the stability of the dendrimers described in this paper toward hydrolysis, we tried to dissolve them in water, but none of them is soluble; only the carbohydrate derivatives **9d-[G$_2$]** (Fig. 1), **10d-[G$_1$]** and **10d-[G$_4$]** are soluble in a mixture of water/THF (3:1). However, dendrimers **9** and **10**, whatever the surface functionalities, possess labile hydrogens in these functions. The corresponding salts should be water-soluble, thus we have reacted sodium hydride (one equivalent per end group) with several dendrimers **9** and **10**. Reactions with **9a-[G$_2$]**, **9c-[G$_2$]**, **10b-[G$_1$]**, and **10c-[G$_1$]** give water-soluble dendrimers. The reaction with **10d-[G$_1$]** does not change its solubility, it is still soluble in a water/THF mixture. The reaction with



Scheme 4. The grafting of up to 48 carboxylic acid, boronic acid, and carbohydrate derivatives on dendrimers.

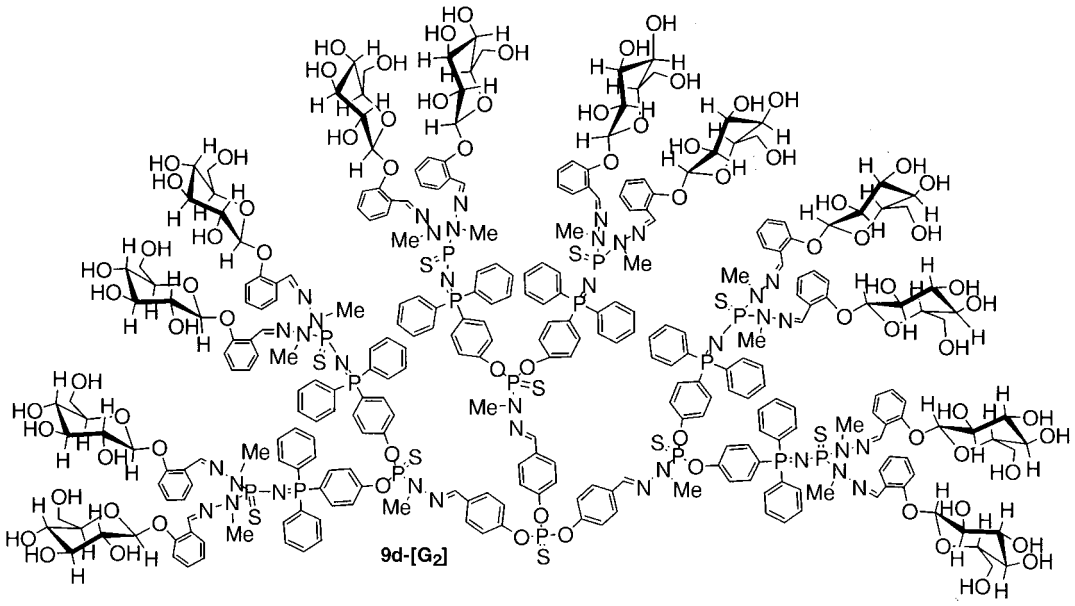


Figure 1. 12 helicin derivatives linked to a second generation dendrimer.

10b-[G_4] gives a dendrimer which is not fully soluble in water, but is soluble in a mixture of water/THF (3:1). Interestingly, evaporation to dryness of the solution gives a dendrimer which becomes directly water-soluble. The ^{1}H NMR spectrum indicates that the dendrimer has retained 14 molecules of THF, which presumably ensure the 'solubility' of the inner layers, whereas the surface is 'solubilized' by water.

The fact that the use of NaH does not induce a cleavage of the dendrimer has been checked: for instance, addition of HCl to the sodium salt of **10b-[G_1]** (suspension in THF)

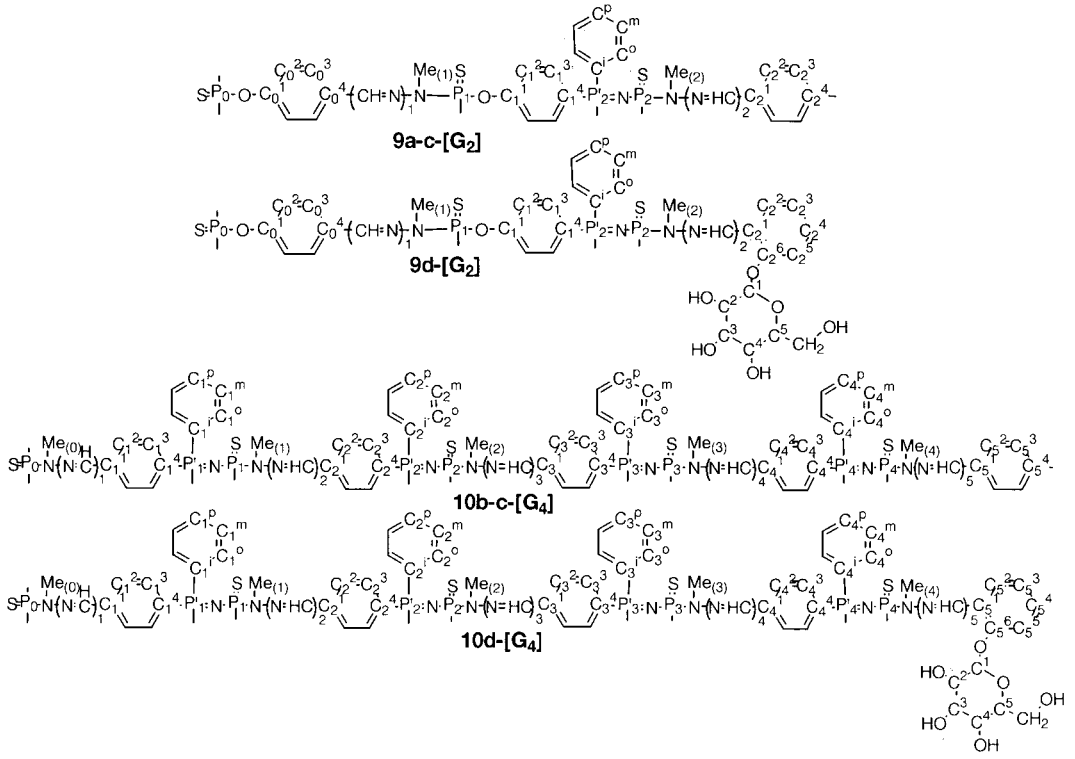


Figure 2. Numbering schemes used for ^{31}P, ^{1}H, and ^{13}C NMR.

allows us to recover **10b-[G$_1$]** intact, and soluble in organic solvents. The stability of the water-solubilized dendrimers has also been checked periodically by NMR. No degradation is observed for the carboxylic acid salt derivatives **10b-[G$_1$]** and **10b-[G$_4$]** even after 7 months in water at room temperature, demonstrating their very high stability.

Conclusion

The formation and isolation of several dendrimers possessing for the first time *N,N*-disubstituted hydrazines as end groups opens the way to a versatile reactivity with functionalized aldehydes. Several interesting functional groups such as carboxylic acids, boronic acids or carbohydrates have been grafted in a very simple way, leading to lipophilic or hydrophilic dendrimers, depending on the type of functional end groups, neutral or ionic. Taking into account the fact that most of the hydrophilic dendrimers described up to now in the literature have been proposed as tools for various biological applications (e.g. transfection, medical imaging, inhibition of viruses), it is important to have not only water soluble, but also water stable, compounds. The phosphorus-containing dendrimers capped with carboxylate derivatives that we have described in this paper are stable for more than 7 months in water, demonstrating the very high stability toward hydrolysis of both the hydrazone external bonds and the whole skeleton of the dendrimer.

Experimental

General

All reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried, distilled and degassed before use. Instrumentation: Bruker AC80, AC200, or AM250 (^{1}H, ^{13}C, ^{31}P NMR), Perkin Elmer 1725X (FT-IR), Electrothermal digital melting point (mp). Compounds **1**,[5] **4**,[7] **7**,[9] $Ph_2PC_6H_4OH$[11] were prepared according to published procedures. The numbering used for NMR is depicted on Fig. 2.

Synthesis of dendrimer 3-[G$_1$]. To a solution of **1** (0.92 g, 1.0 mmol) in THF (5 mL) was added a solution of **2** (2.04 g, 6.6 mmol) in THF (20 mL). The resulting mixture was stirred for 12 h at 40°C, then centrifuged. The solution was evaporated to dryness and the residue was washed 3 times with THF/pentane to afford **3-[G$_1$]** as a white powder (84% yield). ^{31}P {^{1}H} NMR (THF): δ=−6.6 (s, P′$_2$), 51.5 (s, P$_0$), 60.9 (s, P$_1$); ^{1}H NMR ($CDCl_3$): δ=3.40 (d, $^3J_{HP1}$=10.6 Hz, 9H, Me$_{(1)}$), 7.15–7.30 (m, 90H, C_6H_5, C_6H_4), 7.60 (d, $^4J_{HP1}$=2.5 Hz, 3H, CH=N), 7.68 (d, $^3J_{HH}$=8.6 Hz, 6H, C_0^3–H); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=33.0 (d, $^2J_{CP1}$=13.4 Hz, Me$_{(1)}$), 121.3–121.5 (m, C_0^2, C_1^2), 128.4 (s, C_0^3), 128.5 (d, $^3J_{CP'2}$=7.5 Hz, C^m), 128.8 (s, C^p), 132.6 (s, C_0^4), 133.7 (d, $^2J_{CP'2}$=18.5 Hz, C^o), 134.1 (d, $^1J_{CP'2}$=11.3 Hz, C_1^4), 135.0 (d, $^2J_{CP'2}$=20.2 Hz, C_1^3), 136.9 (d, $^1J_{CP'2}$=10.7 Hz, C^i), 138.4 (d, $^3J_{CP1}$=14.0 Hz, CH=N), 151.2 (d, $^2J_{CP}$=6.5 Hz, C_0^1, C_1^1). Anal. Calcd for $C_{132}H_{108}N_6O_9P_{10}S_4$ (2360.3): C, 67.17; H, 4.61; N, 3.56. Found: C, 67.05; H, 4.60; N, 3.51.

Synthesis of dendrimer 5-[G$_2$]. To a solution of dendrimer **3-[G$_1$]** (0.30 g, 0.13 mmol) in CH_2Cl_2 (1 mL) was added a solution of the azide **4** (0.15 g, 0.78 mmol) in CH_2Cl_2 (1 mL). The resulting mixture was stirred for 4 days at 40°C, then evaporated to dryness. The residue was washed 3 times with CH_2Cl_2/pentane (1:5), and 3 times with toluene/pentane (1:5) to afford **5-[G$_2$]** as a white powder (70% yield). ^{31}P {^{1}H} NMR (CH_2Cl_2): δ=11.9 (d, $^2J_{PP}$=17.8 Hz, P′$_2$), 52.1 (s, P$_0$), 60.6 (s, P$_1$), 70.9 (d, $^2J_{PP}$=17.8 Hz, P$_2$); ^{1}H NMR ($CDCl_3$): δ=2.66 (d, $^3J_{HP2}$=11.9 Hz, 36H, Me$_{(2)}$), 3.37 (d, $^3J_{HP1}$=10.8 Hz, 9H, Me$_{(1)}$), 3.46 (br s, 24H, NH_2), 7.28–7.77 (m, 99H, C_6H_5, C_6H_4, CH=N); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=33.1 (br s, Me$_{(1)}$), 39.2 (d, $^2J_{CP2}$=7.2 Hz, Me$_{(2)}$), 121.0 (m, C_0^2, C_1^2), 128.4 (s, C_0^3), 128.5 (d, $^3J_{CP'2}$=12.7 Hz, C^m), 129.4 (dd, $^1J_{CP'2}$=107.0 Hz, $^3J_{CP2}$=2.9 Hz, C_1^4, C^i), 132.4 (s, C^p), 132.5 (d, $^2J_{CP'2}$=10.3 Hz, C^o), 132.7 (s, C_0^4), 134.5 (d, $^2J_{CP'2}$=11.9 Hz, C_1^3), 139.1 (d, $^3J_{CP1}$=11.6 Hz, CH=N), 151.2 (br s, C_0^1), 153.4 (br s, C_1^1). Anal. Calcd for $C_{144}H_{168}N_{30}O_9P_{16}S_{10}$ (3279.3): C, 52.74; H, 5.16; N, 12.81. Found: C, 52.66; H, 5.08; N, 12.83.

General procedure for the synthesis of dendrimers 6-[G′$_n$] (n=0–3) (PPh_2 end groups)

To a mixture of powdered dendrimer **6-[G$_n$]** (n=0, 0.103 g, 0.522 mmol; n=1, 0.150 g, 0.099 mmol; n=2, 0.380 g, 9.08×10^{-2} mmol; n=3, 0.440 g, 4.65×10^{-2} mmol) and powdered (4-formylphenyl)(diphenyl)phosphine **7** (n=0, 0.500 g, 1.72 mmol; n=1, 0.180 g, 6.13 mmol; n=2, 0.320 g, 1.11 mmol; n=3, 0.330 g, 1.12 mmol) was added THF (n=0, 12 mL; n=1, 7 mL; n=2, 10 mL; n=3, 15 mL). The resulting solution was stirred overnight at room temperature, then evaporated to dryness. The residue was washed thrice with pentane/CH_2Cl_2 (10:1) to afford dendrimer **6-[G′$_n$]** as a white powder.

General procedure for the synthesis of dendrimers 6-[G$_n$] (n=0–4) (NH_2 end groups)

To a mixture of powdered dendrimer **6-[G′$_n$]** (n=0, 0.300 g, 0.296 mmol; n=1, 0.120 g, 3.71×10^{-2} mmol; n=2, 0.440 g, 5.89×10^{-2} mmol; n=3, 0.620 g, 3.90×10^{-2} mmol) and powdered azide **4** (n=0, 0.190 g, 0.98 mmol; n=1, 0.046 g, 0.233 mmol; n=2, 0.140 g, 0.718 mmol; n=3, 0.180 g, 0.937 mmol) was added a minimum amount of CH_2Cl_2 to solubilize both reagents (1–2 mL). The resulting solution was stirred at room temperature for 3 days. A small quantity of CH_2Cl_2 was added after 3 days, if an oil was formed. Pentane was added in order to obtain a precipitate, which was recovered by filtration. The precipitate was washed thrice with pentane/CH_2Cl_2 (10:1) to afford dendrimer **6-[G$_n$]** as a white powder.

6-[G′$_0$]: yield: 0.52 g, 99%. Mp 185–187°C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=−5.7 (s, P′$_1$), 73.7 (s, P$_0$); ^{1}H NMR ($CDCl_3$): δ=3.29 (d, $^3J_{HP0}$=8.9 Hz, 9H, Me$_{(0)}$), 7.11 (t, $^3J_{HH}$=$^3J_{HP'1}$=8.0 Hz, 6H, C_1^3H), 7.15–7.32 (m, 30H, C_6H_5), 7.45 (dd, $^3J_{HH}$=8.0 Hz, $^4J_{HH}$=1.4 Hz, 6H, C_1^2H), 7.56 (d, $^4J_{HH}$=1.4 Hz, 3H, CH=N$_{(1)}$); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.54 (d, $^2J_{CP0}$=8.9 Hz, Me$_{(0)}$), 126.36 (d, $^3J_{CP'1}$=7.1 Hz, C_1^2), 128.32 (s, C$_1^p$), 128.52 (d, $^3J_{CP'1}$=7.9 Hz, C$_1^m$), 133.55 (d, $^2J_{CP'1}$=18.9 Hz, C_1^3, C$_1^o$), 135.78 (s, C_1^1), 136.68 (d, $^3J_{CP0}$=

15.0 Hz, CH=N), 136.74 (d, $^{1}J_{CP'1}$=9.2 Hz, C^{i}_{1}), 137.57 (d, $^{1}J_{CP'1}$=11.6 Hz, C^{4}_{1}). MS (FAB^{+}): 1014.31 [M]$^{+}$. Anal. Calcd for $C_{60}H_{54}N_6P_4S$ (1015.08): C, 70.99; H, 5.36; N, 8.27. Found: C, 70.86; H, 5.31; N, 8.21.

6-[G$_1$]: yield: 0.40 g, 90%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=13.0 (d, $^{2}J_{P'1P1}$=17.0 Hz, P′$_1$), 71.3 (d, $^{2}J_{P1P'1}$=17.0 Hz, P$_1$), 73.4 (s, P$_0$); ^{1}H NMR ($CDCl_3$): δ=2.67 (d, $^{3}J_{HP1}$=11.9 Hz, 18H, Me$_{(1)}$), 3.30 (d, $^{3}J_{HP0}$=8.6 Hz, 9H, Me$_{(0)}$), 3.57 (br s, 12H, NH_2), 7.43–7.75 (m, 45H, C_6H_5, C_6H_4, CH=N); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=33.7 (d, $^{2}J_{CP0}$=8.3 Hz, Me$_{(0)}$), 39.8 (d, $^{2}J_{CP1}$=6.8 Hz, Me$_{(1)}$), 126.9 (d, $^{3}J_{CP'1}$=13.1 Hz, C^{2}_{1}), 129.1 (d, $^{3}J_{CP'1}$=12.8 Hz, C^{m}_{1}), 130.1 (dd, $^{1}J_{CP'1}$=106.8 Hz, $^{3}J_{CP1}$= 3.2 Hz, C^{4}_{1}, C^{i}_{1}), 132.9 (d, $^{4}J_{CP'1}$=2.6 Hz, C^{p}_{1}), 133.1 (d, $^{2}J_{CP'1}$=10.7 Hz, C^{o}_{1}), 133.5 (d, $^{2}J_{CP'1}$=11.0 Hz, C^{3}_{1}), 137.1 (d, $^{3}J_{CP0}$=15.0 Hz, CH=N), 139.6 (d, $^{4}J_{CP'1}$=2.9 Hz, C^{1}_{1}). Anal. Calcd for $C_{66}H_{84}N_{21}P_7S_4$ (1516.60): C, 52.23; H, 5.64; N, 19.38. Found: C, 52.09; H, 5.58; N, 19.29.

6-[G′$_1$]: yield: 0.27 g, 88%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=−5.6 (s, P′$_2$), 11.3 (d, $^{2}J_{P'1P1}$=26.5 Hz, P′$_1$), 55.7 (d, $^{2}J_{P1P'1}$=26.5 Hz, P$_1$), 73.4 (s, P$_0$); ^{1}H NMR ($CDCl_3$): δ=3.15 (d, $^{3}J_{HP1}$=8.9 Hz, 18H, Me$_{(1)}$), 3.23 (d, $^{3}J_{HP0}$= 8.5 Hz, 9H, Me$_{(0)}$), 7.10 (t, $^{3}J_{HH}$=$^{3}J_{HP'2}$=7.7 Hz, 12H, C^{3}_{2}H), 7.13–7.37 (m, 102H, C_6H_5, C_6H_4), 7.52 (s, 3H, CH=N$_{(1)}$), 7.54 (s, 6H, CH=N$_{(2)}$), 7.63–7.76 (m, 12H, C^{2}_{2}H); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.7 (d, $^{2}J_{CP1}$=9.8 Hz, Me$_{(1)}$), 33.2 (d, $^{2}J_{CP0}$=7.7 Hz, Me$_{(0)}$), 126.3 (d, $^{3}J_{CP'2}$= 7.2 Hz, C^{2}_{2}), 126.4 (d, $^{3}J_{CP'1}$=7.5 Hz, C^{2}_{1}), 128.4 (d, $^{3}J_{CP'1}$= 13.7 Hz, C^{m}_{1}), 128.5 (d, $^{3}J_{CP'2}$=5.8 Hz, C^{m}_{2}), 128.7 (s, C^{p}_{2}), 129.6 (br d, $^{1}J_{CP'1}$=107.0 Hz, C^{4}_{1}, C^{i}_{1}), 132.2 (br s, C^{p}_{1}), 132.9 (d, $^{2}J_{CP'1}$=10.9 Hz, C^{o}_{1}), 133.3 (d, $^{2}J_{CP'1}$=11.8 Hz, C^{3}_{1}), 133.7 (d, $^{2}J_{CP'2}$=19.7 Hz, C^{3}_{2}, C^{o}_{2}), 134.1 (s, C^{1}_{2}), 136.2 (d, $^{1}J_{CP'2}$=10.5 Hz, C^{4}_{2}), 136.7 (d, $^{3}J_{CP0}$=13.8 Hz, CH=N$_{(1)}$), 137.2 (d, $^{3}J_{CP1}$=7.9 Hz, CH=N$_{(2)}$), 137.3 (d, $^{1}J_{CP'2}$=7.0 Hz, C^{i}_{2}), 139.0 (br s, C^{1}_{1}). Anal. Calcd for $C_{180}H_{162}N_{21}P_{13}S_4$ (3150.31): C, 68.62; H, 5.18; N, 9.33. Found: C, 68.49; H, 5,10; N, 9.25.

6-[G$_2$]: yield: 0.15 g, 99%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=12.6 (d, $^{2}J_{P'1P1}$=27.3 Hz, P′$_1$), 13.2 (d, $^{2}J_{P'2P2}$=15.7 Hz, P′$_2$), 56.1 (d, $^{2}J_{P1P'1}$=27.3 Hz, P$_1$), 71.4 (d, $^{2}J_{P2P'2}$=15.7 Hz, P$_2$), 73.2 (s, P$_0$); ^{1}H NMR ($CDCl_3$): δ=2.68 (dd, $^{3}J_{HP2}$=11.9 Hz, $^{5}J_{HP'2}$=2.9 Hz, 36H, Me$_{(2)}$), 3.19 (br d, $^{3}J_{HP}$=7.4 Hz, 27H, Me$_{(0)}$, Me$_{(1)}$), 3.20 (br s, 24H, NH_2), 7.22–7.76 (m, 135H, C_6H_5, C_6H_4, CH=N); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.9 (d, $^{2}J_{CP1}$=9.4 Hz, Me$_{(1)}$), 33.5 (d, $^{2}J_{CP0}$=7.7 Hz, Me$_{(0)}$), 39.4 (d, $^{2}J_{CP2}$=6.2 Hz, Me$_{(2)}$), 126.1 (d, $^{3}J_{CP'2}$=13.5 Hz, C^{2}_{2}), 126.5 (d, $^{3}J_{CP'1}$=13.0 Hz, C^{2}_{1}), 128.6 (d, $^{3}J_{CP}$=12.8 Hz, C^{m}_{1}, C^{m}_{2}), 129.2 (br d, $^{1}J_{CP'1}$=107.0 Hz, C^{4}_{1}, C^{i}_{1}), 129.9 (br d, $^{1}J_{CP'2}$= 106.4 Hz, C^{4}_{2}, C^{i}_{2}), 132.4 (br s, C^{p}_{1}, C^{p}_{2}), 132.7 (d, $^{2}J_{CP'2}$=10.2 Hz, C^{3}_{2}, C^{o}_{2}), 133.0 (m, C^{3}_{1}, C^{o}_{1}), 136.9 (br d, $^{2}J_{CP}$=14.6 Hz, CH=N$_{(1)}$, CH=N$_{(2)}$), 139.2 (d, $^{4}J_{CP'1}$= 3.3 Hz, C^{1}_{1}), 140.6 (s, C^{1}_{2}). Anal. Calcd for $C_{192}H_{222}N_{51}P_{19}S_{10}$ (4153.35): C, 55.52; H, 5.38; N, 17.19. Found: C, 55.45; H, 5.31; N, 17.09.

6-[G′$_2$]: yield: 0.66 g, 98%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=−5.8 (s, P′$_3$), 11.6 (d, $^{2}J_{P'2P2}$=26.4 Hz, P′$_2$), 12.5 (d, $^{2}J_{P'1P1}$=26.4 Hz, P′$_1$), 56.1 (d, $^{2}J_{PP}$=26.4 Hz, P$_1$, P$_2$), 73.2 (s, P$_0$); ^{1}H NMR ($CDCl_3$): δ=3.16 (m, 63H, Me$_{(0)}$, Me$_{(1)}$, Me$_{(2)}$), 7.10 (t, $^{3}J_{HH}$=$^{3}J_{HP'3}$=7.7 Hz, 24H, C^{3}_{3}H), 7.24–7.44 (m, 255H, C_6H_5, C_6H_4, CH=N$_{(1)}$, CH=N$_{(2)}$), 7.62–7.77 (m, 36H, C^{2}_{3}H, CH=N$_{(3)}$); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.7 (d, $^{2}J_{CP2}$=10.0 Hz, Me$_{(2)}$), 32.9 (d, $^{2}J_{CP1}$=12.6 Hz, Me$_{(1)}$), 33.5 (d, $^{2}J_{CP0}$=9.3 Hz, Me$_{(0)}$), 125.9 (d, $^{3}J_{CP'2}$=13.2 Hz, C^{2}_{2}), 126.3 (d, $^{3}J_{CP'3}$=7.6 Hz, C^{2}_{3}), 126.5 (d, $^{3}J_{CP'1}$=13.0 Hz, C^{2}_{1}), 128.3 (d, $^{3}J_{CP}$=12.5 Hz, C^{m}_{1}, C^{m}_{2}), 128.4 (s, C^{p}_{3}), 128.6 (d, $^{3}J_{CP'3}$=8.0 Hz, C^{m}_{3}), 129.3 (dd, $^{1}J_{CP'1}$=106.0 Hz, $^{3}J_{CP1}$=3.1 Hz, C^{4}_{1}, C^{i}_{1}), 129.9 (br d, $^{1}J_{CP'2}$=109.3 Hz, C^{4}_{2}, C^{i}_{2}), 132.1 (s, C^{p}_{2}), 132.4 (s, C^{p}_{1}), 132.9 (d, $^{2}J_{CP'2}$=10.7 Hz, C^{3}_{2}, C^{o}_{2}), 133.0 (m, C^{3}_{1}, C^{o}_{1}), 133.7 (d, $^{2}J_{CP'3}$=19.0 Hz, C^{3}_{3}, C^{o}_{3}), 134.1 (s, C^{1}_{3}), 136.2 (d, $^{1}J_{CP'3}$=11.6 Hz, C^{4}_{3}), 136.9 (m, CH=N$_{(1)}$, CH=N$_{(2)}$), 137.3 (d, $^{3}J_{CP2}$=8.4 Hz, CH=N$_{(3)}$), 137.3 (d, $^{3}J_{CP'3}$=4.2 Hz, C^{i}_{3}), 139.3 (s, C^{1}_{1}), 140.4 (s, C^{1}_{2}). Anal. Calcd for $C_{420}H_{378}N_{51}P_{31}S_{10}$ (7420.7): C, 67.98; H, 5.13; N, 9.62. Found: C, 67.87; H, 5.07; N, 6.54.

6-[G$_3$]: yield: 0.49 g, 88%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=12.6 (d, $^{2}J_{P'1P1}$=28.5 Hz, P′$_1$), 12.8 (d, $^{2}J_{P'2P2}$=26.8 Hz, P′$_2$), 13.2 (d, $^{2}J_{P'3P3}$=16.5 Hz, P′$_3$), 56.0 (d, $^{2}J_{P2P'2}$=26.5 Hz, P$_2$), 56.1 (d, $^{2}J_{P1P'1}$=28.5 Hz, P$_1$), 71.4 (d, $^{2}J_{P3P'3}$=16.5 Hz, P$_3$), 73.1 (s, P$_0$); ^{1}H NMR ($CDCl_3$): δ=2.68 (d, $^{3}J_{HP3}$=11.8 Hz, 72H, Me$_{(3)}$), 3.21 (br d, $^{3}J_{HP}$=5.7 Hz, 63H, Me$_{(0)}$, Me$_{(1)}$, Me$_{(2)}$), 3.25 (br s, 48H, NH_2), 7.22–7.75 (m, 315H, C_6H_5, C_6H_4, CH=N); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.6 (d, $^{2}J_{CP1}$= 7.6 Hz, Me$_{(1)}$), 33.4 (d, $^{2}J_{CP0}$=7.9 Hz, Me$_{(0)}$), 33.5 (d, $^{2}J_{CP2}$=9.8 Hz, Me$_{(2)}$), 39.4 (d, $^{2}J_{CP3}$=7.1 Hz, Me$_{(3)}$), 126.0 (d, $^{3}J_{CP}$=12.8 Hz, C^{2}_{2}, C^{2}_{3}), 126.7 (d, $^{3}J_{CP'1}$=12.0 Hz, C^{2}_{1}), 128.5 (d, $^{3}J_{CP}$=13.7 Hz, C^{m}_{1}, C^{m}_{2}), 128.6 (d, $^{3}J_{CP'3}$=12.1 Hz, C^{m}_{3}), 129.3 (dd, $^{1}J_{CP'1}$=106.0 Hz, $^{3}J_{CP1}$=3.4 Hz, C^{4}_{1}, C^{i}_{1}), 129.7 (br d, $^{1}J_{CP'2}$=106.0 Hz, C^{4}_{2}, C^{i}_{2}), 130.0 (d, $^{1}J_{CP'3}$=105.9 Hz, C^{4}_{3}, C^{i}_{3}), 132.1 (s, C^{p}_{1}, C^{p}_{2}, C^{p}_{3}), 132.7 (d, $^{2}J_{CP'3}$=11.1 Hz, C^{3}_{3}, C^{o}_{3}), 132.8–133.1 (m, C^{3}_{1}, C^{o}_{1}, C^{3}_{2}, C^{o}_{2}), 137.0 (m, CH=N$_{(1)}$, CH=N$_{(2)}$, CH=N$_{(3)}$), 139.2 (s, C^{1}_{1}), 140.3 (s, C^{1}_{2}), 140.6 (s, C^{1}_{3}). Anal. Calcd for $C_{444}H_{498}N_{111}P_{43}S_{22}$ (9426.8): C, 56.57; H, 5.32; N, 16.49. Found: C, 56.45; H, 5.25; N, 16.42.

6-[G′$_3$]: yield: 0.70 g, 94%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=−5.6 (s, P′$_4$), 11.5 (d, $^{2}J_{P'3P3}$=26.1 Hz, P′$_3$), 12.0 (d, $^{2}J_{P'1P1}$=26.0 Hz, P′$_1$), 12.5 (d, $^{2}J_{P'2P2}$=26.3 Hz, P′$_2$), 56.0 (d, $^{2}J_{PP}$=26.5 Hz, P$_1$, P$_2$), 56.1 (d, $^{2}J_{P3P'3}$=26.1 Hz, P$_3$), 73.1 (s, P$_0$); ^{1}H NMR ($CDCl_3$): δ=3.18 (br d, $^{3}J_{HP}$=7.9 Hz, 135H, Me$_{(0)}$, Me$_{(1)}$, Me$_{(2)}$, Me$_{(3)}$), 7.11 (t, $^{3}J_{HH}$=$^{3}J_{HP'4}$=7.6 Hz, 48H, C^{3}_{4}H), 7.12–7.52 (m, 555H, C_6H_5, C_6H_4, CH=N$_{(1)}$, CH=N$_{(2)}$, CH=N$_{(3)}$), 7.52–7.80 (m, 72H, C^{2}_{4}H, CH=N$_{(4)}$); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.7 (d, $^{2}J_{CP3}$=9.8 Hz, Me$_{(3)}$), 33.0 (d, $^{2}J_{CP}$=10.0 Hz, Me$_{(1)}$, Me$_{(2)}$), 33.6 (d, $^{2}J_{CP0}$=9.4 Hz, Me$_{(0)}$), 125.8 (d, $^{3}J_{CP}$=13.4 Hz, C^{2}_{2}, C^{2}_{3}), 126.3 (d, $^{3}J_{CP'4}$=6.8 Hz, C^{2}_{4}), 126.7 (d, $^{3}J_{CP'1}$=13.0 Hz, C^{2}_{1}), 128.4 (d, $^{3}J_{CP}$=9.9 Hz, C^{m}_{1}, C^{m}_{2}, C^{m}_{3}), 128.5 (s, C^{p}_{4}), 128.6 (d, $^{3}J_{CP'4}$=9.8 Hz, C^{m}_{4}), 129.3 (br d, $^{1}J_{CP'1}$=106.0 Hz, C^{4}_{1}, C^{i}_{1}), 129.6 (br d, $^{1}J_{CP'2}$=107.0 Hz, C^{4}_{2}, C^{i}_{2}), 129.9 (br d, $^{1}J_{CP'3}$=111.0 Hz, C^{4}_{3}, C^{i}_{3}), 132.1 (s, C^{p}_{3}), 132.3 (s, C^{p}_{2}), 132.4 (s, C^{p}_{1}), 132.8 (m, C^{3}_{1}, C^{o}_{1}, C^{3}_{2}, C^{o}_{2}), 132.9 (d, $^{2}J_{CP'3}$=11.3 Hz, C^{3}_{3}, C^{o}_{3}), 133.7 (d, $^{2}J_{CP'4}$=19.6 Hz, C^{3}_{4}, C^{o}_{4}), 134.1 (s, C^{1}_{4}), 136.1 (d, $^{1}J_{CP'4}$=10.1 Hz, C^{4}_{4}), 136.9 (m, CH=N$_{(1)}$, CH=N$_{(2)}$, CH=N$_{(3)}$), 137.2 (d, $^{1}J_{CP'4}$=9.2 Hz, C^{i}_{4}), 137.3 (d, $^{1}J_{CP3}$=12.6 Hz, CH=N$_{(4)}$), 139.3 (s, C^{1}_{1}), 140.4 (s, C^{1}_{3}), 140.6 (s, C^{1}_{2}). Anal. Calcd for $C_{900}H_{810}N_{111}P_{67}S_{22}$ (15962): C, 67.72; H, 5.11; N, 9.74. Found: C, 67.64; H, 5.04; N, 9.68.

6-[G$_4$]: yield: 0.71 g, 91%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=12.7 (d, $^{2}J_{PP}$=26.9 Hz, P′$_1$, P′$_2$, P′$_3$), 13.1 (d, $^{2}J_{P'4P4}$=16.5 Hz,

P′4), 56.1 (d, $^2J_{PP}$=26.9 Hz, P_1, P_2, P_3), 71.3 (d, $^2J_{P4P'4}$=16.5 Hz, P_4), 73.1 (s, P_0); ^{1}H NMR ($CDCl_3$): δ=2.69 (d, $^3J_{HP4}$=11.9 Hz, 144H, $Me_{(4)}$), 3.21 (br d, $^3J_{HP}$=6.5 Hz, 135H, $Me_{(0)}$, $Me_{(1)}$, $Me_{(2)}$, $Me_{(3)}$), 3.47 (br s, 96H, NH_2), 7.24–7.74 (m, 675H, C_6H_5, C_6H_4, CH=N); ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.6 (d, $^2J_{CP1}$=7.7 Hz, $Me_{(1)}$), 33.3 (d, $^2J_{CP}$=9.6 Hz, $Me_{(2)}$, $Me_{(3)}$), 33.6 (d, $^2J_{CP0}$=7.4 Hz, $Me_{(0)}$), 39.3 (d, $^2J_{CP4}$=6.9 Hz, $Me_{(4)}$), 126.0 (d, $^3J_{CP}$= 13.3 Hz, C_2^2, C_3^2, C_4^2), 126.7 (br s, C_1^2), 128.5 (d, $^3J_{CP}$=12.5 Hz, C_1^m, C_2^m, C_3^m), 128.6 (d, $^3J_{CP'4}$=12.7 Hz, C_4^m), 129.3 (br d, $^1J_{CP'1}$=106.0 Hz, C_1^4, C_1^i), 129.6 (br d, $^1J_{CP}$=106.0 Hz, C_2^4, C_2^i, C_3^4, C_3^i), 129.9 (br d, $^1J_{CP'4}$= 106.8 Hz, C_4^4, C_4^i), 132.4 (s, C_1^p, C_2^p), 132.6 (s, C_3^p, C_4^p), 132.7 (d, $^2J_{CP'4}$=11.4 Hz, C_4^3, C_4^o), 133.0 (m, C_1^3, C_1^o, C_2^3, C_2^o, C_3^3, C_3^o), 136.9 (m, $CH=N_{(1)}$, $CH=N_{(2)}$, $CH=N_{(3)}$, $CH=N_{(4)}$), 139.3 (s, C_1^1), 141.2 (s, C_2^1, C_3^1, C_4^1). Anal. Calcd for $C_{948}H_{1050}N_{231}P_{91}S_{46}$ (19974): C, 57.00; H, 5.29; N, 16.19. Found: C, 56.91; H, 5.24; N, 16.11.

General procedure for the synthesis of dendrimers 9a-[G_2] and 9b-[G_2]

To a solution of dendrimer **5-[G_2]** (0.40 g, 0.12 mmol) in THF (10 mL) was added at room temperature a solution of 4-hydroxybenzaldehyde **8a** (0.18 g, 1.50 mmol) or 4-carboxybenzaldehyde **8b** (0.22 g, 1.45 mmol) in THF (5 mL). The resulting solution was stirred for 24 h at room temperature, then evaporated to dryness. The residue was washed three times with THF/pentane (1:5).

9a-[G_2]: yellow powder (94.5% yield). ^{31}P {^{1}H} NMR (THF): δ=8.1 (d, $^2J_{PP}$=25.6 Hz, P′2), 51.5 (s, P_0), 56.4 (d, $^2J_{PP}$=25.6 Hz, P_2), 60.3 (s, P_1); ^{1}H NMR (CD_3COCD_3): δ=3.11 (d, $^3J_{HP2}$=9.3 Hz, 36H, $Me_{(2)}$), 3.41 (d, $^3J_{HP1}$= 10.7 Hz, 9H, $Me_{(1)}$), 6.72 (d, $^3J_{HH}$=8.4 Hz, 24H, H–C_2^3), 7.25–7.55 (m, 63H, C_6H_5, C_6H_4, CH=N), 7.36 (d, $^3J_{HH}$=8.4 Hz, 24H, HC_2^2), 7.75–7.92 (m, 48H, C_6H_5), 9.75 (br s, 12H, OH); ^{13}C {^{1}H} NMR (DMSO-d^6): δ=34.0 (d, $^2J_{CP2}$=10.2 Hz, $Me_{(2)}$), 34.5 (d, $^2J_{CP1}$=9.7 Hz, $Me_{(1)}$), 116.8 (s, C_2^3), 122.5 (m, C_0^2, C_1^2), 127.3 (s, C_0^3), 129.0 (s, C_2^2), 129.1 (s, C_2^1), 130.2 (d, $^3J_{CP'2}$=13.1 Hz, C^m), 131.0 (dd, $^1J_{CP'2}$=104.6 Hz, $^3J_{CP2}$=2.9 Hz, C_1^4, C^i), 133.7 (s, C_0^4), 134.1 (d, $^2J_{CP'2}$=10.2 Hz, C^o), 134.1 (s, C^p), 136.3 (d, $^2J_{CP'2}$=11.6 Hz, C_1^3), 136.7 (d, $^3J_{CP2}$=14.5 Hz, $CH=N_{(2)}$), 138.2 (br s, $CH=N_{(1)}$), 152.2 (br s, C_0^1), 154.6 (br s, C_1^1), 159.1 (s, C_2^4). Anal. Calcd for $C_{228}H_{216}N_{36}O_{21}P_{16}S_{10}$ (4612.7): C, 59.36; H, 4.71; N, 10.93. Found: C, 59.24; H, 4.62; N, 10.86.

9b-[G_2]: white powder (99.5% yield). ^{31}P {^{1}H} NMR (THF): δ=9.8 (d, $^2J_{PP}$=26.3 Hz, P′2), 51.7 (s, P_0), 56.0 (d, $^2J_{PP}$=26.3 Hz, P_2), 60.4 (s, P_1); ^{1}H NMR (CD_3COCD_3): δ=3.20 (d, $^3J_{HP2}$=8.7 Hz, 36H, $Me_{(2)}$), 3.43 (d, $^3J_{HP1}$=10.8 Hz, 9H, $Me_{(1)}$), 7.30–8.10 (m, 159H, C_6H_5, C_6H_4, CH=N); ^{13}C {^{1}H} NMR (DMSO-d_6): δ=32.7 (d, $^2J_{CP2}$=9.9 Hz, $Me_{(2)}$), 32.8 (d, $^2J_{CP1}$=10.0 Hz, $Me_{(1)}$), 121.0–122.0 (m, C_0^2, C_1^2), 125.8 (s, C_2^2), 127.2 (s, C_0^3), 128.8 (d, $^3J_{CP'2}$=12.8 Hz, C^m), 129.1 (dd, $^1J_{CP'2}$=112.9 Hz, $^3J_{CP2}$=3.0 Hz, C_1^4, C^i), 129.6 (s, C_2^3), 129.7 (s, C_2^4), 132.5 (d, $^2J_{CP'2}$=10.9 Hz, C^o), 132.8 (br s, C_0^4, C^p), 134.1 (d, $^3J_{CP2}$=14.2 Hz, $CH=N_{(2)}$), 134.8 (d, $^2J_{CP'2}$=12.8 Hz, C_1^3), 138.9 (br s, $CH=N_{(1)}$), 140.5 (s, C_2^1), 150.8 (br s, C_0^1), 153.2 (br s, C_1^1), 172.3 (s, COOH). IR(KBr): 1700 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{240}H_{216}N_{36}O_{33}P_{16}S_{10}$ (4948.8): C, 58.24; H, 4.39; N, 10.18. Found: C, 58.18; H, 4.32; N, 10.14.

Synthesis of dendrimer 9c-[G_2]. To a solution of dendrimer **5-[G_2]** (0.20 g, 0.06 mmol) in THF (5 mL) was added a solution of acid **8c** (0.12 g, 0.79 mmol) in THF (5 mL). The resulting solution was stirred for 24 h at room temperature, then evaporated to dryness. The yellow residue was rapidly washed three times with methanol to afford dendrimer **9c-[G_2]** as a white powder (95% yield). ^{31}P {^{1}H} NMR (THF): δ=9.0 (d, $^2J_{PP}$=27.2 Hz, P′2), 51.6 (s, P_0), 56.1 (d, $^2J_{PP}$=27.2 Hz, P_2), 60.4 (s, P_1). ^{1}H NMR (DMF-d_7): δ=3.23 (d, $^3J_{HP2}$=7.1 Hz, 36H, $Me_{(2)}$), 3.51 (d, $^3J_{HP1}$= 9.0 Hz, 9H, $Me_{(1)}$), 7.20–8.20 (m, 159H, C_6H_5, C_6H_4, CH=N), 9.1 (br s, 24H, $B(OH)_2$); ^{13}C {^{1}H} NMR (DMF-d_7): δ=32.5–33.5 (m, $Me_{(1)}$, $Me_{(2)}$), 121.5–122.5 (m, C_0^2, C_1^2), 125.8 (s, C_2^2), 128.5 (s, C_0^3), 129.3 (d, $^3J_{CP'2}$=12.4 Hz, C^m), 130.3 (dd, $^1J_{CP'2}$=108.0 Hz, $^3J_{CP2}$=2.6 Hz, C_1^4, C^i), 133.5 (s, C_0^4, C^p), 133.4 (d, $^2J_{CP'2}$=11.2 Hz, C^o), 134.6 (d, $^3J_{CP2}$=16.7 Hz, $CH=N_{(2)}$), 134.9 (s, C_2^3), 135.7 (d, $^2J_{CP'2}$=11.9 Hz, C_1^3), 139.0 (s, C_2^1), 142.0 (br s, $CH=N_{(1)}$), 151.8 (d, $^3J_{CP0}$=7.0 Hz, C_0^1), 154.3 (d, $^3J_{CP1}$=7.2 Hz, C_1^1). Anal. Calcd for $C_{228}H_{228}B_{12}N_{36}O_{33}P_{16}S_{10}$ (4946.5): C, 55.36; H, 4.64; N, 10.19. Found: C, 55.28; H, 4.57; N, 10.12.

Synthesis of dendrimer 9d-[G_2]. To a solution of **5-[G_2]** (0.10 g, 0.03 mmol) in DMF (2 mL) was added at room temperature a solution of helicin **8d** (0.11 g, 0.39 mmol) in DMF (2 mL). The resulting solution was stirred for 24 h, then evaporated to dryness. The residue was washed 3 times with water to afford dendrimer **9d-[G_2]** as a white powder (98% yield). ^{31}P {^{1}H} NMR (DMF): δ=9.3 (d, $^2J_{PP}$=26.3 Hz, P′2), 52.1 (s, P_0), 55.9 (d, $^2J_{PP}$=26.3 Hz, P_2), 60.8 (s, P_1); ^{1}H NMR (DMSO-d_6): δ=3.20–3.80 (m, 117H, Me, CH_2, *H*COH), 4.73 (br t, 12H, OH), 4.86 (br d, $^3J_{HH}$=6.0 Hz, 12H, HC^1), 5.22 (br s, 12H, OH), 5.28 (br s, 12H, OH), 5.62 (br s, 12H, OH), 6.94 (s, 12H, HC_2^3), 7.25 (s, 12H, HC_2^5), 7.30–8.00 (m, 135H, C_6H_5, C_6H_4, CH=N); ^{13}C {^{1}H} NMR (DMSO-d_6): δ=32.6 (d, $^2J_{CP}$=10.5 Hz, $Me_{(2)}$), 32.67 (d, $^2J_{CP}$=10.5 Hz, $Me_{(2)}$), 32.7 (d, $^2J_{CP}$=10.0 Hz, $Me_{(1)}$), 62.3 (s, H_2C), 71.2 (s, C^4), 74.9 (s, C^2), 78.0 (s, C^3 or C^5), 78.6 (s, C^3 or C^5), 103.1 (s, C^1), 116.9 (br s, C_2^5), 121.0–122.0 (m, C_0^2, C_1^2), 122.3 (d, $^4J_{CP}$=3.5 Hz, C_2^1), 124.9 (d, $^3J_{CP2}$=7.2 Hz, $CH=N_{(2)}$), 125.0 (d, $^3J_{CP2}$=5.6 Hz, $CH=N_{(2)}$), 126.0 (br s, C_2^3), 127.8 (m, C_0^3), 128.8 (d, $^3J_{CP'2}$=12.9 Hz, C^m), 128.9 (s, C_2^2), 129.4 (dd, $^1J_{CP'2}$=107.6 Hz, $^3J_{CP2}$=2.5 Hz, C_1^4 or C^i), 129.8 (dd, $^1J_{CP'2}$=108.0 Hz, $^3J_{CP2}$=2.9 Hz, C_1^4 or C^i), 132.3 (s, C_0^4), 132.6 (d, $^2J_{CP'2}$=11.1 Hz, C^o), 132.7 (br s, C_2^4, C^p), 134.9 (dd, $^2J_{CP'2}$=11.8 Hz, $^4J_{CP2}$=2.8 Hz, C_1^3), 138.8 (br s, $CH=N_{(1)}$), 153.1 (br s, C_0^1), 154.3 (br s, C_1^1), 156.6 (s, C_2^2). Anal. Calcd for $C_{300}H_{336}N_{36}O_{81}P_{16}S_{10}$ (6558.4): C, 54.94; H, 5.16; N, 7.68. Found: C, 54.85; H, 5.11; N, 7.61.

General procedure for the synthesis of dendrimers 10b-[G_1] and 10b-[G_4]

To a mixture of powdered dendrimer **6-[G_n]** (n=1, 0.27 g, 0.177 mmol; n=4, 0.11 g, 0.0054 mmol) and 4-carboxybenzaldehyde (n=1, 0.16 g, 1.06 mmol; n=4, 0.04 g, 0.259 mmol) was added THF (n=1, 10 mL; n=4, 5 mL). The resulting solution was stirred overnight at room temperature, then concentrated till the volume was divided by

two. Pentane was added to precipitate **10b-[G$_n$]** as a white powder which was washed thrice with pentane/THF (10:1).

10b-[G$_1$]: yield: 0.36 g, 87%. ^{31}P {^{1}H} NMR (DMSO-d$_6$): δ=15.9 (d, $^2J_{P'1P1}$=26.1 Hz, P′$_1$), 60.6 (d, $^2J_{P1P'1}$=26.1 Hz, P$_1$), 77.9 (s, P$_0$); ^{1}H NMR (DMSO-d$_6$): δ=3.24 (d, $^3J_{HP1}$=8.2 Hz, 18H, Me$_{(1)}$), 3.37 (d, $^3J_{HP0}$=7.1 Hz, 9H, Me$_{(0)}$), 7.50–8.0 (m, 51H, C$_6$H$_5$, C$_6$H$_4$, CH=N), 7.65 (d, $^3J_{HH}$=7.8 Hz, 12H, HC$^2_2$), 7.92 (d, $^3J_{HH}$=7.8 Hz, 12H, HC$^3_2$); ^{13}C {^{1}H} NMR (DMSO-d$_6$): δ=32.7 (d, $^2J_{CP1}$=9.9 Hz, Me$_{(1)}$), 33.3 (d, $^2J_{CP0}$=7.6 Hz, Me$_{(0)}$), 125.9 (s, C$^2_2$), 126.3 (d, $^3J_{CP'1}$=12.5 Hz, C$^2_1$), 128.8 (d, $^3J_{CP'1}$=12.8 Hz, C$^m_1$), 129.2 (dd, $^1J_{CP'1}$=106.2 Hz, $^3J_{CP1}$=3.0 Hz, C$^i_1$), 129.3 (br d, $^1J_{CP'1}$=107.0 Hz, C$^4_1$), 129.6 (s, C$^3_2$), 129.7 (s, C$^4_2$), 132.5 (d, $^2J_{CP'1}$=11.4 Hz, C$^o_1$), 132.6 (s, C$^p_1$), 133.0 (d, $^2J_{CP'1}$= 12.0 Hz, C$^3_1$), 133.9 (d, $^3J_{CP1}$=14.5 Hz, CH=N$_{(2)}$), 137.5 (d, $^3J_{CP0}$=13.6 Hz, CH=N$_{(1)}$), 139.5 (br s, C$^1_1$), 140.7 (s, C$^1_2$), 167.3 (s, C=O). IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{114}H_{108}N_{21}O_{12}P_7S_4$ (2309.32): C, 59.29; H, 4.71; N, 12.73. Found: C, 59.20; H, 4.64; N, 12.68.

10b-[G$_4$]: yield: 0.14 g, 99%. ^{31}P {^{1}H} NMR (THF-d$_8$): δ=14.7 (d, $^2J_{P'4P4}$=28.5 Hz, P′$_4$), 15.3 (br d, $^2J_{PP}$= 26.8 Hz, P′$_1$, P′$_2$, P′$_3$), 59.9 (br d, $^2J_{PP}$=26.9 Hz, P$_1$, P$_2$, P$_3$, P$_4$), 76.6 (s, P$_0$); ^{1}H NMR (THF-d$_8$): δ=3.34 (br s, 279H, Me), 7.30–8.20 (m, 724H, C$_6$H$_5$, C$_6$H$_4$, CH=N), 7.67 (d, $^3J_{HH}$=6.4 Hz, 96H, HC$^2_5$), 7.97 (d, $^3J_{HH}$=6.4 Hz, 96H, HC$^3_2$); ^{13}C {^{1}H} NMR (THF-d$_8$): δ=34.3 (m, Me), 127.8 (br s, C$^2_{1-5}$), 130.4 (d, $^3J_{CP}$=11.9 Hz, C$^m_{1-4}$), 131.5 (s, C$^4_5$), 131.7 (s, C$^3_5$), 132.6 (dd, $^1J_{CP}$=104.6 Hz, $^3J_{CP}$=4.4 Hz, C$^4_{1-4}$), 132.8 (dd, $^1J_{CP}$=106.4 Hz, $^3J_{CP}$=2.9 Hz, C$^i_{1-4}$), 134.2 (m, C$^p_{1-4}$), 135.0 (m, C$^o_{1-4}$, C$^3_{1-4}$, CH=N$_{(5)}$), 137.5 (m, CH=N$_{(1-4)}$), 143.2 (br s, C$^1_{1-4}$), 143.4 (s, C$^1_5$), 168.8 (s, C=O). IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{1332}H_{1242}N_{231}O_{96}P_{91}S_{46}$ (26315): C, 60.79; H, 4.75; N, 12.29. Found: C, 60.69; H, 4.68; N, 12.24.

General procedure for the synthesis of dendrimers 10c-[G$_1$] and 10c-[G$_4$]

To a solution of dendrimer **6-[G$_n$]** (n=1, 0.30 g, 0.198 mmol; n=4, 0.106 g, 0.0053 mmol) in THF (n=1, 5 mL; n=4, 2 mL) was added a solution of 4-formylphenylboronic acid (n=1, 0.18 g, 1.19 mmol, n=4; 0.038 g, 0.255 mmol) in THF (n=1, 5 mL; n=4, 3 mL). A white precipitate appeared, and disappeared after stirring overnight at room temperature. The solution was evaporated to dryness and the residue was washed thrice with pentane/THF (5:1), to afford **10c-[G$_n$]** as a powder, very insoluble in most organic solvents.

10c-[G$_1$]: Pale yellow powder; yield: 0.43 g, 94%. ^{31}P {^{1}H} NMR (DMF-d$_7$): δ=15.3 (d, $^2J_{P'1P1}$=27.3 Hz, P′$_1$), 60.8 (d, $^2J_{P1P'1}$=27.3 Hz, P$_1$), 77.8 (s, P$_0$); ^{1}H NMR (DMF-d$_7$): δ=3.18 (d, $^3J_{HP1}$=9.0 Hz, 18H, Me$_{(1)}$), 3.34 (d, $^3J_{HP0}$= 8.5 Hz, 9H, Me$_{(0)}$), 7.44–7.93 (m, 51H, C$_6$H$_5$, C$_6$H$_4$, CH=N), 7.49 (d, $^3J_{HH}$=8.0 Hz, 12H, HC$^3_2$), 7.78 (d, $^3J_{HH}$=8.0 Hz, 12H, HC$^2_2$); ^{13}C {^{1}H} NMR (DMF-d$_7$): δ=33.0 (d, $^2J_{CP1}$=10.3 Hz, Me$_{(1)}$), 33.8 (d, $^2J_{CP0}$=8.1 Hz, Me$_{(0)}$), 125.8 (s, C$^2_2$), 126.8 (d, $^3J_{CP'1}$=13.7 Hz, C$^2_1$), 129.3 (d, $^3J_{CP'1}$=12.8 Hz, C$^m_1$), 130.3 (dd, $^1J_{CP'1}$=106.0 Hz, $^3J_{CP1}$=3.0 Hz, C$^4_1$), 130.6 (dd, $^1J_{CP'1}$=107.5 Hz, $^3J_{CP1}$= 3.5 Hz, C$^i_1$), 133.2 (s, C$^p_1$), 133.5 (d, $^2J_{CP'1}$=10.9 Hz, C$^o_1$), 133.9 (d, $^2J_{CP'1}$=11.2 Hz, C$^3_1$), 134.4 (br s, C$^4_2$), 135.0 (s, C$^3_2$), 135.7 (d, $^3J_{CP1}$=14.3 Hz, CH=N$_{(2)}$), 138.3 (d, $^3J_{CP0}$= 13.5 Hz, CH=N$_{(1)}$), 139.1 (s, C$^1_2$), 140.3 (d, $^4J_{CP}$=2.8 Hz, C$^1_1$). Anal. Calcd for $C_{108}H_{114}B_6N_{21}O_{12}P_7S_4$ (2308.2): C, 56.20; H, 4.97; N, 12.74. Found: C, 56.08; H, 4.88; N, 12.67.

10c-[G$_4$]: White powder; yield: 0.12 g, 83%. ^{31}P {^{1}H} NMR (DMF-d$_7$): δ=15.4 (d, $^2J_{P'4P4}$=26.6 Hz, P′$_4$), 16.3 (br d, $^2J_{PP}$=27.5 Hz, P′$_1$, P′$_2$, P′$_3$), 60.5 (br d, $^2J_{PP}$=27.5 Hz, P$_1$, P$_2$, P$_3$), 60.7 (br d, $^2J_{P4P'4}$=26.6 Hz, P$_4$), 73.0 (s, P$_0$); ^{1}H NMR(DMF-d$_7$): δ=3.26 (br s, 279H, Me), 7.54–8.00 (m, 723H, C$_6$H$_5$, C$_6$H$_4$, CH=N), 7.56 (d, $^3J_{HH}$=7.6 Hz, 96H, HC$^3_5$), 7.84 (d, $^3J_{HH}$=7.6 Hz, 96H, HC$^2_2$), 8.22 (br s, 96H, OH); ^{13}C {^{1}H} NMR (DMF-d$_7$): δ=33.0 (d, $^2J_{CP5}$=10.0 Hz, Me$_{(5)}$), 33.3 (br d, $^2J_{CP}$=9.4 Hz, Me$_{(1-4)}$), 125.8 (s, C$^2_5$), 126.3 (br d, $^3J_{CP}$=12.5 Hz, C$^2_{1-4}$), 129.2 (d, $^3J_{CP'4}$=12.6 Hz, C$^m_4$), 129.3 (d, $^3J_{CP}$=12.5 Hz, C$^m_{1-3}$), 130.2 (br d, $^1J_{CP'1}$= 106.0 Hz, C$^4_1$, C$^i_1$), 132.9 (br dd, $^1J_{CP}$=105.0 Hz, $^3J_{CP}$= 2.4 Hz, C$^4_{2,3}$, C$^i_{2,3}$), 130.7 (br dd, $^1J_{CP'4}$=109.5 Hz, $^3J_{CP4}$= 2.0 Hz, C$^4_4$, C$^i_4$), 133.2 (m, C$^p_{1-4}$), 133.5 (d, $^2J_{CP'4}$=10.6 Hz, C$^o_4$, C$^3_4$), 133.6 (m, C$^o_{1-3}$, C$^3_{1-3}$), 134.4 (br s, C$^4_5$), 135.0 (s, C$^3_5$), 135.6 (d, $^3J_{CP4}$=14.1 Hz, CH=N$_{(5)}$), 137.6 (m, CH=N$_{(1-4)}$), 139.1 (s, C$^1_5$), 141.4 (m, C$^1_{1-4}$). Anal. Calcd for $C_{1284}H_{1290}B_{48}N_{231}O_{96}P_{91}S_{46}$ (26306): C, 58.62; H, 4.94; N, 12.30. Found: C, 58.54; H, 4.87. N, 12.21.

General procedure for the synthesis of dendrimer 10d-[G$_1$] and 10d-[G$_4$]

To a mixture of powdered dendrimer **6-[G$_n$]** (n=1, 0.20 g, 0.132 mmol, n=4, 0.096 g, 0.0048 mmol) and helicin (n=1, 0.22 g, 0.791 mmol; n=4, 0.066 g, 0.231 mmol) was added DMF (n=1, 3 mL; n=4, 5 mL). The resulting solution was stirred overnight, then evaporated to dryness. The residue was washed thrice with pentane/THF/DMF (10:5:1) to give dendrimer **10d-[G$_n$]** as a powder.

10d-[G$_1$]: White powder; yield: 0.40 g, 98%. ^{31}P {^{1}H} NMR (DMF-d$_7$): δ=15.0 (d, $^2J_{P'1P1}$=28.6 Hz, P′$_1$), 60.9 (d, $^2J_{P1P'1}$=28.6 Hz, P$_1$), 77.8 (s, P$_0$); ^{1}H NMR (DMF-d$_7$): δ=3.23 (d, $^3J_{HP1}$=8.7 Hz, 9H, Me$_{(1)}$), 3.25 (d, $^3J_{HP0}$= 8.7 Hz, 9H, Me$_{(1)}$), 3.30–3.90 (m, 45H, HC-glucose, CH$_2$, Me$_{(0)}$), 4.81 (br s, 6H, OH), 4.90 (md, $^3J_{HH}$=6.5 Hz, 6H, HC^1), 5.25 (br s, 12H, OH), 5.61 (br s, 6H, OH), 6.91 (t, $^3J_{HH}$=7.3 Hz, 6H, HC$^3_2$), 7.23 (m, 12H, HC$^4_2$, HC$^5_2$), 7.56–8.00 (m, 57H, C$_6$H$_5$, C$_6$H$_4$, CH=N); ^{13}C {^{1}H} NMR (DMF-d$_7$): δ=32.93 (d, $^2J_{CP1}$=9.9 Hz, Me$_{(1)}$), 33.03 (d, $^2J_{CP1}$= 9.9 Hz, Me$_{(1)}$), 33.9 (d, $^2J_{CP0}$=7.9 Hz, Me$_{(0)}$), 62.2 (s, CH$_2$), 71.1 (s, C^4), 74.7 (s, C^2), 78.0 (s, C^3 or C^5), 78.2 (s, C^3 or C^5), 102.8 (s, C^1), 117.4 (s, C$^5_2$), 122.8 (s, C$^3_2$), 125.7 (s, C$^2_2$), 126.9 (d, $^3J_{CP'1}$=12.9 Hz, C$^2_1$), 127.0 (s, C$^1_2$), 129.3 (d, $^3J_{CP'1}$=12.5 Hz, C$^m_1$), 129.4 (br s, C$^4_2$), 130.6 (dd, $^1J_{CP'1}$= 106.9 Hz, $^3J_{CP1}$=2.8 Hz, C$^4_1$, C$^i_1$), 131.2 (br d, $^2J_{CP1}$= 11.6 Hz, CH=N$_{(2)}$), 133.2 (s, C$^p_1$), 133.6 (d, $^2J_{CP'1}$=10.9 Hz, C$^o_1$), 133.9 (d, $^2J_{CP'1}$=11.6 Hz, C$^3_1$), 138.5 (br d, CH=N$_{(1)}$), 140.3 (d, $^4J_{CP}$=2.7 Hz, C$^1_1$), 156.1 (s, C$^6_2$). Anal. Calcd for $C_{144}H_{168}N_{21}O_{36}P_7S_4$ (3114.1): C, 55.54; H, 5.43; N, 9.44. Found: C, 55.48; H, 5.37; N, 9.38.

10d-[G$_4$]: Pale yellow powder; yield: 0.12 g, 74%. ^{31}P {^{1}H} NMR (DMF-d$_7$): δ=15.1 (d, $^2J_{P'4P4}$=28.7 Hz, P′$_4$), 16.4 (d, $^2J_{PP}$=27.1 Hz, P′$_1$, P′$_2$, P′$_3$), 60.6 (d, $^2J_{PP}$=27.1 Hz, P$_1$, P$_2$, P$_3$), 60.9 (d, $^2J_{P4P'4}$=28.7 Hz, P$_4$), 77.5 (s, P$_0$); ^{1}H NMR

(DMF-d_7): δ=3.00–4.00 (m, 567H, Me, HC-glucose, CH_2), 4.84 (br s, 48H, OH), 4.93 (m, 48H, HC^1), 5.28 (m, 96H, OH), 5.65 (m, 48H, OH), 6.91 (m, 48H, HC^3_5), 7.24 (m, 96H, HC^4_5, HC^5_5), 7.55–8.26 (m, 771H, C_6H_5, C_6H_4, CH=N); $^{13}C\{^1H\}$ NMR (DMF-d_7): δ=32.97 (d, $^2J_{CP4}$=9.8 Hz, $Me_{(4)}$), 33.04 (d, $^2J_{CP4}$=10.2 Hz, $Me_{(4)}$), 33.4 (d, $^2J_{CP}$=9.3 Hz, $Me_{(0-3)}$), 62.2 (s, CH_2), 71.1 (s, C^4), 74.6 (s, C^2), 78.0 (s, C^3 or C^5), 78.1 (s, C^3 or C^5), 102.8 (s, C^1), 117.4 (s, C^5_5), 122.8 (s, C^3_5), 125.6 (s, C^2_5), 126.5 (m, C^2_{1-4}), 127.0 (s, C^1_5), 129.3 (m, C^m_{1-4}, C^4_5), 130.0 (br d, $^1J_{CP'1}$=106.0 Hz, C^4_1, C^i_1), 130.2 (br d, $^1J_{CP}$=106.0 Hz, $C^4_{2,3}$, $C^i_{2,3}$), 130.8 (dd, $^1J_{CP'4}$=108.4 Hz, $^3J_{CP4}$=2.0 Hz, C^4_4, C^i_4), 131.2 (br d, $CH{=}N_{(5)}$), 133.4 (m, C^p_{1-4}, C^o_{1-4}, C^3_{1-4}), 138.0 (m, $CH{=}N_{(1-4)}$), 141.3 (m, C^1_{1-4}), 156.0 (s, C^6_5). Anal. Calcd for $C_{1572}H_{1722}N_{231}O_{288}P_{91}S_{46}$ (32754): C, 57.64; H, 5.29; N, 9.87. Found: C, 57.57; H, 5.22; N, 9.82.

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