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A new way for the internal functionalization of dendrimers

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Abstract—The selective reaction of amines and hydrazides with only one Cl on each $P(S)Cl_2$ or $P(O)Cl_2$ end group of phosphorus dendrimers, followed by the grafting of hydroxybenzaldehyde on the remaining P–Cl functions, and the subsequent growing of the dendrimer from the aldehyde is described. Allyl and pyrene derivatives have been grafted in this way inside the dendrimers during their growing. This constitutes a new way for the internal functionalization of dendrimers.
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Despite the huge number of reports concerning dendrimers over the last two decades (more than 7000), designing functional dendrimers continue to be the matter of intensive studies. Introducing functions at the periphery is the easiest way for synthetic considerations. Numerous works also concern functions introduced at the core, but in most cases, the dendrimer backbone has no particular function and acts only as support of the periphery. However, in order to enhance the level of sophistication of these special macromolecules, it is highly desirable to introduce functional groups also in the backbone.[1] This requirement has been achieved up to now following two main ways, called *way a*, and *way b* in Scheme 1. *Way a* consists in using a branched monomer bearing three types of functions generally derived from a classical AB_2 monomer in which either one B function has been replaced by C (ABC monomer) or one C function is added (AB_2C monomer).[1,2] *Way b* uses a monomer in which a Z function is introduced in the linear part[1,3] and can be reacted later; we have largely developed this concept previously.[4] Another way (*way c*) should consist in reacting specifically one function on two, on the periphery of the dendrimer and to use the remaining one to continue the growing of the dendrimer. To the best of our knowledge, the use of such a way for functionalizing the interior of dendrimers is unprecedented, even if an example related to this
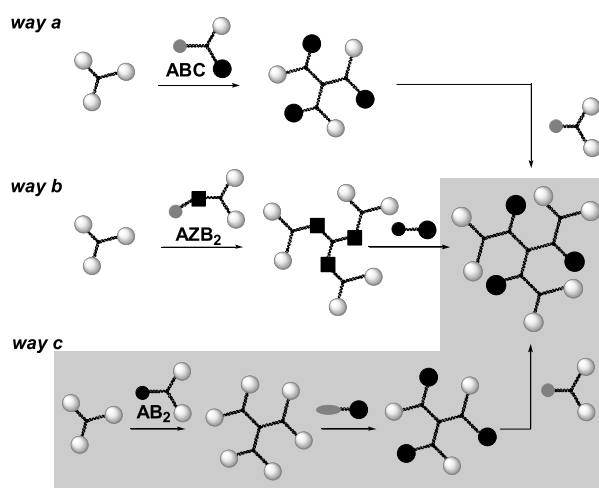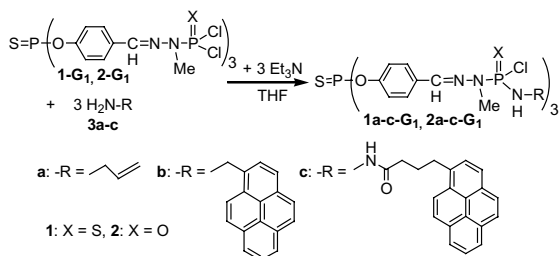

Scheme 1.

concept was described: it consisted in the selective grafting of one dansyl unit on each NH_2 end groups of poly(propylene amine) dendrimers,[5] followed by the grafting of one pre-synthesized dendron on each remaining NH.[6] On the other hand, we have previously reported the possibility to react selectively one on two of each end group[7] of phosphorus-containing dendrimers,[8] in particular for $P(X)Cl_2$ (X = S, O) end groups.[9] In some cases, the remaining Cl are available for further reactions either with amines or phenols. In this paper, we report for the first time that the growing of the dendrimer can be continued starting from the remaining Cl, to afford dendrimers possessing functions inside their structure.

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Scheme 2.

The selective reaction of one Cl on each end group was previously carried out with two simple amines, allylamine (**3a**) and propargylamine, on dendrimers having either P(S)Cl$_2$ (**1**) or P(O)Cl$_2$ (**2**) end groups.[9] In order to check the scope of uses of this reaction, we decided to attempt it with an amine bearing a bulky substituent and also with a hydrazide derivative. Due to the interesting fluorescence properties of pyrene derivatives that we already used as probes for sensing the interior of dendrimers,[10] we chose the aminomethylpyrene **3b** and the pyrenebutanoic hydrazide **3c**. Both reactions were carried out with dendrimers **1-G$_1$** (P(S)Cl$_2$ end groups) and **2-G$_1$** (P(O)Cl$_2$ end groups), in the presence of NEt$_3$ in THF (Scheme 2). The amino derivative **3b** is added at 0 °C, then stirred at room temperature with dendrimers **1-G$_1$** and **2-G$_1$**. The hydrazide **3c** reacts more slowly in these conditions, thus the reaction with dendrimer **1-G$_1$** was carried out at 35 °C.

All these reactions are monitored by ^{31}P NMR (the numbering used for NMR is shown in Fig. 1). The monosubstitution induces an important deshielding of the signal of the P(S) end groups that undergo the reaction, from 63.1 ppm for **1-G$_1$** to ca. 73 ppm for **1a–c-G$_1$**. No trace of disubstitution is detected, as evidenced for **1a-G$_1$**, whose chemical shift corresponding to the disubstitution is known to be different ($\delta = 68.9$ ppm).[11] On the other hand, reactions with dendrimer **2-G$_1$** induce smaller changes in the ^{31}P NMR chemical shift ($\Delta\delta$ less than 2 ppm), but two signals for the end groups are observed in all cases during the course of the reaction, corresponding to P(O)Cl$_2$ and P(O)ClNHR. ^{1}H NMR spectra also provide information, for instance the deshielding of the signal corresponding to the CH$_2$ group of aminomethylpyrene, from 4.6 ppm for **3b** to ca. 5 ppm for **1b-G$_1$** and **2b-G$_1$**.[12]

The next step for growing the dendrimers by our classical method[8] should be the grafting of hydroxybenzaldehyde on the remaining Cl in the presence of a base. Our previous attempts to carry out this reaction on **1a-**
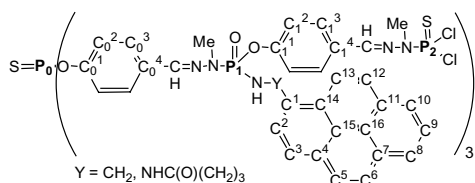
G$_1$ failed (no reaction observed), thus we tried several bases (NEt$_3$, sodium salt, K$_2$CO$_3$, Cs$_2$CO$_3$, etc.) on this compound and on **1b,c-G$_1$**, but either no reaction was observed or the dendrimer backbone was broken in hard conditions (prolonged heating). On the other hand, the reaction of hydroxybenzaldehyde sodium salt occurs easily with dendrimers **2a–c-G$_1$** (P(O)ClNHR end groups), and affords cleanly the expected dendrimers **2a–c-G$_1'$** (Scheme 3).[13] In this case also, ^{31}P NMR is a precious tool for characterizing these compounds. Indeed, the nucleophilic substitution induces an important shielding of the signal corresponding to the P(O) groups from δ ca. 19 ppm for **2a–c-G$_1$** to δ ca. 8 ppm for the amino derivatives **2a,b-G$_1'$** and 0.2 ppm for the hydrazido derivative **2c-G$_1'$**. These data demonstrate again the absence of P(O)Cl$_2$ groups in the starting compounds (**2a–c-G$_1$**), whose substitution with hydroxybenzaldehyde is known to give a different chemical shift ($\delta = -6.8$ ppm).[14]

The second step for growing the dendrimer is the condensation reaction with the phosphorhydrazide **4**. The reaction affords cleanly dendrimers **2a–c-G$_2$**, and induces the appearance of a new signal in ^{31}P NMR ($\delta = 63.3$ ppm) corresponding to P(S)Cl$_2$. Obviously, the condensation reaction is also shown by ^{1}H and ^{13}C NMR spectra, with the disappearance of the signals corresponding to the aldehydes.[15] It can be noted that no reaction is observed between the P–Cl and NH functions of **2a–c-G$_2$**. The sequence of reactions **2a–c-G$_1$** → **2a–c-G$_1'$** → **2a–c-G$_2$** constitutes the whole cycle of synthesis of dendrimers. The synthesis could have been pursued by repeating the nucleophilic substitution with hydroxybenzaldehyde sodium salt and the condensation reaction with the phosphorhydrazide **4**, but our aim was to demonstrate the feasibility of the above mentioned synthetic pathway for the internal functionalization of dendrimers; the achievement of this goal is shown by the obtaining of dendrimers **2a–c-G$_2$** (Fig. 2), and it did not appeared necessary to continue the growing. Nevertheless, the easy implementation of this synthetic pathway is further demonstrated by the synthesis of compound **2a-G$_2'$**, obtained by the reaction of hydroxybenzaldehyde sodium salt with **2a-G$_2$**.[16]

Figure 1. Numbering used for NMR assignments (in CDCl$_3$).
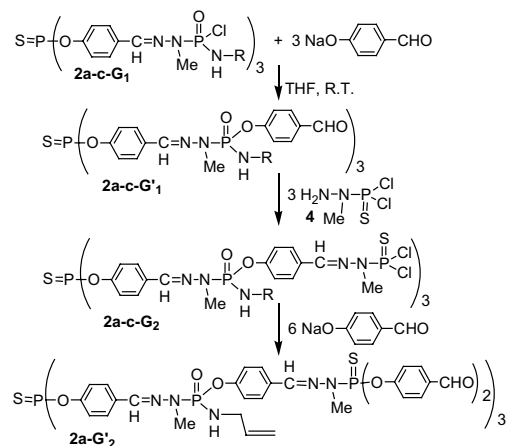
Scheme 3.
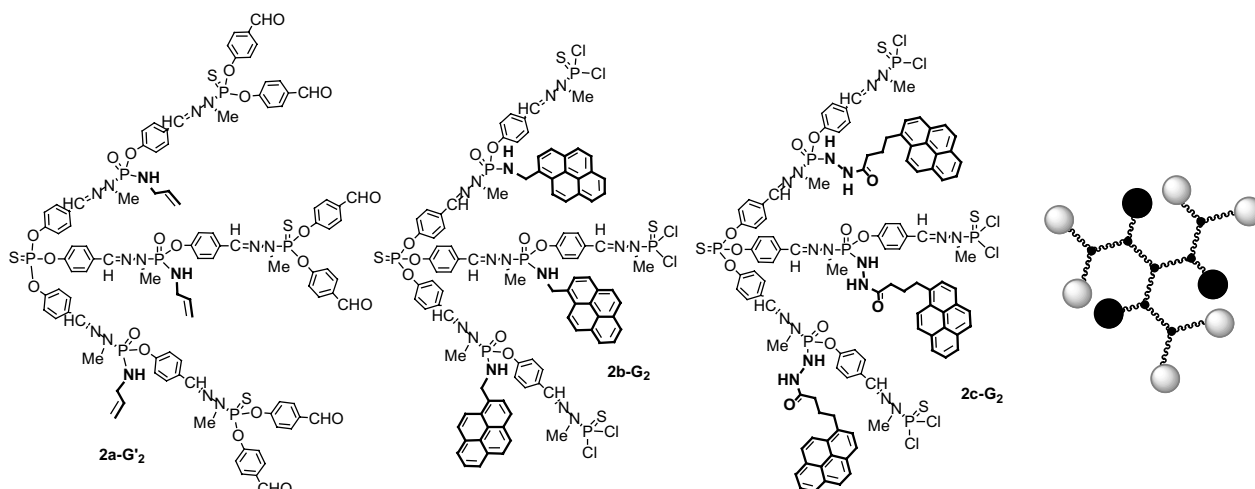
Figure 2. Chemical structure of the largest internally functionalized dendrimers synthesized in each series.

Thus, the specific reactivity of phosphorus allows the easy synthesis of original dendrimers bearing functions both inside and on the periphery. The variety of RNH_2 compounds used in this study shows that this strategy will be applicable to a large number of substituents, and should easily afford highly sophisticated macromolecules.

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12. General procedure for the synthesis of dendrimers **1a–c-G₁** and **2a–c-G₁**. A solution of amine **3a,b** or hydrazide **3c** (1.5 mmol) in THF (20 mL) was added dropwise at 0 °C to a solution of dendrimer **1-G₁** or **2-G₁** (0.5 mmol) in THF (20 mL). This mixture was stirred overnight at room temperature or at 35 °C for 72 h for **1-G₁** and **3c**. After filtration, the solvent was removed under vacuum to give either directly a powder or an oil, which was precipitated by adding pentane. The resulting powder was washed with ether/pentane (5:3) to afford **1a-G₁**,[9] **2a-G₁**[9] as white powders and **1b,c-G₁**, **2b,c-G₁** as yellow powders. Compound **1b-G₁**: 81% yield. ³¹P{¹H} NMR: 52.3 (s, P_0), 72.5 (s, P_1). ¹H NMR: 3.34 (d, $^3J_{HP1}$ = 13.3 Hz, 9H, CH_3NP_1), 5.07 (m, 6H, CH_2), 6.98 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HP0}$ = 1.8 Hz, 6H, C_0^2), 7.36 (d, $^4J_{HP1}$ = 2.4 Hz, 3H, CH=NNP₁), 7.43 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_0^3H), 7.8–8.2 (m, 27H, Pyr). ¹³C{¹H} NMR: 30.8 (d, $^2J_{CP1}$ = 10.5 Hz, CH_3NP_1), 62.6 (s, CH_2), 121.4 (br s, C_0^2), 122.8 (s, C^{13}), 125.0 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.3 (s, C^9), 126.4 (s, C^5), 127.0 (m, C^2, C^6, C^{12}), 128.4 (s, C_0^3), 129.4–132.8 (m, C^7, C^{14}, C_0^4), 133.5 (s, C^1), 138.2 (d, $^3J_{CP1}$ = 15.5 Hz, CH=NNP₁), 150.0 (br s, C_0^1). Anal. Calcd for $C_{75}H_{60}Cl_3N_9O_3P_4S_4$ (1494): C, 60.30; H, 4.05; N, 8.44. Found: C, 60.83; H, 4.01; N, 8.12. Compound **1c-G₁**: 67% yield. ³¹P{¹H} NMR: 52.5 (s, P_0), 73.0 (s, P_1). ¹H NMR: 2.21 (m, 6H, $CH_2CH_2CH_2$), 2.82 (m, 6H, CH_2–Pyr), 3.02 (d, $^3J_{HP1}$ = 7.3 Hz, 9H, CH_3NP_1), 3.41 (t, $^3J_{HH}$ = 7.2 Hz, CH_2CO), 7.15 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HP0}$ = 1.7 Hz, 6H, C_0^2H), 7.44 (d, $^4J_{HP1}$ = 2.5 Hz, 3H, CH=NNP₁), 7.50 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_0^3H), 7.8–8.1 (m, 27H, Pyr). ¹³C{¹H} NMR: 26.5 (s, $CH_2CH_2CH_2$), 30.9 (br s, CH_3NP_1), 32.3 (s, CH_2–Pyr), 34.0 (s, CH_2CO), 121.2 (d, $^3J_{CP0}$ = 3 Hz, C_0^2), 123.3 (s, C^{13}), 124.7 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.7 (s, C^9), 126.6 (s, C^5), 127.3 (m, C^2, C^6, C^{12}), 128.3 (s, C_0^3), 129.4–130.3 (m, C^7, C^{14}), 132.2 (s, C_0^4), 135.9 (s, C^1), 139.1 (d, $^3J_{CP1}$ = 15.4 Hz, CH=NNP₁), 150.1 (d, $^2J_{CP0}$ = 7.8 Hz, C_0^1), 175.9 (s, CO). Anal. Calcd for $C_{84}H_{75}Cl_3N_{12}O_6P_4S_4$ (1707): C, 59.10; H, 4.43; N, 9.85. Found: C, 59.43; H, 4.52; N, 9.95. Compound **2b-G₁**: 78% yield. ³¹P{¹H} NMR: 20.2 (s, P_1), 52.4 (s, P_0). ¹H NMR: 3.22 (d, $^3J_{HP1}$ = 9.9 Hz, 9H, CH_3NP_1), 4.25 (br s, 3H, NH), 4.97 (br m, CH_2), 7.02 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP0}$ = 1.5 Hz, 6H, C_0^2H), 7.40 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_0^3H), 7.47 (d, $^4J_{HP1}$ = 1.5 Hz, 3H, CH=NNP₁), 7.7–8.3 (m, 27H, Pyr).

$^{13}C\{^1H\}$ NMR: 29.8 (d, $^2J_{CP1}$ = 8.5 Hz, CH_3NP_1), 61.1 (s, CH_2), 120.8 (br s, C_0^2), 122.8 (s, C^{13}), 125.0 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.3 (s, C^9), 126.4 (s, C^5), 127.0 (m, C^2, C^6, C^{12}), 127.8 (s, C_0^3), 129.4–132.8 (m, C^7, C^{14}, C_0^4), 133.5 (s, C^1), 138.2 (d, $^3J_{CP1}$ = 7.8 Hz, CH=NNP$_1$), 150.7 (br s, C_0^1). Anal. Calcd for $C_{75}H_{60}Cl_3N_9O_6P_4S$ (1445.7): C, 63.31; H, 4.18; N, 8.72. Found: C, 63.48; H, 4.23; N, 8.68. Compound **2c-G$_1$**: 65% yield. $^{31}P\{^1H\}$ NMR: 52.4 (s, P_0), 18.9 (s, P_1). ^1H NMR: 2.21 (m, 6H, $CH_2CH_2CH_2$), 2.82 (m, 6H, CH_2–Pyr), 3.02 (d, $^3J_{HP1}$ = 7.3 Hz, 9H, CH_3NP_1), 3.41 (t, $^3J_{HH}$ = 7.2 Hz, CH_2CO), 7.15 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HP0}$ = 1.7 Hz, 6H, C_0^2H), 7.44 (d, $^4J_{HP1}$ = 2.5 Hz, 3H, CH=NNP$_1$), 7.50 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_0^3H), 7.8–8.1 (m, 27H, Pyr). $^{13}C\{^1H\}$ NMR: 26.5 (s, $CH_2CH_2CH_2$), 29.9 (d, $^3J_{HP1}$ = 10.5 Hz, CH_3NP_1), 32.3 (s, CH_2–Pyr), 33.5 (s, CH_2CO), 120.9 (d, $^3J_{CP0}$ = 3 Hz, C_0^2), 123.3 (s, C^{13}), 124.7 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.7 (s, C^9), 126.6 (s, C^5), 127.3 (m, C^2, C^6, C^{12}), 127.8 (s, C_0^3), 129.4–130.3 (m, C^7, C^{14}), 131.9 (s, C_0^4), 135.9 (s, C^1), 138.1 (d, $^3J_{CP1}$ = 17.2 Hz, CH=NNP$_1$), 150.5 (d, $^2J_{CP0}$ = 7.8 Hz, C_0^1), 175.9 (s, CO). Anal. Calcd for $C_{84}H_{75}Cl_3N_{12}O_9P_4S$ (1659): C, 60.82; H, 4.56; N, 10.13. Found: C, 61.27; H, 4.59; N, 9.96.

13. General procedure for the synthesis of dendrimers **2a–c-G$_1'$**. Powdered hydroxybenzaldehyde sodium salt (1.2 mmol) was added to a solution of dendrimer **2a–c-G$_1$** (0.4 mmol) in THF (30 mL), and stirred for 1 h at room temperature. The resulting mixture was filtered and the solution was evaporated to dryness to afford a powder which was washed three times with ether. Compound **2a-G$_1$**[9] was isolated as a white powder, **2b–c-G$_1$** as yellow powders. Compound **2b-G$_1'$**: 80% yield. $^{31}P\{^1H\}$ NMR: 7.7 (s, P_1), 52.6 (s, P_0). ^1H NMR: 3.04 (d, $^3J_{HP1}$ = 7.3 Hz, 9H, CH_3NP_1), 4.89 (br s, 3H, NH), 5.45 (br s, 6H, CH_2), 6.90 (d, $^3J_{HH}$ = 8.8 Hz, 6H, C_1^2H), 7.3–7.6 (m, 15H, CH=NNP$_1$, C_0^2H, C_0^3H), 7.65 (d, $^3J_{HH}$ = 8.8 Hz, 6H, C_1^3H), 7.8–8.1 (m, 27H, Pyr), 9.73 (s, 3H, CHO). $^{13}C\{^1H\}$ NMR: 32.3 (d, $^3J_{CP1}$ = 10 Hz, CH_3–N–P$_1$), 62.4 (s, CH_2), 121.4 (br s, C_0^2), 121.6 (br s, C_1^2), 122.8 (s, C^{13}), 125.0 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.3 (s, C^9), 126.4 (s, C^5), 127.0 (m, C^2, C^6, C^{12}), 127.8 (s, C_0^3), 129.4–132.8 (m, C^7, C^{14}, C_1^3, C_0^4, C_1^4), 133.5 (s, C^1), 137.5 (br s, CH=NNP$_1$), 151.0 (br s, C_0^1), 152.8 (br s, C_1^1), 191.4 (CHO). Anal. Calcd for $C_{96}H_{75}N_9O_{12}P_4S$ (1702.7): C, 67.72; H, 4.44; N, 7.40. Found: C, 67.51; H, 4.60; N, 7.36. **2c-G$_1'$**: 75% yield. $^{31}P\{^1H\}$ NMR: 0.2 (s, P_1), 52.4 (s, P_0). ^1H NMR: 2.34 (m, 6H, $CH_2CH_2CH_2$), 2.91 (m, 6H, CH_2–Pyr), 3.48 (d, $^3J_{HP1}$ = 6.9 Hz, 9H, CH_3NP_1), 3.77 (m, CH_2CO), 6.96 (d, $^3J_{HH}$ = 8.7 Hz, 6H, C_1^2H), 7.2–7.8 (m, 15H, CH=NNP$_1$, C_0^2H, C_0^3H), 7.50 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_1^3 H), 7.8–8.1 (m, 27H, Pyr), 9.89 (s, 3H, CHO). $^{13}C\{^1H\}$ NMR: 27.5 (s, $CH_2CH_2CH_2$), 31.9 (d, $^3J_{CP1}$ = 10.5 Hz, CH_3NP_1), 33.8 (s, CH_2–Pyr), 34.1 (s, CH_2CO), 121.2 (d, $^3J_{CP0}$ = 3.4 Hz, C_0^2), 121.5 (d, $^3J_{CP1}$ = 3.8 Hz, C_1^2), 123.3 (s, C^{13}), 124.7 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.7 (s, C^9), 126.6 (s, C^5), 127.3 (m, C^2, C^6, C^{12}), 127.9 (s, C_0^3), 129.4–130.3 (m, C^7, C^{14}), 131.5 (s, C_1^3), 132.2 (s, C_0^4), 132.9 (s, C_1^4), 135.9 (s, C^1), 137.3 (d, $^3J_{CP1}$ = 15.0 Hz, CH=NNP$_1$), 150.8 (d, $^2J_{CP0}$ = 7.8 Hz, C_0^1), 155.7 (d, $^2J_{CP1}$ = 3.2 Hz, C_1^1), 174.8 (s, CO), 190.5 (s, CHO). Anal. Calcd for $C_{105}H_{90}N_{12}O_{15}P_4S$ (1916): C, 65.83; H, 4.73; N, 8.77. Found: C, 65.84; H, 4.92; N, 8.66.

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15. General procedure for the synthesis of dendrimers **2a–c-G$_2$**. Powdered dendrimer **2a–c-G$_1'$** (0.3 mmol) was added to a solution of phosphorhydrazide **4** (0.9 mmol) in CHCl$_3$ (5 mL) and stirred at room temperature for 30 min. The solution was evaporated to dryness and the resulting powder was washed with pentane/ether to afford **2a-G$_2$** as

a white powder and **2b,c-G$_2$** as yellow powders. Compound **2a-G$_2$**: 99% yield. $^{31}P\{^1H\}$ NMR: 7.8 (s, P_1), 52.7 (s, P_0), 63.3 (s, P_2). ^1H NMR: 3.15 (d, $^3J_{HP}$ = 7.3 Hz, 9H, Me–N–P$_1$), 3.2 (br m, 3H, NH), 3.45 (d, $^3J_{HP}$ = 13 Hz, 9H, Me–N–P$_2$), 3.81 (m, 6H, –CH$_2$), 5.09 (dd, $^3J_{HHcis}$ = 10 Hz, $^2J_{HHgem}$ = 1.4 Hz, 3H, =CH$_2$), 5.24 (dd, $^3J_{HHtrans}$ = 17 Hz, $^2J_{HHgem}$ = 1.4 Hz, 3H, =CH$_2$), 5.9 (m, 3H, =CH), 7.2–7.7 (m, 30H, ArH, CH=N). $^{13}C\{^1H\}$ NMR: 31.8 (d, $^2J_{CP}$ = 13.5 Hz, CH$_3$–N–P$_2$), 31.9 (d, $^2J_{CP}$ = 8 Hz, CH$_3$–N–P$_1$), 44.1 (s, –CH$_2$), 115.9 (s, =CH$_2$), 121.2 (d, $^3J_{CP}$ = 5 Hz, C_0^2), 121.5 (d, $^3J_{CP}$ = 4 Hz, C_1^2), 127.9 (s, C_0^3), 128.8 (s, C_1^3), 130.8 (s, C_0^4), 133.0 (s, C_1^4), 135.9 (d, $^3J_{CP}$ = 6 Hz, CH=), 136.5 (d, $^3J_{CP}$ = 14.8 Hz, CH=NNP$_1$), 140.8 (d, $^3J_{CP}$ = 19 Hz, CH=NNP$_2$), 150.8 (d, $^2J_{CP}$ = 8 Hz, C_0^1), 152.2 (d, $^2J_{CP}$ = 7 Hz, C_1^1). Anal. Calcd for $C_{57}H_{66}Cl_6N_{15}O_9P_7S_4$ (1663): C, 41.17; H, 4.00; N, 12.63. Found: C, 41.05; H,3.94; N, 12.51. Compound **2b-G$_2$**: 93% yield. $^{31}P\{^1H\}$ NMR: 7.7 (s, P_1), 52.6 (s, P_0), 63.3 (s, P_2). ^1H NMR: 3.12 (d, $^3J_{HP1}$ = 7.3 Hz, 9H, CH_3NP_1), 3.37 (d, $^3J_{HP1}$ = 14 Hz, 9H, CH_3NP_2), 4.81 (br s, 3H, NH), 5.52 (br s, 64H, CH$_2$), 6.9–7.6 (m, 30H, CH=N, C_{0-1}^2H, C_{0-1}^3H), 7.8–8.1 (m, 27H, Pyr). $^{13}C\{^1H\}$ NMR: 32.0 (d, $^2J_{CP}$ = 13 Hz, CH_3NP_2), 32.2 (d, $^2J_{CP}$ = 10 Hz, CH$_3$–N–P$_1$), 62.4 (s, CH_2), 121.3 (br s, C_0^2), 121.6 (br s, C_1^2), 122.8 (s, C^{13}), 125.0 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.3 (s, C^9), 126.4 (s, C^5), 127.0 (m, C^2, C^6, C^{12}), 127.8 (s, C_0^3), 128.1 (s, C_1^3), 129.4–132.8 (m, C^7, C^{14}, C_2^3, C_0^4, C_1^4), 133.5 (s, C^1), 136.9 (br s, CH=NNP$_1$), 140.2 (br s, CH=NNP$_2$), 150.9 (br s, C_0^1), 152.5 (br s, C_1^1). Anal. Calcd for $C_{99}H_{84}Cl_6N_{15}O_9P_7S_4$ (2186): C, 54.41; H, 3.87; N, 9.61. Found: C, 54.12; H, 3.82; N, 9.97. Compound **2c-G$_2$**: 91% yield. $^{31}P\{^1H\}$ NMR: 0.2 (s, P_1), 52.4 (s, P_0), 63.2 (s, P_2). ^1H NMR: 2.41 (m, 6H, $CH_2CH_2CH_2$), 2.98 (m, 6H, CH_2–Pyr), 3.15 (d, $^3J_{HP1}$ = 7.3 Hz, 9H, CH_3 NP$_1$), 3.47 (d, $^3J_{HP1}$ = 14 Hz, 9H, CH_3NP_2), 3.86 (m, 6H, CH_2CO), 7.1–7.8 (m, 30H, CH=N, C_{0-1}^2H, C_{0-1}^3H), 7.8–8.1 (m, 27H, Pyr). $^{13}C\{^1H\}$ NMR: 27.5 (s, $CH_2CH_2CH_2$), 31.7 (d, $^2J_{CP}$ = 13 Hz, CH_3NP_2), 31.9 (d, $^2J_{CP}$ = 10 Hz, CH$_3$–N–P$_1$), 33.8 (s, CH_2–Pyr), 34.1 (s, CH_2CO), 121.2 (s, C_0^2), 121.5 (s, C_1^2), 123.3 (s, C^{13}), 124.7 (m, C^3, C^8, C^{10}, C^{15}, C^{16}), 125.7 (s, C^9), 126.6 (s, C^5), 127.3 (m, C^2, C^6, C^{12}), 128.3 (s, C_0^3), 128.8 (s, C_1^3), 129.4–130.3 (m, C^7, C^{14}), 130.8 (s, C_0^4), 133.0 (s, C_1^4), 135.9 (s, C^1), 136.5 (d, $^3J_{CP1}$ = 14.8 Hz, CH=NNP$_1$), 140.6 (d, $^3J_{CP1}$ = 14.8 Hz, CH=NNP$_2$), 150.7 (s, C_0^1), 152.3 (br s, C_1^1), 175.9 (s, CO). Anal. Calcd for $C_{108}H_{99}Cl_6N_{18}O_{12}P_7S_4$ (2399): C, 54.08; H, 4.16; N, 10.51. Found: C, 54.41; H, 4.29; N, 10.21.

16. Synthesis of dendrimer **2a-G$_2'$**. Same procedure as for **2a-G$_1'$**, with 0.6 mmol of hydroxybenzaldehyde sodium salt and 0.1 mmol of dendrimer **2a-G$_2$** in THF (10 mL). Compound **2a-G$_2'$**: 80% yield. $^{31}P\{^1H\}$ NMR: 8.0 (s, P_1), 52.7 (s, P_0), 60.9 (s, P_2). ^1HNMR: 3.15 (d, $^3J_{HP}$ = 7.3 Hz, 9H, CH_3 NP$_1$), 3.34 (d, $^3J_{HP}$ = 11 Hz, 9H, CH_3NP_2), 3.7 (m, 6H, –CH$_2$), 5.07 (d, $^3J_{HHcis}$ = 10 Hz, 3H, =CH$_2$), 5.22 (d, $^3J_{HHtrans}$ = 17 Hz, 3H, =CH$_2$), 5.8 (m, 3H, =CH), 6.9–7.8 (m, 54H, ArH, CH=N), 9.9 (s, 6H, CHO). $^{13}C\{^1H\}$ NMR: 31.8 (d, $^2J_{CP}$ = 8.8 Hz, CH_3NP_1), 32.7 (d, $^2J_{CP}$ = 13.3 Hz, CH_3NP_2), 43.9 (s, –CH$_2$), 115.7 (s, =CH$_2$), 120.9 (d, $^3J_{CP}$ = 4 Hz, C_1^2), 121.3 (d, $^3J_{CP}$ = 4.3 Hz, C_0^2), 121.8 (d, $^3J_{CP}$ = 5 Hz, C_2^2), 127.7 (s, C_0^3), 128.1 (s, C_1^3), 131 (s, C_0^4), 131.3 (s, C_2^3), 132.9 (s, C_1^4), 133.4 (s, C_2^4), 135.7 (d, $^3J_{CP}$ = 6 Hz, CH=), 136.5 (d, $^3J_{CP}$ = 15 Hz, CH=NNP$_1$), 139.6 (d, $^3J_{CP}$ = 13.5 Hz, CH=NNP$_2$), 150.9 (d, $^2J_{CP}$ = 8.4 Hz, C_0^1), 151.6 (d, $^2J_{CP}$ = 7.3 Hz, C_1^1), 155.0 (d, $^2J_{CP}$ = 7 Hz, C_2^1), 190.7 (s, CHO). IR(KBr): $v_{C=O}$ 1700 cm^{-1}. Anal. Calcd for $C_{99}H_{96}N_{15}O_{21}P_7S_4$ (2177): C, 54.62; H, 4.44; N, 9.65. Found: C, 54.68; 4.47; N, 9.57.