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Synthesis and Properties of Dendrimers Possessing the Same Fluorophore(s) Located Either Peripherally or Off-Center

Grégory Franc,[†] Serge Mazères,[‡] Cédric-Olivier Turrin,[†] Laure Vendier,[†] Carine Duhayon,[†] Anne-Marie Caminade,*[,†] and Jean-Pierre Majoral*[,†]

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France, and Institut de Pharmacologie et de Biologie Structurale (CNRS-UPS, UMR 5089), 205 route de Narbonne, 31077 Toulouse Cedex 4, France

caminade@lcc-toulouse.fr; majoral@lcc-toulouse.fr

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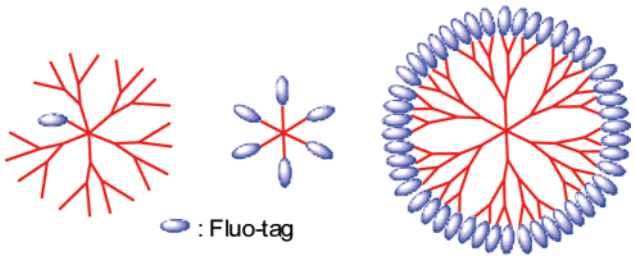

Two series of phosphorus dendrimers functionalized by maleimide derivatives are synthesized, as well as three new monomeric maleimide derivatives, of which two are characterized by X-ray diffraction. The first series of phosphorus dendrimers possesses maleimide derivatives as end groups (6−48, from generation 0 to generation 3). The second series of dendrimers possesses a single copy of the same maleimide derivative linked "off-center" to a cyclotriphosphazene core, leading to dissymmetrical dendrimers; this series is synthesized from generation 0 to generation 2. The fluorescence properties of both series of dendrimers and of monomers are studied, affording new information. First, the presence of labile hydrogen extinguishes the fluorescence. Second, the grafting of the fluorophore(s) directly to the core affords highly fluorescent compounds. Finally, an original influence of the branches possessing phosphorhydrazone linkages toward the fluorescence properties is shown.

Introduction

Dendrimers[1] constitute one of the most active areas of research in chemistry due to the numerous fields they have cross-fertilized, such as catalysis, materials science, nanotechnologies, or biology/medicine. The physicochemical characteristics of these hyperbranched and monodisperse macromolecules are also the subject of numerous studies, often carried out with the aim of determining the influence of the dendritic scaffold on a precise property. In this perspective, numerous works have taken advantage of the use of fluorescence as a highly sensitive tool.[2]

Despite the relatively large number of fluorescent dendrimers already synthesized possessing fluorophores in various locations (periphery,[3] core,[4] or branches[5]), there is no example to date concerning a single type of fluorophore linked either "off-center"[6] to the core or to the entire surface (peripherally) of the

[†] Laboratoire de Chimie de Coordination du CNRS.
[‡] Institut de Pharmacologie et de Biologie Structurale.

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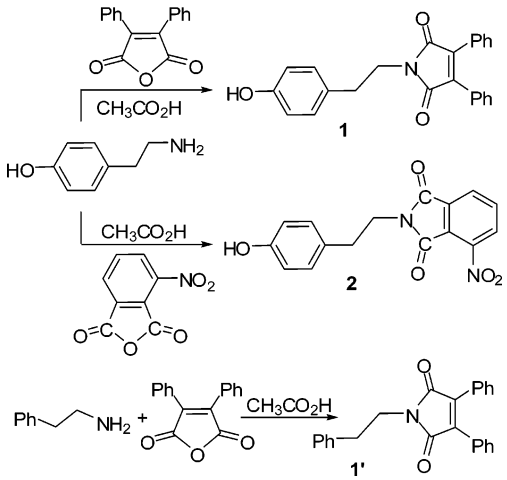
same family of dendrimers, despite the interest of grafting a functional probe to facilitate the detailed investigation of the properties of such macromolecules. However, there exists one example in which a single anthracene is linked either to the core, or to a particular layer, or to a single place of the surface of a poly(benzyl ether) dendron and not to the entire surface as in our case.[7] We have already reported that the scaffold of phosphorus-containing dendrimers is generally compatible with fluorescence experiments, in particular for phthalocyanine cores[8] or pyrene derivatives included in the interior.[9] Furthermore, some fluorescent phosphorus dendrimers were shown to possess interesting properties for the creation of organic light emitting diodes (OLEDs),[10] as brilliant organic nanodots,[11] for the elucidation of biological mechanisms,[12] and for medical imaging.[13] In this paper, we report the synthesis of two series of fluorescent dendrimers in which a same maleimide derivative is grafted either peripherally (from generation 0 to 3) or off-center (from generation 0 to 2) to phosphorus dendrimers. In both cases, the fluorophore is linked via a single chemical function, allowing a direct comparison of the properties, contrary to the cases in which the fluorophore constitutes the branches or the core, for which at least two chemical functions are needed.

Results and Discussion

The easiest way to functionalize the surface of phosphorus-containing dendrimers consists of grafting functional phenols. Thus, our first aim was to synthesize fluorescent probes bearing a phenol. Maleimide fluorophores constitute a versatile family of fluorophores;[14] thus, we decided to synthesize a phenol maleimide. Compound **1** is obtained by reaction of diphenyl maleic anhydride with tyramine in acetic acid (Scheme 1) and is isolated in 95% yield after workup. The analogous compound **1′** (no OH group) is synthesized for comparison purposes, applying the same method but from phenethylamine. Another

SCHEME 1



fluorescent probe linked to a phenol (**2**) is synthesized in the same way, starting from 3-nitrophthalic anhydride. Compound **2** is isolated in 87% yield as a relatively poorly soluble powder (Scheme 1). The ^{1}H NMR chemical shift of the signal corresponding to the amino CH_2 group is at $\delta = 3.84$ ppm for **2**, very close to the value found for **1** (3.86). These compounds are also characterized by ^{13}C NMR and mass spectrometry.

Synthesis of Dendrimers Possessing Fluorophores Located Peripherally. Having in hand both phenols **1** and **2**, we tried to graft them to hexachlorocyclotriphosphazene **3** under basic conditions to obtain the generation 0 of the peripherally functionalized dendrimers. The reaction of 6 equiv of phenol **1** in the presence of cesium carbonate is slow and needs 2 days at 40 °C to go to completion. Monitoring the progress of the reaction by ^{31}P NMR shows the presence of numerous intermediates, each of them displaying complex patterns of types AA′B or ABC, whereas the completion of the reaction is characterized by a singlet at δ ^{31}P = 8.78 ppm for the hexasubstituted compound **4-G$_0$** (Scheme 2). ^{13}C NMR also displays the shielding of the signal corresponding to the ipso carbon (C_0^1) of the phenoxy group, from 154.8 ppm in **1** to 149.43 ppm in **4-G$_0$**. The MALDI-TOF spectrum confirmed the full substitution of the cyclotriphosphazene. We tried to perform the same experiment using phenol **2** instead of phenol **1**, but this reaction rapidly led to insoluble compounds, thus no more attempts to use phenol **2** were done.

Since phenol **1** was cleanly grafted on P−Cl bonds, we used it in the continuation of this work to obtain higher generations of peripherally functionalized phosphorus dendrimers. The first-generation dendrimer **3-G$_1$**[15] possessing 6 P(S)Cl$_2$ end groups is reacted with 12 equiv of the phenol **1** (Scheme 3). Despite the higher number of functional groups in this compound compared to **3-G$_0$**, the reaction proceeds more rapidly (one night at room temperature). The ^{31}P NMR spectrum displays a slight shift of the peripheral phosphorus, from 62.5 ppm for **3-G$_1$** to 63.4 ppm for **4-G$_1$**. Furthermore, an intermediate signal at δ 69.8 ppm is observed during the synthetic process, corresponding to the monosubstitution (P(S)Cl(OAryl) end groups). Then, the same reaction is carried out with the second- (**3-G$_2$**) and the third-generation (**3-G$_3$**) dendrimers and 24 or 48 equiv of phenol **1**, leading to the peripherally functionalized dendrimers

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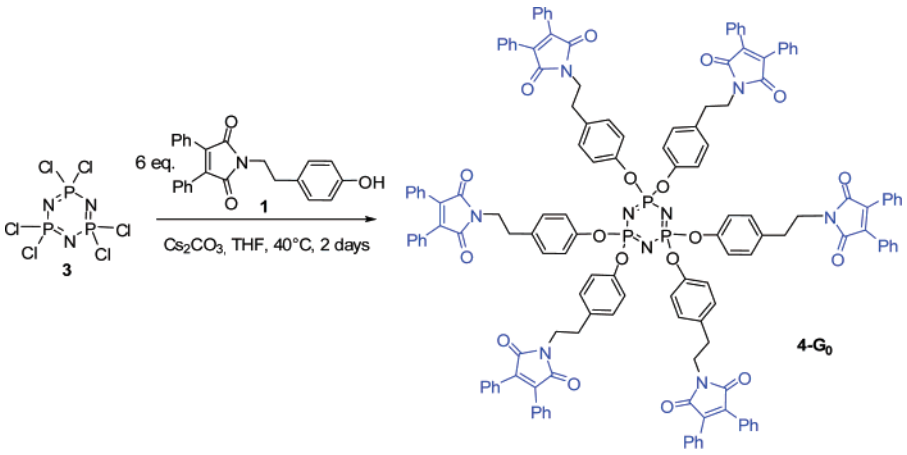
SCHEME 2



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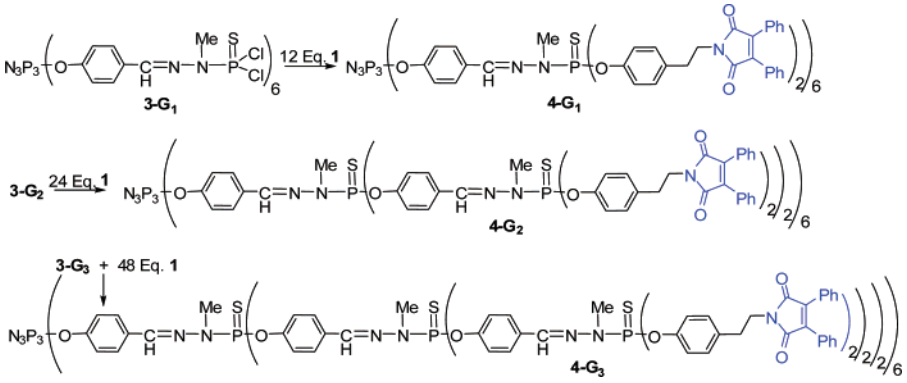

4-G$_2$ and **4-G$_3$**, respectively (Scheme 3). In both cases, the ^{31}P NMR spectra display the same deshielding/shielding process of the signal corresponding to the end groups, as already illustrated with the first generation, in addition to the signals corresponding to the internal structure. MALDI-TOF analyses are unusable to ascertain the purity of all of the phosphorus hydrazone dendrimers, due to intrinsic fragmentation/rearrangement processes.[16] However, the full substitution is shown by the presence of a single signal for the end groups with the precision of ^{31}P NMR (estimated at 0.5%).

Synthesis of Dendrimers Possessing a Fluorophore Located Off-Center. The second series of dendrimers we intended to synthesize for comparison with the first series should bear one maleimide group off-center. For this purpose, we needed to differentiate the reactivity of one chlorine among six in the hexachlorocyclotriphosphazene. We have already proposed a few examples of such nonsymmetric substitutions,[17] which can be accomplished either by reacting first one Cl with one type of functional compound and then the five remaining Cl with 5 equiv of another functional compound or by reacting first 5 equiv of one functional compound then 1 equiv of another functional compound with the single remaining Cl. We tried both approaches but found the second one to be more suitable with the reagents we used. Thus, 1 equiv of the phenol **1** is reacted in the presence of cesium carbonate with the monochloropentaaldehyde derivative **5-G$_0$** (obtained by reaction of 5 equiv of hydroxybenzaldehyde with $N_3P_3Cl_6$) (Scheme 4). The reaction proceeds gently overnight at room temperature to afford the first compound in the off-center series **6-G$_0$** in 85% yield after chromatography. The ^{31}P NMR spectrum of compound **5-G$_0$** is very complex and displays two series of signals, two doublets centered at 3.5 ppm, corresponding to the fully substituted phosphorus and one doublet of doublet centered at 19.1 ppm, corresponding to the phosphorus bearing one chlorine. Replacement of the Cl by the phenol of compound **1** renders the cyclotriphosphazene core more symmetric from the point of view of phosphorus; thus, only a single multiplet is observed for the core at $\delta = 8.04$ ppm. In fact, the whole molecule **6-G$_0$** is dissymmetrical, as shown in particular by the presence of

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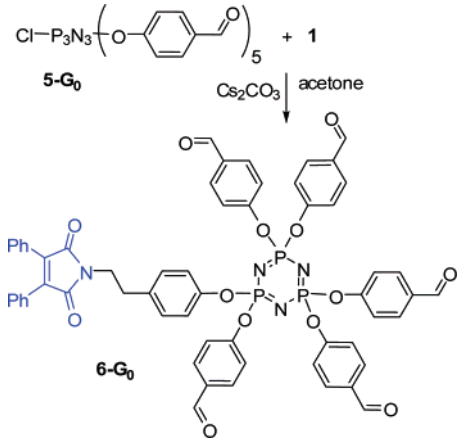

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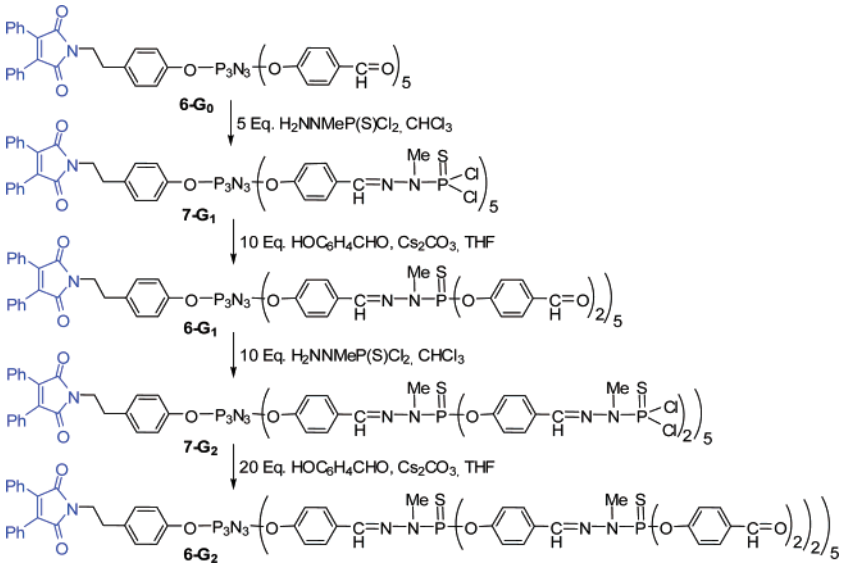
SCHEME 5



three signals in a 1:2:2 ratio for the CHO groups in ^{1}H NMR. The signal integrating for 1H corresponds to the phenoxybenzaldehyde connected to the phosphorus bearing also the newly grafted tyramine derivative. Each of both signals integrating for 2H should correspond to the two aldehydes located on each side relative to the cyclotriphosphazene core.

Starting from compound **6-G$_0$**, the synthesis of the off-center family necessitates the growing of the dendritic branches from the five aldehydes, using our classical two-step synthetic procedure.[18] Thus, the phosphorhydrazide $H_2NNMeP(S)Cl_2$ is condensed with the aldehydes, leading to the first generation of the unsymmetrical dendrimer **7-G$_1$** (Scheme 5). Interestingly, the unsymmetrical character of this family of compounds is detectable by ^{31}P NMR, which displays three signals for the $P(S)Cl_2$ end groups in an approximate 1:2:2 ratio at $\delta = 62.60$, 62.67, and 62.71 ppm, respectively. The full condensation is shown by the disappearance of the signals corresponding to the aldehydes by ^{1}H and ^{13}C NMR; contrary to our classical dendrimers, IR spectroscopy is not efficient to monitor the completion of the reaction, since the aldehydes and the C═O groups of the fluorophore give a large single band. The next synthetic step necessitates the replacement of Cl by hydroxybenzaldehyde. This reaction is carried out overnight at room temperature in the presence of cesium carbonate to afford the first-generation **6-G$_1$** possessing 10 aldehyde end groups (Scheme 5).

Three different signals are again observed in the ^{31}P NMR spectrum for the five P(S) groups of compound **6-G$_1$**. Furthermore, the sensitivity of the aldehyde groups to act as sensors in ^{1}H NMR for the detection of dissymmetry in dendritic structures[19] is confirmed here. Indeed, four different signals are observed in a 2:2:4:2 ratio in the ^{1}H NMR and two signals in the ^{13}C NMR also for the aldehydes. The second generation with $P(S)Cl_2$ end groups is obtained by reacting the dendrimer **6-G$_1$** with $H_2NNMeP(S)Cl_2$ (Scheme 5). The completion of the reaction is shown by ^{1}H NMR as well as by ^{13}C NMR, with the disappearance of the signals corresponding to the aldehydes. An interesting feature is observed by ^{31}P NMR for dendrimer **7-G$_2$**; indeed, three signals are detected for the $P(S)Cl_2$ end groups, showing that the dissymmetry still exists and is still detectable for this generation. The last dendrimer that we synthesized in this series is obtained by reacting 20 equiv of hydroxybenzaldehyde with 1 equiv of dendrimer **7-G$_2$** (Scheme 5). The reaction proceeds gently overnight to afford the dendrimer **6-G$_2$**. Here again, the dissymmetry is detectable by ^{31}P NMR for the signals of the phosphorus pertaining to the first and second layers.

Having in hand two series of dendrimers bearing fluorophores located either on the periphery (**4-G$_n$**) or off-center (**6-G$_n$**), we decided to study their photophysical properties to determine the influence of the dendritic skeleton.

Photophysical Properties of Dendrimers 4-G$_n$ and 6-G$_n$. In order to establish a measurement of the photophysical properties, we decided first to investigate the properties of the monomeric fluorophores **1** and **1′**. The maximum of the UV−vis spectrum of **1** is at 365 nm in THF and at 370 nm in dichloromethane (DCM). This solvatochromic effect is classically related to the polarity of the solvents.[20] Both series of dendrimers **4-G$_n$** and **6-G$_n$** behave analogously to compound **1** concerning the λ_{max} values; however, the value of ϵ_{max} is very different for the series **4-G$_n$** as expected (Table 1). Figure 1 indicates that there is a linear increase of the ϵ_{max} values with the number of chromophores, confirming the absence of large defects, as previously observed.[21] The ϵ_{max} values are slightly different in both solvents; such a phenomenon was previously reported for other types of dendrimers and chromophores.[22]

Most maleimide derivatives do not have a very high quantum yield, but it is generally sufficient to perform fluorescence studies.[23] The fluorescence of compound **1** is measured in THF and in CH_2Cl_2, using $\lambda = 315$ and 370 nm in THF and $\lambda = 320$ and 380 nm in DCM as wavelengths for excitation. The

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TABLE 1.

compd	N^{br} fluor	ϵ_{max} (365 nm) THF	ϵ_{max} (370 nm) DCM	λ_{exc} THF	λ_{em} THF	Φ^b THF	λ_{exc} DCM	λ_{em} DCM	Φ^b DCM
1	1	2600	3400	315/370	*483/495*	n.a.	320/380	*506*	8
1′	1	3320	3470	300/375	*499*	57	300/375	*506*	52
6-G$_0$	1	3300	3300	300/375	*499*	77	302/376	*506*	77
6-G$_1$	1	3450	3200	(324)[a]/375	*499*	22	320/375	*506*	24
6-G$_2$	1	3600	3200	(325)[a]/375	*499*	20	(325)[a]/378	*506*	14
4-G$_0$	6	15600	21500	300/375	*499*	78	302/376	*506*	72
4-G$_1$	12	35400	37900	300/375	*499*	49	305/375	*506*	33
4-G$_2$	24	68800	79300	300/375	*499*	43	320/375	*506*	29
4-G$_3$	48	135400	163000	310/375	*499*	39	320/375	*506*	23

[a] Shoulder. [b] Relative to coumarin 6 (EtOH), 78%.

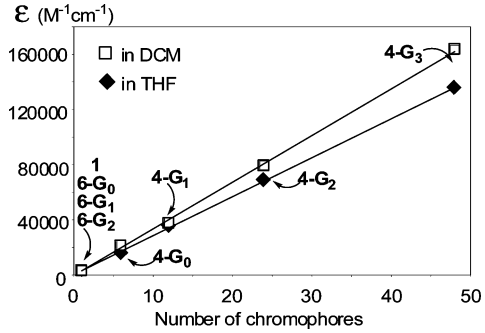

FIGURE 1. Variation of ϵ_{max} with the number of chromophores in DCM and THF for the series **4-G*n*** and **6-G*n***.

emission wavelength in both cases is at 495 nm in THF and 506 nm in DCM, exhibiting a large Stokes shift estimated to be 6555 cm^{-1} in DCM and 6825 cm^{-1} in THF according to $(1/\lambda_{max.exc} - 1/\lambda_{max.em}) \times 10^7$.[24] Such values indicate an important difference in the properties and structures between the ground state S_0 and the first excited state S_1 and have been attributed for maleimide derivatives to an increased coplanarity of the phenyl rings with the maleimide ring in the excited state.[25] However, to our surprise, the fluorescence quantum yield Φ of **1** is extremely low and even nonmeasurable in THF. Such behavior could hamper any useful measurements with the dendrimers we have synthesized. Nevertheless, it was noted in a paper describing the properties of a series of maleimide derivatives that compounds possessing a NH bond have systematically a much lower quantum yield than the corresponding N-Me derivatives, but no explanation was given.[23] Compound **1′** differs only from **1** by the absence of the OH group; thus, we decided to measure also its fluorescence properties. Fortunately, the quantum yield obtained for **1′** is quite convenient (57% in THF, 52% in DCM). In order to determine if the OH group of compound **1** could be able to interact with the fluorophore moiety of the same compound, we tried to determine the structure of **1** by X-ray diffraction, as well as that of **1′**, for comparison.

Single crystals of compounds **1** and **1′** were grown from ether solutions in both cases. The ORTEP drawing of the packing for compound **1** is shown in Figure 2. The most important information afforded by this structure is the strong interaction of the OH group of the phenol with one of the oxygen atom of the maleimide part of another molecule ($d_{O\cdots H} = 2.072$ Å $< \Sigma_{\text{van der Waals radii}} = 2.885$ Å), giving a bent "dimer". On the other hand, the ORTEP drawing of compound **1′** shows that the packing induces a flattening of this compound compared to **1** (Figure 3).

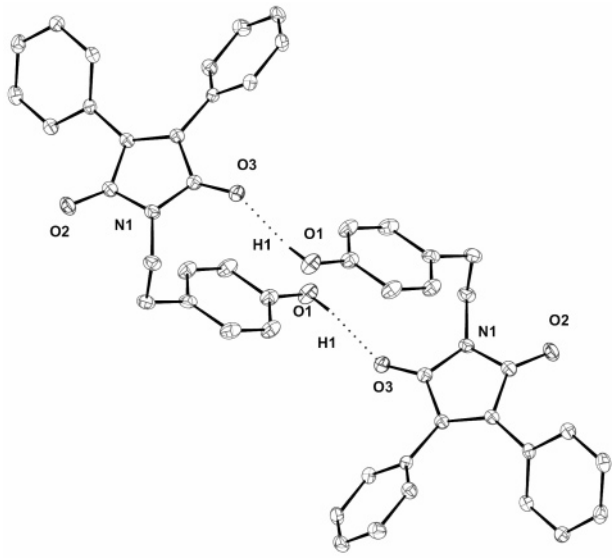

FIGURE 2. ORTEP drawing of two molecules of compound **1**, showing the association (hydrogen atoms not shown for clarity, except OH).

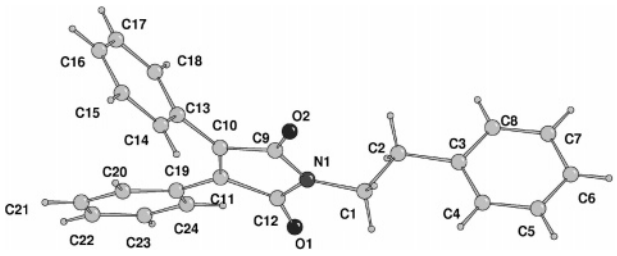

FIGURE 3. ORTEP drawing of compound **1′**.

In view of the strong hydrogen bonding between two molecules of **1**, we believe that such interaction persists at least in part in solution and induces the nonradiative deactivation pathway observed, such phenomenon being impossible with **1′**. Thus, we may assume that grafting compound **1** to the dendrimer should allow recovery of a measurable fluorescence since the labile H will no longer exist. To our delight, the fluorescence quantum yield measurements for compound **4-G$_0$** possessing six chromophoric units is high (78% in DCM relative to coumarine 6 in EtOH) and even higher than any of the previously described maleimide derivatives, demonstrating that our assumption concerning the role of H bonding was right. As previously observed with compounds **1** and **1′**, the Stokes shift

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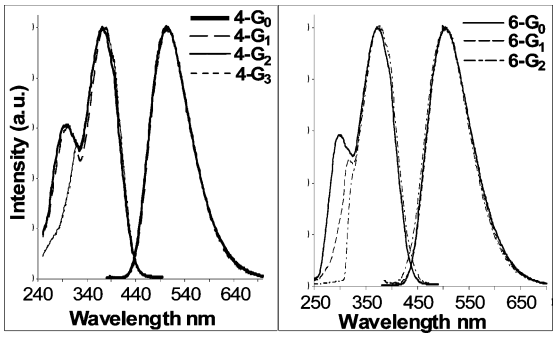

FIGURE 4. Excitation/emission spectra for the series **4-G*n*** (left) and **6-G*n*** (right) in DCM.

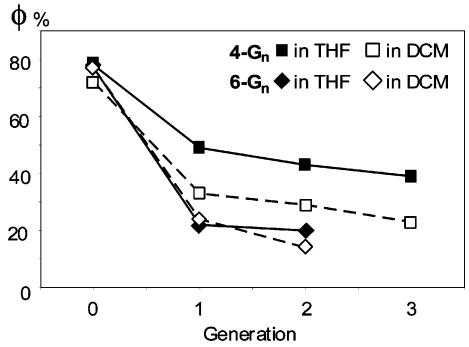

FIGURE 5. Decrease of the quantum yield when the generation increases, for both series of dendrimers **4-G*n*** (peripheral fluorophores) and **6-G*n*** (off-center fluorophore).

is also high for **4-G$_0$** (6625 cm^{-1} in THF, 6905 in DCM). After generation 0, the quantum yields of the series of dendrimers **4-G*n*** (n = 1−3) were measured (Table 1, Figure 4).

Surprisingly, an important decrease of the quantum yield is observed for the first generation (49%) and confirmed with the second (43%) and third (39%) generations in THF, and the results are even worse in DCM (Table 1, Figure 5). Such a phenomenon was previously described for other types of dendrimers bearing fluorophores as end groups[21] and was generally attributed to an increase in the steric hindrance, inducing an interaction between fluorophores in close proximity, leading to a nonradiative deactivation process. However, we think that such explanation is not valid in our case. Indeed, the reaction time needed to synthesize the generation zero indicates that this compound is sterically crowded, whereas the other generations (from 1 to 3) are less. Comparing the chemical structure of dendrimers **4-G$_0$** and **4-G$_1$**, it is obvious that the main difference between both compounds is the aryl phosphorhydrazone linkage. We have already demonstrated that several types of fluorophores directly linked to this linkage totally lost their fluorescence properties, which could be recovered only if a spacer was added between the fluorophore and this linkage.[10] In the present case, the spacer is constituted by the tyramine; thus, the quenching phenomenon should be avoided. However, the tyramine linkage is very flexible, and some interaction might occur between the fluorophore and the dendritic structure.

The series of compounds **6-G*n*** might be useful to confirm this assertion. Indeed, in this series, the fluorophore is surrounded by the branches even at the first generation; thus, if an interaction exists between the fluorophore and the branches, it should be maximized within this series. The quantum yield of compound **6-G$_0$** is high (77%) and compares perfectly well with the value measured for **4-G$_0$** (78%). The value measured for **6-G$_1$** is poor (22%) both in THF and DCM and much lower than the value measured for **4-G$_1$** (49%). The addition of another layer (compound **6-G$_2$**) has practically no influence (Φ = 20% in DCM). These data demonstrate that the influence of the branches upon the fluorophore close to the core is more important than the solvent, showing that the fluorophore is readily encapsulated by the branches. However, in the literature, the branches generally induce a protection of the fluorophore (concept of "site isolation") and an increased fluorescence,[6] even with the same phosphorhydrazone branches,[8b] contrary to our present observations.

Conclusion

We have described the first example of two series of dendrimers constituted of the same branches and bearing the same fluorophore either as end groups or off-center. This last series is particularly interesting since it is built by the differentiation of one function among six on cyclotriphosphazene. The dissymmetrical character of this series (**6-G*n***) is shown by ^{31}P, ^{1}H, and ^{13}C NMR, which display the presence of different signals for P(S) and CHO groups of the same generation, clearly distinguishable even for the second generation. The photophysical data of both series of dendrimers allowed us to draw original conclusions. First, the presence of a phenol group in the starting monomeric fluorophore of the maleimide type induces the quasi-disappearance of the fluorescence, presumably due to a deactivation through hydrogen bonding, as shown by X-ray diffraction. Second, the grafting of such fluorophore directly to cyclotriphosphazene affords compounds possessing the highest fluorescence quantum yield measured to date in the maleimide series, confirming the dramatic role of substituents on these fluorophores. Third, we have shown an original influence of the branches on the fluorescence of the end groups, which is dramatically confirmed in the case of the off-center family. Such behavior illustrates that the dendritic scaffold is not at all an "innocent" spectator but may play a key role for some properties.

Experimental Section

NMR numbering is illustrated in Figure 6.

Compound 1. 2,3-Diphenylmaleic anhydride (1 g, 4 mmol) and tyramine (0.548 g, 4 mmol) were dissolved in the minimum amount of acetic acid. The resulting slurry mixture was heated under vigorous stirring at 160−170 °C for 90 min in an open flask to afford a dark viscous oil. The mixture was cooled to room temperature, and 50 mL of distilled water was added. The resulting yellow precipitate was filtered off and if necessary purified by column chromatography (CH_2Cl_2/*n*-pentane) to afford **1** as a yellow powder in 95% yield (1.40 g). Crystallization from Et_2O gave single crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 2.94 ("t", $^{3}J_{HH}$ = 7.6 Hz, 2H, C^{a}H), 3.87 ("t", $^{3}J_{HH}$ = 7.6 Hz, 2H, C^{b}H), 5.65 (s, 1H, OH), 6.79 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, $C_0{}^{2}$H), 7.13 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, $C_0{}^{3}$H), 7.27−7.45 (m, 10H, C^{o}H, C^{m}H, C^{p}H). ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 34.2 (s, C^{a}), 40.3 (s, C^{b}), 115.8 (s, $C_0{}^{2}$), 128.96 (s, C^{i}), 129.00 (s, C^{m}), 130.26 (s, C^{o}), 130.28 (s, C^{p}), 130.48 (s, $C_0{}^{3}$), 130.51 (s, $C_0{}^{4}$), 136.5 (s, C=C), 154.8 (s, $C_0{}^{1}$), 171.2 (s, C=O) ppm. IR (KBr): 1692 cm^{-1} ($\nu_{C=O}$). Mp (uncorrected): 181−183 °C.

Compound 1′. 2,3-Diphenylmaleic anhydride (400 mg, 1.59 mmol) and phenylethylamine (201 mg, 1.64 mmol) were dissolved in the minimum amount of acetic acid. The resulting slurry mixture was heated under vigorous stirring at 160−170 °C for 60 min in an open flask to afford a dark viscous oil. The mixture was cooled

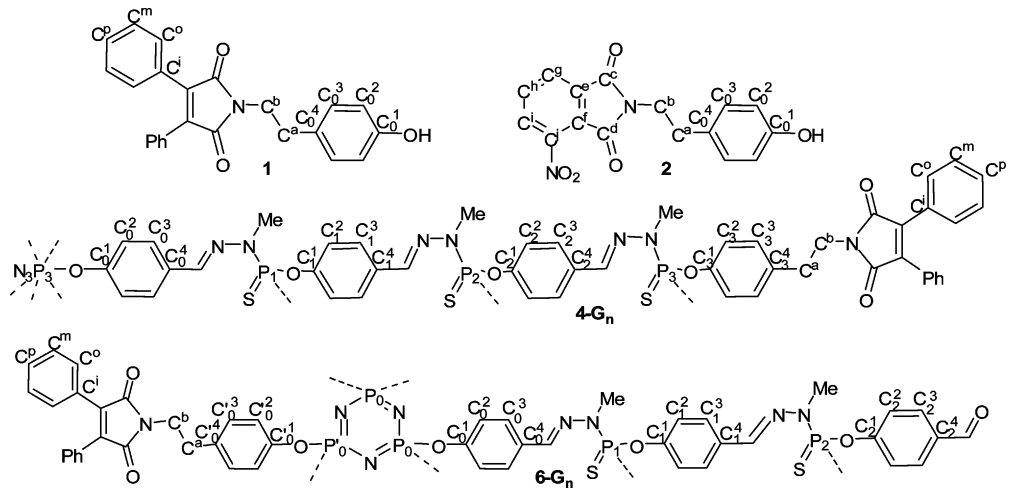

FIGURE 6. Numbering used for NMR.

to room temperature, and 50 mL of distilled water was added. The aqueous phase was extracted twice with 35 mL of CH_2Cl_2. The collected organic phases were dried on magnesium sulfate and concentrated under reduced pressure. The crude residue was eluted on a plug of silica with Et_2O to afford **1′** as a yellow powder in 98% yield (553 mg) after solvent removal. Crystallization from Et_2O gave single crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, 300.13 MHz): $\delta = 3.03$ ("t", $^3J_{HH} = 7.5$ Hz, 2H, C^aH), 3.92 ("t", $^3J_{HH} = 7.5$ Hz, 2H, C^bH), 7.26−7.60 (m, 15H, H_{ar}). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.89 MHz): $\delta = 34.7$ (s, C^a), 39.7 (s, C^b), 126.7 (s, C_0^1), 128.56 (s, C^m), 128.60 (s, C^i), 128.9 (s, C_0^2), 129.82 (s, C_0^3), 129.86 (s, C^o, C^p), 136.2 (s, C═C), 138.1 (s, C_0^4), 170.6 (s, C═O) ppm. IR (KBr): 1697 cm^{-1} ($\nu_{C=O}$). Mp (uncorrected): 162−166 °C.

Compound 2. 3-Nitrophthalic anhydride (750 mg, 3.88 mmol) and tyramine (586 mg, 4 mmol) were dissolved in the minimum amount of acetic acid. The slurry mixture was heated under vigorous stirring at 160 °C for 90 min in an open flask to afford a dark viscous oil. The mixture was cooled to room temperature, and 50 mL of distilled water was added. The resulting yellow precipitate was filtered off and dried to afford **2** as a brownish powder in 87% yield (1.05 g). ^{1}H NMR (CD_3OCD_3, 300.13 MHz): $\delta = 2.91$ ("t", $^3J_{HH} = 7.5$ Hz, 2H, C^aH), 3.84 ("t", $^3J_{HH} = 7.5$ Hz, 2H, C^bH), 6.76 (d, $^3J_{HH} = 8.4$ Hz, 2H, C_0^2H), 7.10 (d, $^3J_{HH} = 8.4$ Hz, 2H, C_0^3-H), 8.05−8.22 (m, 3H, H_{ar}). ^{13}C-{^{1}H} NMR (CD_3OCD_3, 75.46 MHz): $\delta = 33.1$ (s, C^a), 39.9 (s, C^b), 115.3 (s, C_0^2), 123.4 (s, C^f), 126.4 (s, C^i), 128.1 (s, C^g), 128.9 (s, C_0^4), 129.7 (s, C_0^3), 134.2 (s, C^e), 135.9 (s, C^h), 145.0 (s, C^j), 156.1 (s, C_0^1), 163.1 (s, C^c═O), 165.7 (s, C^d═O) ppm. IR (KBr): 1709 cm^{-1} ($\nu_{C=O}$). MS (DCI) m/z = 330 $[M + NH_4]^+$. Mp (uncorrected): 198−200 °C.

Compound 4-G$_0$. Compound **1** (310 mg, 0.840 mmol) and cesium carbonate (555 mg, 1.70 mmol) were added at 0 °C to a solution of hexachlorocyclotriphosphazene **3** (45.6 mg, 0.131 mmol) in THF (20 mL). The reaction mixture was stirred at 40 °C for 2 days. After the mixture was cooled to room temperature, salts were removed by centrifugation, and the clear solution was concentrated under reduced pressure and subjected to flash chromatography (pentane/Et_2O, 7:3 to CH_2Cl_2) to afford **4-G$_0$** as a yellow powder in 85% yield (261 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 121.49 MHz): $\delta = 8.78$ (s, P═N); ^{1}H NMR ($CDCl_3$, 300.13 MHz): $\delta = 3.00$ ("t", $^3J_{HH} = 7.8$ Hz, 12H, C^aH), 3.88 ("t", $^3J_{HH} = 7.8$ Hz, 12H, C^bH), 6.95 (d, $^3J_{HH} = 8.4$ Hz, 12H, C_0^2H), 7.14 (d, $^3J_{HH} = 8.4$ Hz, 12H, C_0^3H), 7.28−7.43 (m, 36H, C^mH, C^pH), 7.45 (d, $^3J_{HH} = 6.9$ Hz, 24H, C^oH). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.46 MHz): $\delta = 34.0$ (s, C^a), 39.6 (s, C^b), 121.2 (s, C_0^2), 128.55 (s, C^m), 128.67 (s, C^i), 129.80 (2 s, C_0^3, C^p), 129.90 (s, C^o), 134.7 (s, C_0^4), 136.2 (s, C═C), 149.4 (m, C_0^1), 170.5 (s, C═O) ppm. MS (MALDI-TOF, dithranol matrix): m/z = 2343.57 $[M]^+$.

Dendrimer 4-G$_1$. Compound **1** (300 mg, 0.811 mmol) was added to a mixture of **3-G$_1$**[15] (114 mg, 0.062 mmol) and cesium carbonate (529 mg, 1.62 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature overnight. Salts were then removed by centrifugation, and the clear solution was concentrated under reduced pressure. The residue was then dissolved in the minimum amount of THF (*ca.*1 mL) and precipitated with a mixture of pentane and Et_2O (9:1). The resulting powder was filtered off and then flash chromatographed to afford **4-G$_1$** as a yellow powder in 65% yield (236 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 202.53 MHz): δ = 8.51 (s, P═N), 63.39 (s, P_1═S). ^{1}H NMR ($CDCl_3$, 500.13 MHz): $\delta = 2.89$ ("t", $^3J_{HH} = 7.6$ Hz, 24H, C^aH), 3.15 (d, $^3J_{HP} = 10.2$ Hz, 18H, NMe), 3.78 ("t", $^3J_{HH} = 7.6$ Hz, 24H, C^bH), 7.03 (d, $^3J_{HH}$ = 10 Hz, 12H, C_0^2H), 7.12 (m, 48H, C_1^2H, C_1^3H), 7.27−7.37 (m, 72H, C^mH, C^pH), 7.38−7.44 (m, 48H, C^oH), 7.59 (s, 6H, CH═N), 7.65 (d, $^3J_{HH} = 10$ Hz, 12H, C_0^3H). ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.80 MHz): $\delta = 33.0$ (d, $^3J_{CP} = 12.6$ Hz, CH_3NP_1), 34.0 (s, C^a), 39.5 (s, C^b), 121.4 (s, C_0^2), 121.6 (s, C_1^2), 128.3 (s, C_0^3), 128.5 (s, C^m, C^i), 129.9 (s, C^p, C^o), 130.0 (s, C_1^3), 132.2 (s, C_0^4), 135.3 (s, C_1^4), 136.1 (s, C═C), 138.6 (br s, CH═NNP_1), 149.2 (d, $^2J_{CP} = 7.5$ Hz, C_1^1), 151.3 (s, C_0^1), 170.5 (s, C═O) ppm. IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$).

Dendrimer 4-G$_2$. Compound **1** (150 mg, 0.405 mmol) was added to a mixture of **3-G$_2$**[15] (77 mg, 0.016 mmol) and cesium carbonate (264 mg, 0.810 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature overnight. Salts were then removed by centrifugation, and the clear solution was concentrated under reduced pressure. The residue was then dissolved in the minimum amount of THF (ca.1 mL) and precipitated with a mixture of pentane and Et_2O (9:1). The resulting powder was filtered off and then flash chromatographied to afford **4-G$_2$** as a yellow powder in 83% yield (170 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 101.25 MHz): δ = 8.42 (s, P═N), 62.42 (s, P_1═S), 63.21 (s, P_2═S). ^{1}H NMR ($CDCl_3$, 500.3 MHz): $\delta = 2.89$ (br s, 48H, C^aH), 3.15 (m, 54H, $CH_3NP_{1,2}$), 3.74 (br s, 48H, C^bH), 6.92−7.63 (m, 426H, H_{Ar}, CH═N). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.85 MHz): $\delta = 32.94$ (d, $^3J_{CP} = 12.4$ Hz, $CH_3NP_{1,2}$), 33.93 (s, C^a), 39.46 (s, C^b), 121.43 (s, C_0^2), 121.62 (s, C_2^2), 121.8 (s, C_1^2), 128.4 (s, C_0^3, C_1^3), 128.5 (s, C^m, C^i), 129.85 (s, C^o, C^p), 129.94 (s, C_2^3), 132.2 (s, C_0^4), 132.4 (s, C_1^4), 135.3 (s, C_2^4), 136.1 (s, C═C), 138.7 (br s, CH═NNP_2), 138.8 (br s, CH═NNP_1), 149.3 (d, $^2J_{CP} = 7$ Hz, C_2^1), 151.2 (d, $^2J_{CP} = 7$ Hz, C_0^1, C_1^1), 170.4 (s, C═O) ppm. IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$).

Dendrimer 4-G$_3$. Compound **1** (200 mg, 0.542 mmol) was added to a mixture of **3-G$_3$**[15] (110.4 mg, 0.010 mmol) and cesium

carbonate (351 mg, 1.08 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature overnight. Salts were then removed by centrifugation, and the clear solution was concentrated under reduced pressure. The residue was then dissolved in the minimum amount of THF (ca.1 mL) and precipitated with a mixture of pentane and Et_2O (9:1). The resulting powder was filtered off and then flash chromatographed to afford **4-G$_3$** as a yellow powder in 98% yield (270 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ = 7.99 (br s, P=N), 62.45 (s, P_1=S, P_2=S), 63.05 (s, P_3=S). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 2.86 (br s, 96H, C^aH), 3.14 (br s, 126H, $CH_3NP_{1,2,3}$), 3.77 (br s, 96H, C^bH), 6.75−7.80 (m, 882H, H_{Ar}, CH=N). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.46 MHz): δ = 32.9 (br d, $^3J_{CP}$= 12.6 Hz, $CH_3NP_{1,2,3}$), 33.9 (s, C^a), 39.4 (s, C^b), 121.6 (br s, $C_0{}^2$, $C_3{}^2$), 121.8 (br s, $C_1{}^2$, $C_2{}^2$), 128.3 (s, $C_0{}^3$, $C_1{}^3$, $C_2{}^3$), 128.5 (s, C^m, C^i), 129.8 (s, C^p, C^o), 129.9 (s, $C_3{}^3$), 132.4 (br s, $C_0{}^4$, $C_1{}^4$, $C_2{}^4$), 135.2 (s, $C_3{}^4$), 136.0 (s, C=C), 138.1−139.1 (m, CH=N), 149.3 (d, $^2J_{CP}$ = 6.9 Hz, $C_3{}^1$), 151.2 (m, $C_0{}^1$, $C_1{}^1$, $C_2{}^1$), 170.4 (s, C=O) ppm. IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$).

Compound 5-G$_0$. The sodium salt of 4-hydroxybenzaldehyde (1.3 g, 9 mmol) was added to a solution of $N_3P_3Cl_6$ (0.6 g, 1.73 mmol) in THF (150 mL) at 0 °C, and then the mixture was stirred to room temperature overnight. After evaporation of the solvent, the residue was purified by column flash chromatography (hexane/ethyl acetate 5:1) to give **5-G$_0$** as a colorless oil in 85% yield (1.13 g). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.50 MHz): δ = 3.53 (2 d, $^2J_{PP}$ = 88.1 Hz, $^2J_{PP}$ = 85.0 Hz, P_0), 19.09 (dd, $^2J_{PP}$ = 88.1 Hz, $^2J_{PP}$ = 85.0 Hz, P'_0). ^{1}H NMR (CD_3OCD_3-d_6, 300.13 MHz): δ = 7.24 (m, 10H, $C_0{}^2$H), 7.79 (m, 10H, $C_0{}^3$H), 9.95 (3 s; 5H, CHO). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.48 MHz): δ = 121.6 (m, $C_0{}^2$), 131.5 (s, $C_0{}^3$), 133.9 (s, $C_0{}^4$), 134.0 (s, $C_0{}^4$), 154.3 (d, $^2J_{CP}$ = 17.1 Hz, $C_0{}^1$), 190.4 (s, CHO), 190.5 (s, CHO) ppm.

Dendrimer 6-G$_0$. Cesium carbonate (656 mg, 1 mmol) and compound **5-G$_0$** (780 mg, 1 mmol) were added to a solution of **1** (370 mg, 1 mmol) in acetone (5 mL). The reaction mixture was stirred overnight at room temperature and then centrifuged. The supernatant was then concentrated under reduced pressure. The resulting yellow oil was flash chromatographed to afford **6-G$_0$** as a yellow powder in 85% yield (947 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 121.50 MHz): δ = 8.04 (m, P=N). ^{1}H NMR ($CDCl_3$, 500.3 MHz): δ = 3.03 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C^aH), 3.88 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C^bH), 7.06 (d, $^3J_{HH}$ = 8.5 Hz, 2H, $C'_0{}^2$H), 7.24−7.29 (m, 12H, $C_0{}^2$H, $C'_0{}^3$H), 7.35−7.46 (m, 10H, C^oH, C^mH, C^pH), 7.81−7.89 (m, 10H, $C_0{}^3$H), 9.98 (s, 1H, CHO), 9.99 (s, 2H, CHO), 10.00 (s, 2H, CHO). ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 33.4 (s, C^a), 39.2 (s, C^b), 120.8 (m, $C'_0{}^2$), 121.3 (m, $C_0{}^2$), 128.3 (s, C^o), 129.1 (s, C^i), 129.6 (s, C^p), 129.8 (s, C^m), 130.2 (s, $C'_0{}^3$), 131.21 (s, $C_0{}^3$), 131.24 (s, $C_0{}^3$), 131.26 (s, $C_0{}^3$), 134.06 (s, $C_0{}^4$), 134.15 (s, $C_0{}^4$), 134.17 (s, $C_0{}^4$), 136.3 (s, $C'_0{}^4$), 136.4 (s, C=C), 148.8 (m, $C'_0{}^1$), 154.5 (m, $C_0{}^1$), 154.7 (m, $C_0{}^1$), 170.2 (s, C=O), 190.49 (s, CHO), 190.55 (s, CHO) ppm. IR(KBr): 1702 cm^{-1} ($\nu_{C=O}$). MS (FAB) m/z = 1109 $[MH]^+$.

Dendrimer 7-G$_1$. A freshly prepared solution (0.24 mol·L^{-1} in chloroform) of *N*-methyldichlorothiophosphorhydrazide (7 mL, 1.68 mmol) was added at 0 °C to a solution of **6-G$_0$** (310 mg, 0.279 mmol) in chloroform (1 mL). The solution was stirred for 3 h and then concentrated under reduced pressure (ca. 1 mL). A 20 mL portion of pentane was added to the residue, and the resulting precipitate was filtered off and dried under reduced pressure. The powder was finally dissolved in the minimum amount of CH_2Cl_2 and precipitated with pentane to afford **7-G$_1$** as a yellow powder in 91% yield (486 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ = 8.52 (m, P=N), 62.60 (s, P_1=S), 62.67 (s, P_1=S), 62.71 (s, P_1=S); ^{1}H NMR ($CDCl_3$, 500.3 MHz): δ = 2.95 (t, $^3J_{HH}$ = 7.8 Hz, 2H, C^aH), 3.45 (d, $^3J_{HP}$ = 13.9 Hz, 6H, CH_3NP_1), 3.48 (d, $^3J_{HP}$ = 13.8 Hz, 9H, CH_3NP_1), 3.80 (t, $^3J_{HH}$ = 7.8 Hz, 2H, C^bH), 6.92 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $C'_0{}^2$H), 6.98 (d, $^3J_{HH}$ = 8.7 Hz, 4H, $C_0{}^2$H), 7.07 (d, $^3J_{HH}$ = 8.7 Hz, 6H, $C_0{}^2$H), 7.08 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $C'_0{}^3$H), 7.35−7.48 (m, 10H, C^oH, C^mH, C^pH), 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 4H, $C_0{}^3$H), 7.62 (d, $^3J_{HH}$ = 8.7 Hz, 6H, $C_0{}^3$H), 7.65 (s, 3H, CH=N), 7.68 (s, 2H, CH=N). ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 31.9 (d, $^3J_{CP}$ = 12.3 Hz, CH_3NP_1), 32.0 (d, $^3J_{CP}$ = 12.6 Hz, CH_3NP_1), 34.0 (s, C^a), 39.4 (s, C^b), 121.2 (br s, $C'_0{}^2$), 121.3 (br s, $C_0{}^2$), 121.43 (br s, $C_0{}^2$), 128.46 (s, C^i), 128.6 (s, $C_0{}^3$, C^m), 129.9 (s, $C'_0{}^3$, C^p), 130.0 (s, C^o), 131.18 (s, $C_0{}^4$), 131.27 (s, $C_0{}^4$), 131.31 (s, $C_0{}^4$), 135.1 (s, $C'_0{}^4$), 136.3 (s, C=C), 140.7 (d, $^3J_{CP}$ = 17.6 Hz, CH=NNP_1), 140.7 (d, $^3J_{CP}$ = 17.7 Hz, CH=NNP_1), 148.9 (br s, $C'_0{}^1$), 151.67 (br s, $C_0{}^1$), 151.77 (br s, $C_0{}^1$), 151.82 (br s, $C_0{}^1$), 170.6 (s, C=O).

Dendrimer 6-G$_1$. A mixture of 4-hydroxybenzaldehyde (141 mg, 1.15 mmol), cesium carbonate (756.8 mg, 2.35 mmol), and compound **7-G$_1$** (202 mg, 0.105 mmol) in THF (10 mL) was stirred at room temperature overnight. Salts were then removed by centrifugation, and the clear solution was concentrated under reduced pressure. The residue was then flash chromatographed (THF/*n*-pentane, 1:1 to 1:0) to afford **6-G$_1$** as a yellow powder in 80% yield (234 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 202.5 MHz): δ = 8.29 (m, P=N), 60.62 (2 s, P_1=S), 60.66 (s, P_1=S); ^{1}H NMR ($CDCl_3$, 500.3 MHz): δ = 2.89 (t, $^3J_{HH}$ = 7.8 Hz, 2H, C^aH), 3.34 (d, $^3J_{HP}$ = 10.6 Hz, 6H, CH_3NP_1), 3.36 (d, $^3J_{HP}$ = 10.6 Hz, 9H, CH_3NP_1), 3.74 (m, 2H, C^bH), 6.88 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $C'_0{}^2$H), 6.98 (d, $^3J_{HH}$ = 8.6 Hz, 4H, $C_0{}^2$H), 7.05 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $C'_0{}^3$H), 7.09 (d, $^3J_{HH}$ = 8.6 Hz, 6H, $C_0{}^2$H), 7.34−7.42 (m, 30H, $C_1{}^2$H, C^oH, C^mH, C^pH), 7.55−7.63 (m, 10H, $C_0{}^3$H), 7.65 (s, 3H, CH=N), 7.68 (s, 2H, CH=N), 7.81−7.86 (m, 20H, $C_1{}^3$H), 9.91 (s, 2H, CHO), 9.92 (s, 2H, CHO), 9.93 (s, 4H, CHO), 9.93 (s, 2H, CHO). ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 32.9 (br d, $^3J_{CP}$ = 12.6 Hz, CH_3NP_1), 33.9 (s, C^a), 39.3 (s, C^b), 121.1 (br s, $C'_0{}^2$), 121.3 (br s, $C_0{}^2$), 121.5 (br s, $C_0{}^2$), 122.0 (br s, $C_1{}^2$), 128.29 (s, $C_0{}^3$), 128.32 (s, $C_0{}^3$), 128.4 (s, C^i), 128.6 (s, C^m), 129.81 (s, C^o), 129.85 (s, C^p), 130.0 (s, $C'_0{}^3$), 131.5 (br s, $C_1{}^3$), 131.7 (s, $C_0{}^4$), 131.8 (s, $C_0{}^4$), 133.7 (s, $C_1{}^4$), 135.2 (s, $C'_0{}^4$), 136.1 (s, C=C), 139.5 (s, CH=NNP_1), 149.0 (s, $C'_0{}^1$), 151.4 (br s, $C_0{}^1$), 151.6 (br s, $C_0{}^1$), 154.99 (s, $C_1{}^1$), 155.05 (s, $C_1{}^1$), 155.09 (s, $C_1{}^1$), 170.5 (s, C=O), 190.72 (s, CHO), 190.74 (s, CHO) ppm.

Dendrimer 7-G$_2$. A freshly prepared solution (0.16 mmol in chloroform) of *N*-methyldichlorothiophosphorhydrazide (6.4 mL) was added at 0 °C to compound **6-G$_1$** (260 mg, 0.094 mmol). The reaction mixture was stirred at room temperature until completion (ca. 40 min) and then precipitated with pentane. The powder was filtered off, dissolved in the minimum amount of THF (ca. 1 mL), and precipitated with pentane. These washings were repeated thrice to afford **7-G$_2$** as a yellow powder in 76% yield (313 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 121.49 MHz): δ = 8.35 (m, P=N), 61.95 (s, P_1=S), 61.99 (s, P_1=S), 62.80 (s, P_2=S), 62.83 (s, P_2=S), 62.85 (s, P_2=S); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 2.89 (t, $^3J_{HH}$ = 8.4 Hz, 2H, C^aH), 3.32 (m, 15H, CH_3NP_1), 3.43 (d, $^3J_{HP}$ = 13.8 Hz, 12H, CH_3NP_2), 3.44 (d, $^3J_{HP}$ = 13.8 Hz, 18H, CH_3NP_2), 3.76 (t, $^3J_{HH}$ = 8.4 Hz, 2H, C^bH), 6.92 (d, $^3J_{HH}$ = 8.1 Hz, 2H, $C'_0{}^2$H), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 4H, $C_0{}^2$H), 6.98−7.08 (m, 8H, $C'_0{}^3$H, $C_0{}^2$H), 7.22−7.28 (m, 20H, $C_1{}^2$H), 7.30−7.43 (m, 10H, C^oH, C^mH, C^pH), 7.57−7.71 (m, 45H, $C_0{}^3$H, $C_1{}^3$H, CH=N). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.46 MHz): δ = 31.9 (d, $^3J_{CP}$ = 13.1 Hz, CH_3NP_1), 33.1 (d, $^3J_{CP}$ = 12.5 Hz, CH_3NP_2), 33.9 (s, C^a), 39.4 (s, C^b), 121.1 (br s, $C'_0{}^2$), 121.4 (br s, $C_0{}^2$), 121.9 (br s, $C_1{}^2$), 128.3 (s, $C_0{}^3$), 128.4 (s, C^i), 128.6 (s, C^m), 128.8 (br s, $C_1{}^3$), 129.8 (s, C^o, C^p), 130.0 (s, $C'_0{}^3$), 131.6 (s, $C_1{}^4$), 131.9 (s, $C_0{}^4$), 132.0 (s, $C_0{}^4$), 135.2 (s, $C'_0{}^4$), 136.1 (s, C=C), 139.0 (d, $^3J_{CP}$ = 13.6 Hz, CH=NNP_1), 140.6 (d, $^3J_{CP}$ = 18.8 Hz, CH=NNP_2), 149.0 (s, $C'_0{}^1$), 151.4 (br s, $C_0{}^1$), 151.8 (m, $C_1{}^1$), 170.5 (s, C=O) ppm.

Dendrimer 6-G$_2$. A mixture of 4-hydroxybenzaldehyde (155 mg, 1.27 mmol), cesium carbonate (825 mg, 2.53 mmol), and compound **7-G$_2$** (250 mg, 0.057 mmol) in THF (10 mL) was stirred at room temperature overnight. Salts were then removed by centrifugation, and the clear solution was concentrated under reduced pressure. The residue was then flash chromatographed (ether/THF 1:0 to 1:1) to afford **6-G$_2$** as a yellow powder in 72% yield (248 mg). ^{31}P-{^{1}H} NMR ($CDCl_3$, 121.49 MHz): δ = 8.35 (m, P=N), 60.27 (s, P_2=S), 60.30 (s, P_2=S), 62.23 (s, P_1=S), 62.29 (s, P_1=S). ^{1}H NMR

($CDCl_3$, 300.13 MHz): δ = 2.85 (m, 2H, C^aH), 3.25−3.45 (m, 45H, $CH_3NP_{1,2}$), 3.71 (m, 2H, C^bH), 6.80−7.90 (m, 169H, H_{Ar}, CH═N), 9.92 (br s, CHO, 20H). ^{13}C-{^1H} NMR ($CDCl_3$, 75.46 MHz): δ = 32.9 (d, $^3J_{CP}$ = 13.0 Hz, $CH_3NP_{1,2}$), 33.9 (s, C^a), 39.4 (s, C^b), 121.3 (br s, C_0^2, $C'_0{}^2$), 122.0 (d, $^3J_{CP}$ = 4.7 Hz, C_1^2, C_2^2), 128.4 (s, C_0^3, C_1^3), 128.6 (s, C^i, C^m), 129.8 (s, C^o, C^p), 130.0 (s, $C'_0{}^3$), 131.5 (s, C_2^3), 132.0 (s, C_0^4, C_1^4), 136.1 (s, C═C), 139.1 (d, $^3J_{CP}$ = 12.6 Hz, CH═NNP_1), 139.5 (d, $^3J_{CP}$ = 12.6 Hz, CH═NNP_2), 148.1 (br s, $C'_0{}^1$), 151.4 (d, $^2J_{CP}$ = 6.9 Hz, C_0^1, C_1^1), 155.1 (d, $^2J_{CP}$ = 6.8 Hz, C_2^1), 170.5 (s, C═O), 190.7 (br s, CHO) ppm.

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Supporting Information Available: Copy of ^1H, ^{13}C, and ^{31}P NMR spectra of all new compounds. Crystallographic information files (CIF) for compounds **1** and **1′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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