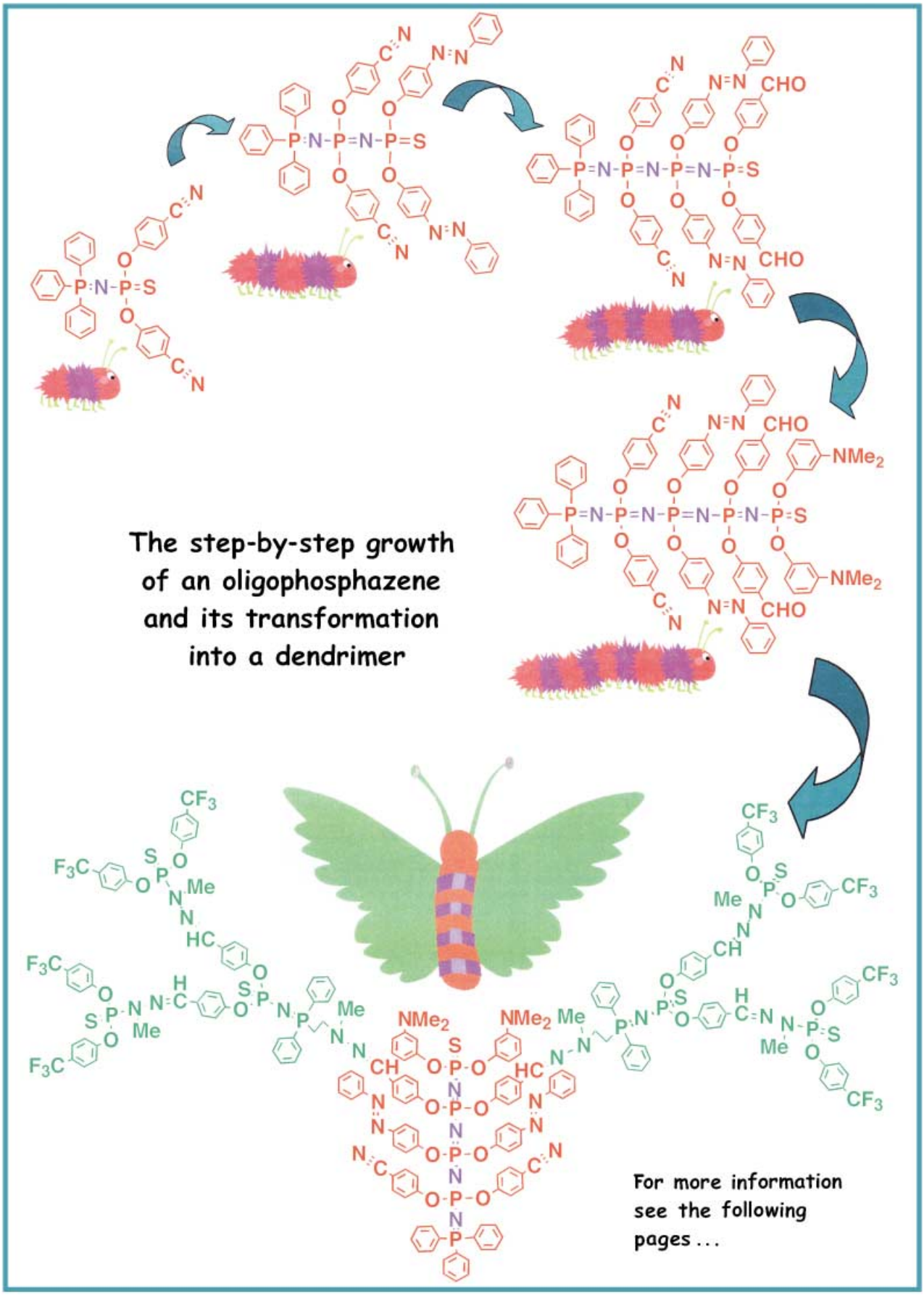

 DOI: 10.1002/chem.200204630

The First Linear Multiphosphazene Having Five Different Types of Side Groups and Its Use as the Core of a Dendrimeric Species

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Abstract: The step-by-step synthesis of the first oligophosphazenes having more than two types of side functions is described. These multifunctionalized oligophosphazenes possess up to four phosphazene linkages and up to four types of functional side groups. These compounds may serve as models for a better understanding of electronic delocalization phenomena in linear inorganic chains, and constitute novel cores for the synthesis of new dendrimeric species possessing several types of functions as end groups, at the level of the core, and within the branches.

Keywords: alkylation · azides · chain structures · dendrimers · phosphazenes

Introduction

The phosphazene linkage plays a key role in several aspects of chemistry, in particular for the construction of inorganic polymers[1] and strong bases.[2] Linear polyphosphazenes ($[\text{-N=PR}_2\text{-}]_n$) have many applications, for instance as flame-retardants, electrolytes in batteries, or biomedically important materials.[3] The structural diversity of polyphosphazenes is enormous; in addition to the general cases in which the R substituents are the same along the chain, polyphosphazenes that possess two types of substituents, placed either at specific sites ($[\text{-N=PRR}'\text{-}]_n$) or at random ($([\text{-N=PR}_2\text{-}]_x[\text{-N=PR}'_2\text{-}]_y)_n$) are known, as well as some examples of compounds that have three or even four side groups, generally consisting of block copolymers ($([\text{-N=PRR}'\text{-}]_x[\text{-N=PR}''\text{R}'''\text{-}]_y)_n$).[4] On the other hand, small and well-defined oligophosphazenes (linear chain of three or four P=N linkages) are less well known, and their structural diversity is limited. To the best of our knowledge, only one example of a defined oligomer possessing at least three linearly alternating P=N linkages and at least two types of substituents on phosphorus was previously described, namely $P_3N_3F_5\text{-N=PF}_2\text{-N=PCl}_2\text{-N=PCl}_3$.[5]

Such inorganic oligomers might also be used as a tool for a better understanding of the bonding in polyphosphazenes; however, it might also be used as a novel core for a dendrimeric species. Indeed, the grafting of one,[6] two,[7] or a large number[8] of dendrons to organolinear oligomers or polymers was previously reported, but there is no example of dendrons grafted to a linear inorganic and multifunctionalized oligomer.

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We report here the first examples of a series of perfectly defined oligophosphazenes possessing up to four P=N linkages and five different types of substituents on the phosphorus atoms, four of them being different functional groups, as well as their use for the grafting of two dendrons in a specific location on the oligophosphazene linkage.

Results and Discussion

The only way to obtain a well-defined and specifically functionalized oligomer is by creating it by means of a step-by-step process. To build the oligophosphazene backbone, we chose to use the three-step process that we have already applied for the internal functionalization of dendrimers.[9] The first step is a Staudinger reaction between a thiophosphorylated azide and a phosphine to create a P=N-P=S linkage. The second step is an alkylation of the P=S group with alkyl triflates to induce a weakening of the P–S bond. The third step is the desulfurization reaction with $P(NMe_2)_3$ to generate a tricoordinate phosphorus atom that is able to react in a Staudinger reaction. We have already demonstrated the feasibility of the three steps; however, we never tried to repeat them several times. Furthermore, these reactions were carried out either in the absence of any functional group on the dendrimer, or in the presence of an aldehyde as the sole functional group.

Thus, the first crucial point for the multistep building of oligophosphazenes is the choice of the functionalized azides, since the functional groups must not react during the multistep process, particularly when alkyl triflates are used. We already knew that the aldehyde groups are compatible, but we needed to check several other groups. For this purpose, we built several $R_3P\text{=N-P(S)(OAr)}_2$ models, and tested their reactivity. Arylnitride, arylmalonitrile, and azobenzene

DOI: 10.1002/chem.200204630

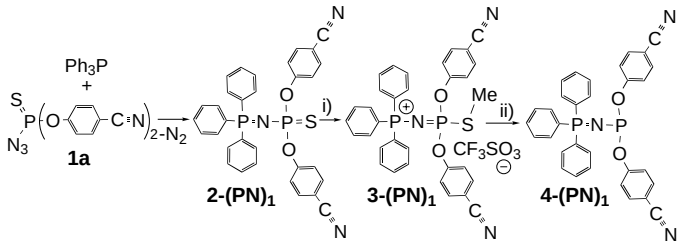
Table 1. $^{31}P\{^1H\}$ NMR data (δ; ^2J[Hz]) in $CDCl_3$.

Compound	P_0	$J(P_0,P_1)$	P_1	$J(P_1,P_2)$	P_2	$J(P_2,P_3)$	P_3	$J(P_3,P_4)$	P_4	P_5	$J(P_5,P'_5)$	P'_5	P_6
2-(PN)$_1$	15.3	30.1	50.3										
3-(PN)$_1$	23.2[a]	20.2	23.4[b]										
4-(PN)$_1$	12.9	56.7	144.8										
2-(PN)$_2$	15.8	23.8	−14.6	58.1	46.9								
3-(PN)$_2$	20.0	26.1	−17.2	54.8	22.2								
4-(PN)$_2$	14.8	25.0	−11.9	78.0	137.0								
2-(PN)$_3$	16.2	23.0	−16.3	52.3	−17.8	55.5	45.0						
3-(PN)$_3$	18.4	26.1	−16.3	55.5	−19.1	55.9	20.8						
2-(PN)$_4$	16.6	24.1	−16.4	54.4	−19.7	53.7	−20.9	56.6	46.5				
6-G$_1$										11.9	30.5	53.1	61.6
7-G$_1$										18.7	33.2	52.4	61.6
8-G$_2$	16.3	25.0	−16.3	54.1	−18.8	54.9	−20.2	57.2	46.4	18.2	34.2	52.4	61.6

[a] Or P_1. [b] Or P_0.

groups do not react with alkyl triflates. Therefore, they could be used as functional groups at any step. On the other hand, aryldimethylamino groups are partly alkylated (as expected) and thus, they could be used only in the last step of the construction. The second crucial point concerns the tricoordinate phosphorus atom generated during the desulfurization process: it must not weaken the structure. The arylmalonitrile group was eliminated from our selection because it induces such a problem.

Having carried out these preliminary experiments, we began the synthesis of the oligophosphazene. The first step is the Staudinger reaction between triphenylphosphine and the thiophosphinoazide **1a** to give the thiophosphorylated monophosphazene **2-(PN)$_1$** in quantitative yield (Scheme 1).



Scheme 1. The first three steps for the building of the oligophosphazenes. i) CF_3SO_3Me; ii) $P(NMe_2)_3$, $-[MeSP(NMe_2)_3][CF_3SO_3]$.

The ^{31}P NMR spectrum of **2-(PN)$_1$** consists of two doublets at $\delta = 15.3$ (PPh_3) and 50.3 ppm (P=S) with $^2J(P,P) = 30.1$ Hz (Table 1). Single crystals of **2-(PN)$_1$** were obtained from THF/pentane (1/20) (Table 2). The X-ray crystal structure of **2-(PN)$_1$** is shown in Figure 1.[10]

The second step of the construction of the oligophosphazene is the methylation of the thiophosphoryl group with CF_3SO_3Me to afford compound **3-(PN)$_1$** in very good yield. The ^{31}P NMR spectrum of **3-(PN)$_1$** consists of an AB system at $\delta = 23.2 - 23.4$ ppm. Thus, the alkylation induces a shielding of the signal corresponding to the thiophosphoryl group ($\Delta\delta = -27$), as expected, but also a deshielding of the signal corresponding to the PPh_3 group ($\Delta\delta = 8$). Single crystals of **3-(PN)$_1$** were obtained from chloroform (Table 2). The X-ray crystal structure of **3-(PN)$_1$** is shown in Figure 2.[10]

Compounds **2-(PN)$_1$** and **3-(PN)$_1$** differ only by the presence of the methyl group linked to S in **3-(PN)$_1$**, thus it is interesting to note the structural variations induced by the alkylation (Table 3): it induces a lengthening of the P–S bond,

Table 2. X-ray data for **2-(PN)$_1$** and **3-(PN)$_1$**.

	2-(PN)$_1$	**3-(PN)$_1$**
formula	$C_{32}H_{23}N_3O_2P_2S$	$C_{34}H_{26}F_3N_3O_5P_2S_2$
fw	575.53	739.64
crystal dimensions [mm]	0.45 × 0.50 × 0.12	0.50 × 0.37 × × 0.15
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a [Å]	11.6605(11)	11.7970(9)
b [Å]	8.4315(6)	13.6570(12)
c [Å]	28.816(3)	21.1917(15)
β [°]	97.694(12)	95.452(9)
V [Å]	2807.6(4)	3398.8(5)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.362	1.445
μ [mm^{-1}]	0.265	0.314
$F000$	1192	1520
λ [Å]	0.71073	0.71073
$2\theta_{max}$ [°]	52.3	52.5
T [K]	160(2)	180(2)
scan mode	ϕ rotation	ϕ rotation
no. of reflections collected	21171	33037
no. of unique reflections	5525	6671
no. of variables	361	443
absorption correction	semiempirical	semiempirical
$T_{min} - T_{max}$	0.556–0.864	0.524–0.851
GOF on F^2	1.029	1.026
$R1$ (all data)	0.0499	0.0654
$WR2$ (all data)	0.0858	0.1067
$R1$ ($I > 2\sigma(I)$)	0.0332	0.0406
$WR2$ ($I > 2\sigma(I)$)	0.0799	0.0961
ρ_{max}, ρ_{min}	0.269, −0.864	0.613, −0.354

Abstract in French: *La synthèse étape par étape des premiers oligophosphazènes ayant plus de deux fonctions latérales différentes est décrite. Ces oligophosphazènes plurifonctionnalisés possèdent jusqu'à 4 liaisons phosphazène et 4 types de groupements fonctionnels latéraux. Ces composés peuvent servir de modèles pour une meilleure compréhension des phénomènes de délocalisation électronique dans des chaînes inorganiques linéaires, et ils constituent des cœurs originaux pour la synthèse de nouvelles espèces dendrimériques ayant plusieurs types de fonctions en surface, au niveau du cœur et dans les branches.*

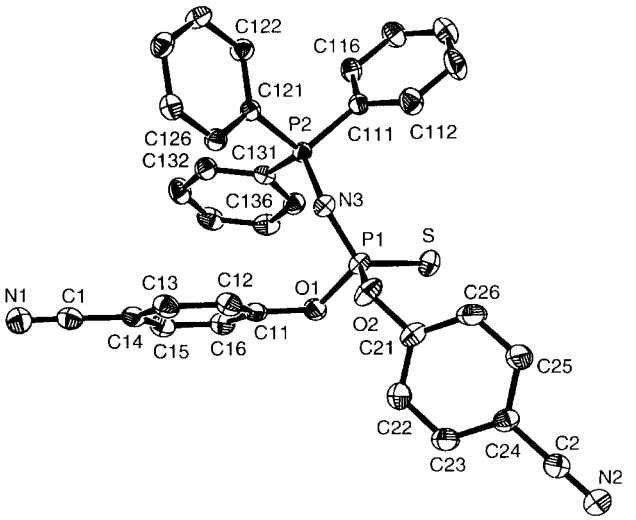


Figure 1. Structure of compound **2-(PN)$_1$** (ORTEP drawing; hydrogen atoms are omitted for clarity).

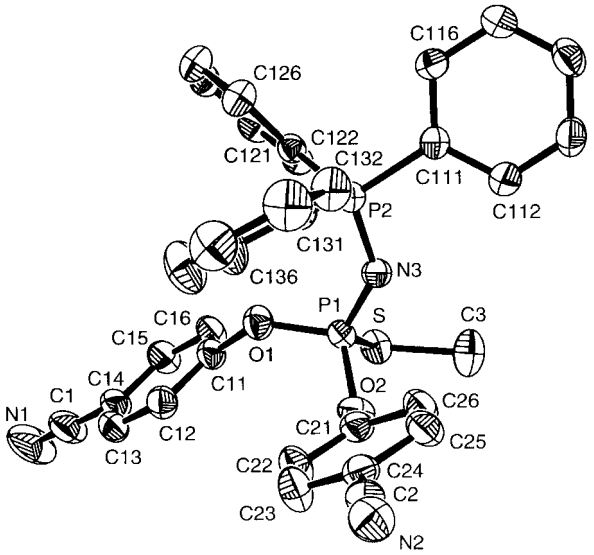


Figure 2. The cationic part of compound **3-(PN)$_1$** (ORTEP drawing; hydrogen atoms are omitted for clarity).

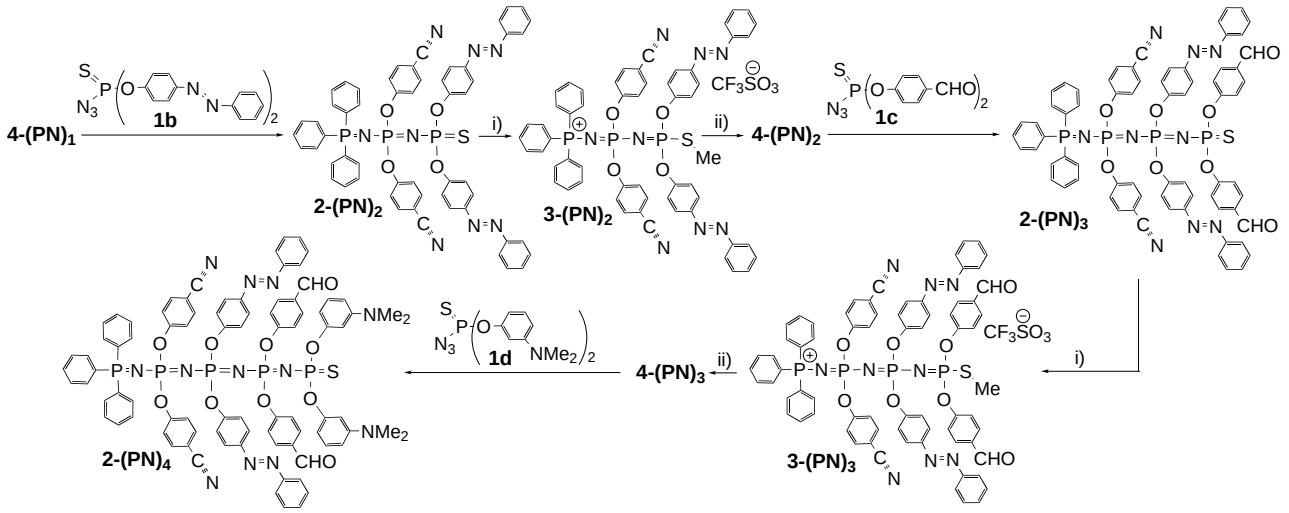
Table 3. Bond lengths [Å] and angles [°] for the P2–N3–P1(–O–C)$_2$–S fragment of **2-(PN)$_1$** and **3-(PN)$_1$**, and variations between both structures.

Parameter	**2-(PN)$_1$**	**3-(PN)$_1$**	Δ**2-(PN)$_1$** → **3-(PN)$_1$**
P1–S	1.9267(6)	2.0397(9)	+0.113
P1–N3	1.5734(14)	1.5370(19)	−0.036
N3–P2	1.5806(15)	1.5951(19)	+0.014
P1–O1	1.6308(12)	1.5726(18)	−0.058
P1–O2	1.6146(14)	1.5749(17)	−0.040
O1–C1	1.386(2)	1.407(3)	+0.022
O2–C2	1.384(2)	1.410(3)	+0.026
N3-P1-S	123.24(6)	117.20(8)	−6.0
P1-N3-P2	134.67(10)	137.65(13)	+3.0

as expected, but it also induces a slight shortening of the N–P(S) bond and a slight lengthening of the Ph_3P–N bond. This indicates at least a partial delocalization of the charge along the inorganic backbone of **3-(PN)$_1$**. There is also a shortening of the P–OAryl bonds in **3-(PN)$_1$**.

The third step of the construction of the oligophosphazene consists in breaking the P–S bond to obtain a tricoordinate phosphorus atom (P^{III}). Reaction of **3-(PN)$_1$** with $P(NMe_2)_3$ induces the transfer of the S–Me group and leads to **4-(PN)$_1$** (Scheme 1). This compound is very sensitive to oxidation, thus it was not isolated but only characterized by ^{31}P NMR spectroscopy. It has a very characteristic value of the chemical shift, namely $\delta = 144.8$ ppm (d, $^2J(P,P) = 56.7$ Hz) for the P^{III} center.

The sequence of three reactions can be repeated starting with **4-(PN)$_1$**. Indeed, the tricoordinate phosphorus atom of **4-(PN)$_1$** reacts readily with the azide **1b** to afford the diphosphazene **2-(PN)$_2$** that contains two nitrile and two azobenzene functional groups[11] (Scheme 2). The methylation of **2-(PN)$_2$** gives the expected **3-(PN)$_2$**, which is desulfurized by $P(NMe_2)_3$ to afford **4-(PN)$_2$**. A third cycle of reactions can begin with **4-(PN)$_2$** and the azide **1c** to afford **2-(PN)$_3$**. To the best of our knowledge, this compound is the first linear triphosphazene possessing three types of functional groups. The three-step cycle can be applied again, starting from **2-(PN)$_3$**. The azide **1d** is reacted in the last step to afford **2-(PN)$_4$**, the first tetraphosphazene functionalized by four



Scheme 2. Repetitive multistep synthesis of the tetraphosphazene **2-(PN)$_4$**. i) CF_3SO_3Me; ii) $P(NMe_2)_3$, $-[MeSP(NMe_2)_3][CF_3SO_3]$.

different types of functions (nitrile, azobenzene, aldehyde, and amine) (Scheme 2). According to our previous experiments, the use of the azide **1d** precludes the continuation of the growth of the phosphazene chain because the NMe_2 groups will react during the alkylation step.

All these mono-, di-, tri-, and tetraphosphazenes are characterized by multinucleus NMR and mass spectrometry (FAB); however, the most important tool is ^{31}P NMR spectroscopy (Table 1). As an illustration, Figure 3 gives the ^{31}P NMR spectrum of compound **2-(PN)$_4$**, as well as its simulated spectrum, which is in perfect agreement with the real one. The spectrum is complex, as expected, but all the five phosphorus atoms can be precisely identified.

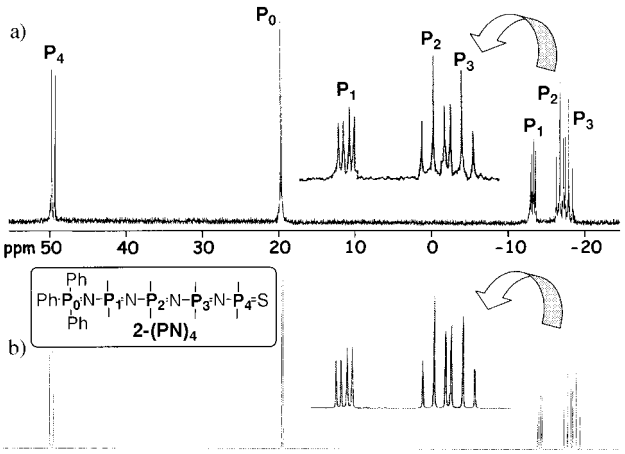


Figure 3. a) ^{31}P NMR spectrum of the tetraphosphazene **2-(PN)$_4$**. b) Simulated ^{31}P NMR spectrum of **2-(PN)$_4$**.

Such a series of compounds offers a very unique opportunity to study the possibility of an electronic delocalization along an inorganic chain. Indeed, it is obvious that the π system in oligo- or polyphosphazenes is very different from that of organic polymers. A study of the electronic structure of oligophosphazenes by means of density functional theory (DFT) calculations suggested that the π bonding is induced by a negative hyperconjugation that involves electron donation from the lone pair π (N) orbitals to the σ* (P–X) orbitals[12] (X = substituent); such delocalization is mostly confined in the vicinity of the P-N-P region, the so-called "island π bonding".[13] Thus, the possibility of delocalization through several phosphazene linkages is an open question. The presence of a charge and the structural modification that it induces could help to answer this question. A few charged, small oligophosphazenes were previously reported,[14] but their symmetrical structure was not adequate ($[R_3P{=}N\text{-}PR_2{=}N\text{-}PR_3]^+$ is equivalent to $[R_3P\text{-}N{=}PR_2\text{-}N{=}PR_3]^+$). On the other hand, the series of oligophosphazenes studied here could help to answer this question using ^{31}P NMR spectroscopy, which is again the best tool to characterize such behavior. Indeed, the chemical shift of the phosphorus atom of the Ph_3P group at the beginning of the chain (noted P_0) is sensitive to the alkylation that occurs on sulfur. Figure 4 displays the variation of the chemical shift value of all phosphorus atoms for each compound from **2-(PN)$_1$** to **2-(PN)$_4$** and from **3-(PN)$_1$** to **3-(PN)$_3$**. The behavior of the P_0 atom is totally different from that of P_1, P_2, and P_3 atoms. Indeed, the chemical shifts of the latter vary from $\delta \approx 50$ ppm in the P=S form (**2-(PN)$_x$**) to ≈24 ppm in the P-S-Me form (**3-(PN)$_x$**) and ≈ −15 ppm in the P=N form (**2-(PN)$_{x+1}$**). Their chemical shift values remain almost constant for all the subsequent reactions. In marked contrast to such behavior, the chemical shift value of P_0 varies at each step of the oligophosphazene construction. It oscillates around $\delta = 17$ with progressively decreasing amplitude when the alkylation site is remote. The phenomenon remains sensitive, even for the **2-(PN)$_3$** → **3-(PN)$_3$** reaction that occurs seven bonds away from P_0. Thus, this data suggests that the charge introduced during the alkylation step is delocalized throughout the inorganic phosphazene chain; however, with a decreasing effectiveness as the site of alkylation moves away from the beginning of the chain.

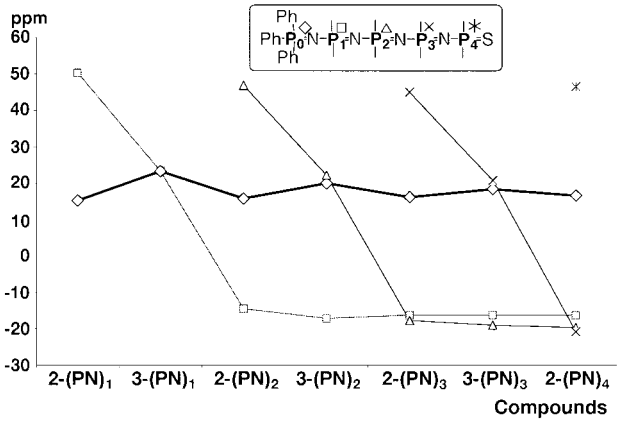
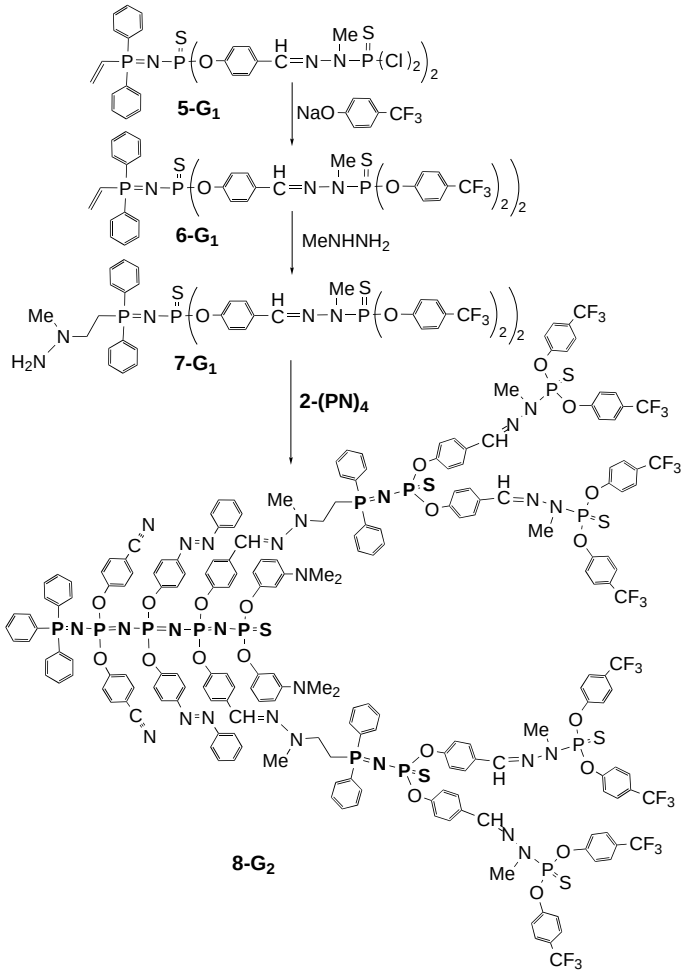


Figure 4. Variation of the ^{31}P NMR chemical shifts of all phosphorus atoms for compounds **2-(PN)$_1$** to **2-(PN)$_4$** and **3-(PN)$_1$** to **3-(PN)$_3$**.

In addition to this novel property, the other important feature of compound **2-(PN)$_4$** is the presence of four types of functional groups. Because no well-defined inorganic oligomer was used as a dendrimer core up to now, we decided to test this compound. The aldehyde groups appear to be the most compatible with the chemistry of our dendrimers. Thus, we designed dendron **7-G$_1$**, that has a *N*,*N*-disubstituted hydrazine core and trifluoro-*p*-cresol end groups. This compound was synthesized by an adaptation of the procedure we had already reported for the synthesis of dendrons.[15] Starting from dendron **5-G$_1$**, four equivalents of the sodium salt of trifluoro-*p*-cresol were reacted with the $P(S)Cl_2$ end groups, leading to dendron **6-G$_1$**; then methyl hydrazine was reacted with the core to give dendron **7-G$_1$**. The condensation reaction between two equivalents of dendron **7-G$_1$** and the tetraphosphazene **2-(PN)$_4$** occurs readily to afford the dendrimeric species **8-G$_2$**, which was isolated in very good yield (95%) after workup (Scheme 3). The condensation reaction is characterized in ^1H NMR by the disappearance of the signal corresponding to the aldehyde groups. Compound **8-G$_2$** was also characterized by ^{31}P NMR spectroscopy: in addition to the signals corresponding to the tetraphosphazene chain, three series of signals (two doublets and one singlet) appear (Table 1). The condensation is also confirmed by a slight shielding of the doublet corresponding to the PPh_2 group of



Scheme 3. Regioselective grafting of two dendrons on the oligophosphazene **2-(PN)$_4$**.

the dendron from $\delta = 18.7$ ppm for **7-G$_1$** to $\delta = 18.2$ ppm for **8-G$_2$**. This very novel dendrimeric species possesses several types of functional groups at the core, in the branches, and on the surface, and consists of phosphazene linkages not only at the core but also within the branches.

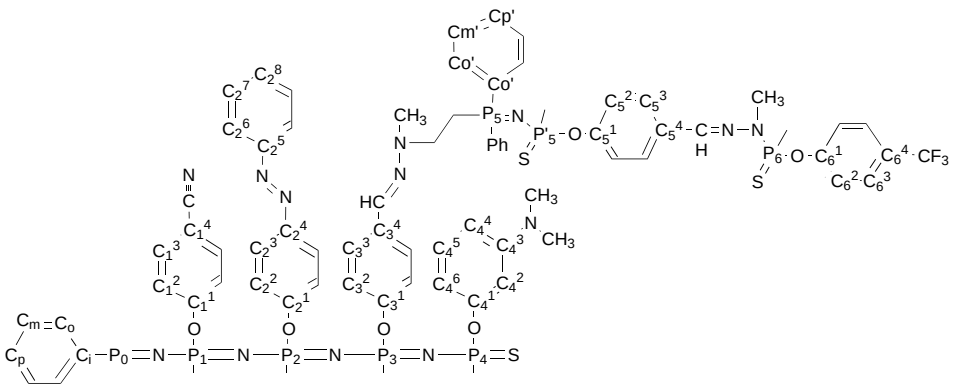
Conclusion

We have demonstrated, for the first time, the possibility of building a series of oligophosphazenes that contain up to four different functionalized side groups that can be precisely placed on the backbone. These compounds were found to be useful for a better understanding of the delocalization effects in inorganic chains, but also as a novel core of dendrimeric species. Indeed, the condensation reaction of two equivalents of dendrons on aldehyde functions gave rise to an unusual type of dendrimeric species with a multifunctionalized oligophosphazene core and eight trifluoromethyl groups as end groups, linked to the oligophosphazene chain through phosphazene linkages. Obviously, these methods of synthesis could be applied to other functions (at the core or on the surface), to vary the potential uses of such compounds.

Experimental Section

All manipulations were carried out with standard high-vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and ether over sodium/benzophenone, pentane and CH_2Cl_2 over phosphorus pentoxide, toluene over sodium); they were degassed prior to use in the case of experiments that used derivatives with tricoordinate phosphorus atoms. All compounds that contained azo groups were protected against light during manipulation to avoid the isomerization of these bonds. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded with Bruker AC200, AC250, DPX300, or AMX400 spectrometers. References for NMR chemical shifts were 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^{1}H and ^{13}C NMR, CF_3CO_2H for ^{19}F NMR. The ^{13}C NMR signals were assigned on the basis of J_{mod}, two-dimensional HMBC, and HMQC, broad-band or CW ^{31}P decoupling experiments, when necessary. The numbering used for NMR assignments is depicted in Scheme 4. The program MestRe-C was used to generate the simulated spectra. Mass spectra (FAB) were recorded on a Finnigan Mat TSQ700. Compounds **1a**,[15] **1c**,[16] **1d**,[15] and the first-generation dendron **5-G$_1$**[15] were synthesized as described previously. All ^{31}P NMR data are gathered in Table 1.

Compound 1b: A solution of 4-hydroxyazobenzene (0.39 g, 1.97 mmol) and NEt_3 (0.275 mL, 1.97 mmol) in THF (20 mL) was stirred for 30 min. This mixture was added dropwise at $-100\,^\circ$C to a solution of trichlorophosphine sulfide (0.1 mL, 0.985 mmol) in THF (10 mL). The resulting mixture was slowly allowed to reach room temperature, and was then stirred for 12 h at this temperature. The mixture was filtered to eliminate the precipitated triethylamine hydrochloride. The resulting solution was evaporated to dryness. The residue was dissolved in acetone (20 mL), and sodium azide (64 mg, 0.985 mmol) was added. This solution was stirred for 24 h at room temperature, and then evaporated to dryness. THF (20 mL) was added to the residue, and the mixture was centrifuged to eliminate sodium chloride. The resulting solution was evaporated to dryness to yield an oily orange liquid that was purified by column chromatography on silica (AcOEt/Hexane: 3/7). Compound **1b** was obtained as a waxy orange oil in 32% yield. ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 58.8$ ppm (s); ^{1}H NMR ($CDCl_3$): $\delta = 7.41$ (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,P) = 1.9 Hz, 4H; HC^2), 7.44–7.58 (m, 6H; HC^7, HC^8), 7.92 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.7 Hz; HC^6), 7.98 ppm (dd, ^3J(H,H) = 8.8 Hz, ^5J(H,P) = 0.9 Hz, 4H; HC^3); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 121.7$ (d, ^3J(C,P) = 4.4 Hz, C^2), 122.8 (s, C^6), 124.3 (s, C^3), 129.0 (s, C^7), 131.1 (s, C^8), 150.3 (d, ^5J(C,P) = 2.9 Hz, C^4), 151.4 (d, ^2J(C,P) = 8.8 Hz, C^1), 152.3 ppm (s, C^5); IR (KBr): $\tilde{\nu} = 2150\ cm^{-1}$ (N_3); elemental analysis calcd (%) for $C_{24}H_{18}N_7O_2PS$ (499.5): C 57.71, H 3.63, N 19.63; found: C 57.63, H 3.58, N 19.51.



Scheme 4. Numbering scheme used for the NMR assignments

Compound 2-(PN)$_1$: A solution of **1a** (0.288 g, 0.845 mmol) in dichloromethane (3 mL) was added to a solution of triphenylphosphine (0.233 g, 0.888 mmol) in dichloromethane (3 mL) at room temperature. This solution was stirred for 12 h, and then evaporated to dryness. The resulting powder was washed three times with THF/pentane (1/20) to give **2-(PN)$_1$** as a white powder in 99% yield. Single crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature in a mixture of THF/pentane (1/20). ^{1}H NMR ($CDCl_3$): $\delta = 7.23$ (d, ^3J(H,H) = 8.0 Hz, 4H; C_1^2H), 7.40–7.65 ppm (m, 19H; H_{arom}); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 107.9$ (s, C_1^4), 118.6 (s, CN), 122.5 (d, ^3J(C,P) = 5.4 Hz, C_1^2), 128.8 (dd, ^1J(C,P) = 106.0 Hz, ^3J(C,P) = 3.7 Hz, C_i), 128.9 (d, ^3J(C,P) = 13.9 Hz, C_m), 132.7 (d, ^2J(C,P) = 9.7 Hz, C_o), 133.2 (d, ^4J(C,P) = 3.5 Hz, C_1^3), 133.6 (s, C_p), 155.3 ppm (d, ^2J(C,P) = 10.1 Hz, C_1^1); IR (KBr): $\tilde{\nu} = 2225$ cm^{-1} (CN); elemental analysis calcd (%) for $C_{32}H_{23}N_3O_2P_2S$ (575.6): C 66.78, H 4.03, N 7.30; found: C 66.73, H 3.99, N 7.25.

Compound 3-(PN)$_1$: Methyl triflate (40 μL, 0.35 mmol) was added dropwise at room temperature to a solution of **2-(PN)$_1$** (0.201 g, 0.35 mmol) in CH_2Cl_2 (2 mL). The resulting solution was stirred for 20 min, and then evaporated to dryness. The residue was washed three times with THF/pentane (1/20) to give **3-(PN)$_1$** as a white powder in 95% yield. Single crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature in chloroform. ^{1}H NMR ($CDCl_3$): $\delta = 2.53$ (d, ^3J(H,P) = 17.3 Hz, 3H; S-CH_3), 7.25–7.62 ppm (m, 23H; H_{arom}); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 13.7$ (d, ^2J(C,P) = 5.1 Hz, S-CH_3), 110.7 (s, C_1^4), 117.5 (s, CN), 122.0 (d, ^3J(C,P) = 3.6 Hz, C_1^2), 123.8 (d, ^1J(C,P) = 112.7 Hz, C_i), 129.7 (d, ^3J(C,P) = 11.9 Hz, C_m), 132.0 (d, ^2J(C,P) = 10.4 Hz, C_o), 134.6 (br s, C_1^3, C_P), 151.8 ppm (d, ^2J(C,P) = 9.8 Hz, C_1^1) ($CF_3SO_3^-$ not detected); ^{19}F{^{1}H} NMR ($CDCl_3$): $\delta = -2.0$ ppm (s, CF_3); IR (KBr): $\tilde{\nu} = 2225$ cm^{-1} (CN); elemental analysis calcd (%) for $C_{34}H_{26}F_3N_3O_5P_2S_2$ (739.7): C 55.21, H 3.54, N 5.68; found: C 55.14, H 3.48, N 5.60.

Compound 4-(PN)$_1$: Hexamethylphosphorustriamide (HMPT, 117 μL, 0.64 mmol) was added dropwise at room temperature to a solution of **3-(PN)$_1$** (0.476 g, 0.64 mmol) in dichloromethane (5 mL). The resulting solution was stirred for 2 h, and then evaporated to dryness. The residue was extracted with toluene, then the solution was evaporated to dryness to afford **4-(PN)$_1$** as a highly air-sensitive white powder (70% yield).

Compound 2-(PN)$_2$: A solution of **1b** (0.093 g, 0.186 mmol) in THF (5 mL) was added at room temperature to a solution of **4-(PN)$_1$** (0.101 g, 0.186 mmol) in THF (5 mL). The solution was stirred for 12 h and then evaporated to dryness to afford an oil, which was purified by column chromatography on silica (ethyl acetate/pentane (1/4)). **2-(PN)$_2$** was isolated as an orange oil in 85% yield. ^{1}H NMR ($CDCl_3$): $\delta = 7.07$ (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,P) = 1.3 Hz, 4H; HC_1^2), 7.20 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,P) = 1.5 Hz, 4H; HC_2^2), 7.39–7.65 (m, 25H; H_{arom}), 7.77 (d, ^3J(H,H) = 8.8 Hz, 4H; HC_2^3), 7.91 ppm (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.4 Hz, 4H; HC_2^6); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 108.5$ (s, C_1^4), 118.2 (s, CN), 121.8 (d, ^3J(C,P) = 4.2 Hz, C_2^2), 121.9 (d, ^3J(C,P) = 5.8 Hz, C_1^2), 122.8 (s, C_2^6), 123.9 (s, C_2^3), 127.6 (dd, ^1J(C,P) = 114.3 Hz, ^3J(C,P) = 3.9 Hz, C_i), 129.0 (d, ^3J(C,P) = 13.4 Hz, C_m), 129.1 (s, C_2^7), 130.9 (s, C_2^8), 132.5 (d, ^2J(C,P) = 11.6 Hz, C_o), 133.2 (s, C_P), 133.6 (s, C_1^3), 149.1 (s, C_2^4), 152.6 (s, C_2^5), 154.1 (d, ^2J(C,P) = 9.9 Hz, C_2^1), 154.5 ppm (d, ^2J(C,P) = 8.2 Hz, C_1^1); IR (KBr): $\tilde{\nu} = 2225$ cm^{-1} (CN); MS (FAB): m/z (%): 1015 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{56}H_{41}N_8O_4P_3S$ (1015.0): C 66.27, H 4.07, N 11.04; found: C 66.35, H 4.15, N 10.91.

Compound 3-(PN)$_2$: Methyl triflate (20 μL, 0.177 mmol) was added dropwise at room temperature to a solution of **2-(PN)$_2$** (0.177 g, 0.174 mmol) in dichloromethane (2 mL). The resulting solution was stirred for 20 min, and then evaporated to dryness, to afford an oil, which was washed three times with CH_2Cl_2/pentane (1/20). **3-(PN)$_2$** was isolated as an orange oil in 95% yield. ^{1}H NMR ($CDCl_3$): $\delta = 2.63$ (d, ^3J(H,P) = 18.0 Hz, 3H; S-CH_3), 6.94 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,P) = 1.0 Hz, 4H; HC_1^2), 7.16 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,P) = 1.7 Hz, 4H; HC_2^2), 7.28–7.56 (m, 22H; H_{arom}), 7.66 (ttd, ^3J(H,H) = 7.1 Hz, ^4J(H,H) = 1.5 Hz, ^5J(H,P) = 1.7 Hz, 3H, HC_P), 7.84 (d, ^3J(H,H) = 8.6 Hz, 4H, HC_2^3), 7.93 ppm (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.4 Hz, 4H, HC_2^6); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 13.6$ (d, ^2J(C,P) = 5.5 Hz, S-CH_3), 110.1 (s, C_1^4), 117.5 (s, CN), 121.0 (d, ^3J(C,P) = 5.0 Hz, C_2^2), 121.4 (d, ^3J(C,P) = 5.8 Hz, C_1^2), 123.1 (s, C_2^6), 124.7 (s, C_2^3), 125.7 (dd, ^1J(C,P) = 108.1 Hz, ^3J(C,P) = 4.3 Hz, C_i), 129.3 (s, C_2^7), 129.6 (d, ^3J(C,P) = 13.8 Hz, C_m), 131.8 (s, C_2^8), 132.1 (d, ^2J(C,P) = 11.8 Hz, C_o), 133.8 (s, C_P), 134.4 (s, C_1^3), 150.6 (d, ^2J(C,P) = 11.1 Hz, C_2^1), 150.7 (s, C_2^4), 152.2 (s, C_2^5), 152.9 ppm (d, ^2J(C,P) = 9.8 Hz, C_1^1), ($CF_3SO_3^-$ not detected); ^{19}F{^{1}H} NMR ($CDCl_3$): $\delta = -2.0$ ppm (s, CF_3); IR (KBr): $\tilde{\nu} = 2225$ cm^{-1} (CN); elemental analysis calcd (%) for $C_{58}H_{44}F_3N_8O_7P_3S_2$ (1179.1): C 59.08, H 3.76, N 9.50; found: C 59.21, H 3.85, N 9.44.

Compound 4-(PN)$_2$: HMPT (32 μL, 0.174 mmol) was added dropwise at room temperature to a solution of **3-(PN)$_2$** (0.205 g, 0.174 mmol) in CH_2Cl_2 (3 mL). The solution was stirred for 2 h, and then evaporated to dryness. The residue was extracted with toluene, then the solution was evaporated to dryness to afford **4-(PN)$_2$** as a highly air-sensitive orange powder in 72% yield.

Compound 2-(PN)$_3$: A solution of **1c** (0.061 g, 0.174 mmol) in THF (5 mL) was added at room temperature to a solution of **4-(PN)$_2$** (0.171 g, 0.174 mmol) in THF (5 mL). The solution was stirred for 12 h, and then evaporated to dryness. The resulting powder was washed three times with THF/pentane (1/20) to afford **2-(PN)$_3$** as an orange powder in 83% yield. ^{1}H NMR ($CDCl_3$): $\delta = 7.10$ (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,P) = 0.9 Hz, 4H; HC_1^2), 7.15 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,P) = 0.9 Hz, 4H; HC_2^2), 7.28 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,P) = 0.9 Hz, 4H; HC_3^2), 7.40–7.63 (m, 25H; H_{arom}), 7.67 (d, ^3J(H,H) = 8.7 Hz, 4H; HC_2^3), 7.75 (d, ^3J(H,H) = 8.7 Hz, 4H; HC_3^3), 7.97 (dd, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.5 Hz, 4H; HC_2^6), 9.84 ppm (s, 2H; CHO); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 109.2$ (s, C_1^4), 118.5 (s, CN), 121.8 (d, ^3J(C,P) = 5.0 Hz, C_2^2), 122.2 (d, ^3J(C,P) = 5.6 Hz, C_1^2), 122.2 (d, ^3J(C,P) = 5.1 Hz, C_3^2), 123.3 (s, C_2^6), 124.4 (s, C_2^3), 127.6 (dd, ^1J(C,P) = 107.7 Hz, ^3J(C,P) = 3.9 Hz, C_i), 129.6 (d, ^3J(C,P) = 13.2 Hz, C_m), 129.6 (s, C_2^7), 131.5 (s, C_3^3), 131.6 (s, C_2^8), 132.8 (s, C_3^4), 132.8 (d, ^2J(C,P) = 11.4 Hz, C_o), 133.9 (d, ^4J(C,P) = 2.9 Hz, C_P) , 134.2 (s, C_1^3), 149.8 (d, ^5J(C,P) = 1.3 Hz, C_2^4), 152.9 (s, C_2^5), 153.6 (d, ^2J(C,P) = 8.6 Hz, C_2^1), 154.5 (d, ^2J(C,P) = 8.8 Hz, C_1^1), 157.3 (d, ^2J(C,P) = 8.8 Hz, C_3^1), 191.4 ppm (s, CHO); IR (KBr): $\tilde{\nu} = 1702$ (CHO), 2228 cm^{-1} (CN). MS (FAB): m/z (%): 1302 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{70}H_{51}N_9O_8P_4S$ (1302.2): C 64.57, H 3.95, N 9.68; found: C 64.49, H 3.90, N 9.61.

Compound 3-(PN)$_3$: Methyl triflate (4.1 μL, 0.036 mmol) was added dropwise at room temperature to a solution of **2-(PN)$_3$** (0.043 g, 0.033 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 20 min, and then evaporated to dryness. The residue was washed three times with CH_2Cl_2/pentane (1/20). **3-(PN)$_3$** was isolated as an orange powder in 95% yield. ^{1}H NMR ($CDCl_3$): $\delta = 2.61$ (d, ^3J(H,P) = 18.3 Hz, 3H; S-CH_3), 6.90–7.93 (m, 49H; H_{arom}), 9.82 ppm (s, 2H; CHO); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 13.8$ (d, ^2J(C,P) = 5.8 Hz, S-CH_3), 109.7 (s, C_1^4), 117.7 (s, CN), 120.8 (d, ^3J(C,P) = 5.8 Hz, C_2^2), 121.0 (d, ^3J(C,P) = 5.0 Hz, C_1^2), 121.6 (d, ^3J(C,P) = 5.8 Hz, C_3^2), 123.1 (s, C_2^6), 124.4 (s, C_2^3), 126.4 (dd, ^1J(C,P) = 108.3 Hz, ^3J(C,P) = 3.5 Hz, C_i), 129.3 (s, C_2^7), 129.4 (d, ^3J(C,P) = 13.9 Hz, C_m), 131.7 (s, C_2^8), 131.9 (s, C_3^3), 132.1 (d, ^2J(C,P) = 10.3 Hz, C_o), 133.9 (br s, C_P), 134.2 (s, C_1^3), 134.6 (s, C_3^4), 150.1 (br s, C_2^4), 151.6 (d, ^2J(C,P) = 8.3 Hz, C_3^1), 152.3 (s, C_2^5), 153.3 (br d, ^2J(C,P) = 11.5 Hz, C_2^1), 153.4 (br d, ^2J(C,P) = 8.1 Hz, C_1^1), 190.4 ppm (s, CHO), ($CF_3SO_3^-$ not detected); ^{19}F{^{1}H} NMR ($CDCl_3$): $\delta = -2.0$ ppm (s, CF_3); IR (KBr): $\tilde{\nu} = 1701$ (CHO), 2227 cm^{-1} (CN); elemental analysis calcd (%) for $C_{72}H_{54}F_3N_9O_{11}P_4S_2$ (1466.3): C 58.98, H 3.71, N 8.60; found: C 58.92, H 3.65, N 8.45.

Compound 2-(PN)$_4$: HMPT (6 μL, 0.034 mmol) was added dropwise at room temperature to a solution of **3-(PN)$_3$** (0.048 g, 0.033 mmol) in dichloromethane (3 mL). The solution was stirred for 2 h, and then evaporated to dryness. The residue was extracted with toluene, and then the solution was evaporated to dryness. The resulting compound was not characterized, but used directly. It was dissolved in THF (5 mL), and then a solution of **1d** (0.0125 g, 0.033 mmol) in THF (5 mL) was added at room temperature. The resulting solution was stirred for 12 h, and then evaporated to dryness to afford a powder that was washed three times with THF/pentane (1/20). **2-(PN)$_4$** was isolated as an orange powder in 70% yield. ^{1}H NMR ($CDCl_3$): $\delta = 2.78$ (s, 12H; NMe_2), 6.40 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,P) = 2.3 Hz, 2H; HC_4^6), 6.53 (d, ^4J(H,P) = 1.6 Hz, 2H; HC_4^2), 6.58 (br d, ^3J(H,H) = 8.0 Hz, 2H; HC_4^4), 6.98 (t, ^3J(H,H) = 8.1 Hz, 2H; HC_4^5), 7.05–7.20 (m, 12H; HC_1^2, HC_2^2, HC_3^2), 7.35–7.63 (m, 29H; H_{arom}), 7.68 (d, ^3J(H,H) = 8.9 Hz, 4H; HC_3^3), 7.95 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.6 Hz, 4H; HC_2^6), 9.79 ppm (s, 2H; CHO); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 40.8$ (s, NMe_2), 106.4 (d, ^3J(C,P) = 5.7 Hz, C_4^2), 108.6 (s, C_4^4), 109.2 (d, ^5J(C,P) = 1.1 Hz, C_1^4), 109.9 (d, ^3J(C,P) = 4.9 Hz, C_4^6), 117.8 (s, CN), 121.8 (m, C_2^2, C_1^2), 122.2 (d, ^3J(C,P) = 5.3 Hz, C_3^2), 123.3 (s, C_2^6), 124.4 (s, C_2^3), 127.5 (dd, ^1J(C,P) = 111.9 Hz, ^3J(C,P) = 4.1 Hz, C_i), 129.5 (s, C_4^5), 129.6 (d, ^3J(C,P) = 13.2 Hz, C_m), 129.6 (s, C_2^7), 131.4 (s, C_3^3), 131.6 (s, C_2^8), 132.7 (d, ^2J(C,P) = 11.4 Hz, C_o), 132.8 (s, C_3^4), 133.8 (d, ^4J(C,P) = 2.8 Hz, C_P), 134.3

(s, C_1^3), 149.8 (br s, C_2^4), 151.8 (s, C_4^3), 152.9 (s, C_2^5), 153.4 (d, ^2J(C,P) = 8.9 Hz, C_4^1), 153.6 (d, ^2J(C,P) = 9.2 Hz, C_2^1), 154.4 (d, ^2J(C,P) = 9.3 Hz, C_1^1), 156.7 (d, ^2J(C,P) = 8.5 Hz, C_3^1), 191.3 ppm (s, CHO); IR (KBr): $\tilde{\nu}$ = 1702 (CHO), 2228 cm^{-1} (CN); elemental analysis calcd (%) for $C_{86}H_{71}N_{12}O_{10}P_5S$ (1619.5): C 63.78, H 4.42, N 10.38; found: C 63.66, H 4.37, N 10.25.

Dendron 6-G$_1$: Trifluoro-*p*-cresol, sodium salt (0.192 g, 1.18 mmol) was added to a solution of dendron **5-G$_1$** (0.246 g, 0.288 mmol) in THF (10 mL). The resulting mixture was stirred for 12 h at room temperature, centrifuged, and then evaporated to dryness. The residue was washed three times with THF/pentane (1/5) to afford **6-G$_1$** as a pale yellow powder in 93% yield. ^{1}H NMR ($CDCl_3$): δ = 3.39 (d, ^3J(H,P) = 11.1 Hz, 6H; P_6-N-CH_3), 6.15 (ddd, ^3J(H,P) = 24.0 Hz, ^3J(H,H)$_a$ = 18.3 Hz, ^2J(H,H) = 1.2 Hz, 1H; H_c), 6.40 (ddd, ^3J(H,P) = 45.9 Hz, ^3J(H,H)$_a$ = 12.5 Hz, ^2J(H,H) = 1.2 Hz, 1H; H_b), 6.87 (dddd, ^2J(H,P) = 30.6 Hz, ^3J(H,H)$_c$ = 18.3 Hz, ^3J(H,H)$_b$ = 12.5 Hz, ^4J(H,P) = 1.2 Hz, 1H; H_a), 7.29 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,P) = 1.8 Hz, 4H; HC_5^2), 7.36 (br d, ^3J(H,H) = 8.4 Hz, 8H; HC_6^2), 7.48 ("t"d, ^3J(H,H) = 7.8 Hz, ^4J(H,P) = 3.3 Hz, 4H; HC'_m), 7.54–7.65 (m, 8H, HC'_p, HC_5^3; CH=N), 7.62 (br d, ^3J(H,H) = 8.4 Hz, 8H; HC_6^3), 7.68 ppm (ddd, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.5 Hz, ^3J(H,P) = 13.2 Hz, 4H; HC'_o); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 32.8 (d, ^2J(C,P) = 13.5 Hz, P_6-N-CH_3), 121.7 (d, ^3J(C,P) = 4.8 Hz, C_6^2), 121.9 (d, ^3J(C,P) = 5.7 Hz, C_5^2), 123.6 (q, ^1J(C,F) = 271.8 Hz, CF_3), 126.8 (br q, ^3J(C,F) = 3.2 Hz, C_6^3), 127.4 (d, ^1J(C,P) = 97.4 Hz, C_{Ha}), 127.5 (q, ^2J(C,F) = 33.0 Hz, C_6^4), 127.9 (s, C_5^3), 128.6 (d, ^3J(C,P) = 13.2 Hz, C'_m), 128.8 (part of doublet of C'_i), 130.4 (s, C_5^4), 132.0 (d, ^2J(C,P) = 11.4 Hz, C'_o), 132.6 (s, C'_p), 136.7 (s, CH_2=), 139.9 (d, ^3J(C,P) = 13.8 Hz, C_5^4-*C*H=N), 152.8 (d, ^2J(C,P) = 6.7 Hz, C_6^1), 153.2 ppm (d, ^2J(C,P) = 8.8 Hz, C_5^1); ^{19}F{^{1}H} NMR ($CDCl_3$): δ = 13.9 ppm (s, CF_3); elemental analysis calcd (%) for $C_{58}H_{45}F_{12}N_5O_6P_4S_3$ (1356.1): C 51.37, H 3.34, N 5.16; found: C 51.25, H 3.27, N 5.03.

Compound 7-G$_1$: $MeNHNH_2$ (30 equiv, 173 μL, 3.25 mmol) was added to a solution of **6-G$_1$** (0.147 g, 0.108 mmol) in THF (10 mL). The resulting mixture was stirred for 2 h at room temperature and then evaporated to dryness. The residue was washed with THF/pentane (1/5) to afford **7-G$_1$** as a white powder in 96% yield. ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3H; CH_3-N-NH_2), 2.65 (m, 2H; CH_2-CH_2-P_5), 2.82 (br s, 2H; NH_2), 3.08 (m, 2H; CH_2-P_5), 3.40 (d, ^3J(H,P) = 10.8 Hz, 6H; P_6-N-CH_3), 7.30 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,P) = 1.5 Hz, 4H; HC_5^2), 7.37 (br d, ^3J(H,H) = 8.4 Hz, 8H; HC_6^2), 7.47 ("t"d, ^3J(H,H) = 7.5 Hz, ^4J(H,P) = 3.3 Hz, 4H; HC'_m), 7.52–7.68 (m, 8H, HC'_p, HC_5^3; CH=N), 7.62 (br d, ^3J(H,H) = 8.4 Hz, 8H; HC_6^3), 7.74 ppm (ddd, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.5 Hz, ^3J(H,P) = 12.9 Hz, 4H; HC'_o); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 25.8 (d, ^1J(C,P) = 66.4 Hz, CH_2-P_5), 33.4 (d, ^2J(C,P) = 13.6 Hz, P_6-N-CH_3), 50.9 (s, CH_3-N-NH_2), 54.9 (s, CH_2-CH_2-P_5), 122.3 (d, ^3J(C,P) = 4.8 Hz, C_6^2), 122.6 (d, ^3J(C,P) = 5.1 Hz, C_5^2), 124.2 (q, ^1J(C,F) = 272.0 Hz, CF_3), 127.4 (br q, ^3J(C,F) = 3.2 Hz, C_6^3), 128.4 (s, C_5^3), 129.2 (d, ^3J(C,P) = 13.5 Hz, C'_m), 129.4 (dd, ^1J(C,P) = 105.8 Hz, ^3J(C,P) = 5.8 Hz, C'_i), 131.0 (s, C_5^4), 131.8 (d, ^2J(C,P) = 10.5 Hz, C'_o), 132.9 (d, ^4J(C,P) = 2.7 Hz, C'_p), 140.5 (d, ^3J(C,P) = 13.7 Hz, C_5^4-*C*H=N), 153.4 (d, ^2J(C,P) = 6.1 Hz, C_6^1), 153.7 ppm (d, ^2J(C,P) = 9.0 Hz, C_5^1), (C_6^4 not detected); ^{19}F{^{1}H} NMR ($CDCl_3$): δ = 13.9 ppm (s, CF_3); elemental analysis calcd (%) for $C_{59}H_{51}F_{12}N_7O_6P_4S_3$ (1402.2): C 50.54, H 3.67, N 6.99; found: C 50.48, H 3.59, N 7.03.

Compound 8-G$_2$: A solution of **7-G$_1$** (0.0213 mg, 15.2 μmol) in THF (5 mL) was added at room temperature to a solution of **2-(PN)$_4$** (0.0123 g, 7.6 μmol) in THF (5 mL). The solution was stirred for 12 h, and then evaporated to dryness. The residue was washed three times with THF/pentane (1/20), to afford **8-G$_2$** as an orange powder in 95% yield. ^{1}H NMR ($CDCl_3$): δ = 2.69 (s, 6H; CH_3-N-CH_2-CH_2-P_5), 2.72 (s, 12H; NMe_2), 3.07 (m, 4H; CH_2-CH_2-P_5), 3.37 (d, ^3J(H,P) = 10.8 Hz, 12H; P_6-N-CH_3), 3.60 (m, 4H; CH_2-P_5), 6.34 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,P) = 2.4 Hz, 2H; HC_4^6), 6.55–6.62 (m, 4H; HC_4^2, HC_4^4), 6.80–7.92 ppm (m, 125H; H_{arom}, CH=N); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 24.8 (d, ^1J(C,P) = 63.5 Hz, CH_2-P_5), 33.4 (d, ^2J(C,P) = 13.4 Hz, P_6-N-CH_3), 38.1 (s, CH_3-N-CH_2-CH_2-P_5), 40.8 (s, NMe_2), 52.0 (s, CH_2-CH_2-P_5), 106.6 (d, ^3J(C,P) = 5.7 Hz, C_4^2), 108.4 (s, C_4^4), 108.9 (s, C_1^4), 110.2 (d, ^3J(C,P) = 4.9 Hz, C_4^6), 118.6 (s, CN), 121.5 (d, ^3J(C,P) = 5.0 Hz, C_2^2), 121.8 (d, ^3J(C,P) = 5.0 Hz, C_1^2), 122.3 (d, ^3J(C,P) = 4.8 Hz, C_3^2, C_6^2), 122.4 (d, ^3J(C,P) = 4.7 Hz, C_5^2), 123.2 (s, C_2^6), 124.4 (s, C_2^3), 124.4 (q, ^1J(C,F) = 272.0 Hz, CF_3), 126.7 (s, C_3^3), 127.4 (br q, ^3J(C,F) = 2.8 Hz, C_6^3), 127.9 (dd, ^1J(C,P) = 109.2 Hz, ^3J(C,P) = 3.9 Hz, C_i), 128.4 (s, C_5^3), 129.2 (d, ^3J(C,P) = 12.7 Hz, C'_m), 129.3 (dd, ^1J(C,P) = 107.3 Hz, ^3J(C,P) = 5.3 Hz, C'_i), 129.4 (s, C_4^5), 129.5 (s, C_2^7), 129.5 (d, ^3J(C,P) = 13.1 Hz, C_m), 131.1 (br s, C_3^4, C_5^4), 131.5 (s, C_2^8), 131.8 (d, ^2J(C,P) = 10.5 Hz, C'_o), 132.7 (d, ^2J(C,P) = 11.3 Hz, C_o), 132.9 (br s, C'_p), 133.7 (br s, C_p), 134.1 (s, C_3^5), 134.2 (s, C_1^3), 140.5 (d, ^3J(C,P) = 13.8 Hz, C_5^4-*C*H=N), 149.6 (br s, C_2^4), 151.5 (d, ^2J(C,P) = 8.6 Hz, C_3^1), 151.7 (s, C_4^3), 152.9 (s, C_2^5), 153.4 (br d, ^2J(C,P) = 6.8 Hz, C_6^1), 153.7 (d, ^2J(C,P) = 9.1 Hz, C_5^1), 153.7 (d, ^2J(C,P) = 9.0 Hz, C_2^1), 153.8 (d, ^2J(C,P) = 9.1 Hz, C_4^1), 154.5 ppm (d, ^2J(C,P) = 9.4 Hz, C_1^1), (C_6^4 not detected); ^{19}F{^{1}H} NMR ($CDCl_3$): δ = 13.9 (s, CF_3); IR (KBr): $\tilde{\nu}$ = 2225 cm^{-1} (CN); elemental analysis calcd (%) for $C_{204}H_{169}F_{24}N_{26}O_{20}P_{13}S_7$ (4387.8): C 55.84, H 3.88, N 8.30; found: C 55.76, H 3.82, N 8.22.

X-ray structure analysis: Data collection was performed at low temperature (T = 160 K) for **2-(PN)$_1$** and (T = 180 K) for **3-(PN)$_1$** on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Standard reflections were monitored periodically; they showed no change during data collection, corrections were made for Lorentz and polarization effects. Absorption corrections (Difabs)[17] were applied. Structures were solved by direct methods with SIR 92,[18] and some difference Fourier maps techniques, then refined by least-squares procedures on a F^2 with SHELXL 97.[19] All hydrogen atoms were located on a difference Fourier maps and refined with a riding model and isotropic thermal parameters fixed at 20% higher than those of the carbon atoms to which they are connected. For both structures all non-hydrogen atoms were anisotropically refined, and weighting schemes were applied in the last cycles of refinement; the weights were calculated with the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecules were drawn with the program ORTEP 32[20] with 50% probability displacement ellipsoids for non-hydrogen atoms.

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Received: December 3, 2002 [F4630]

