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First 'layer-block' dendrimer built with a regular alternation of two types of repeat units up to the fourth generation

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Summary — The synthesis of the first regular 'layer-block' dendrimer **1-[G$_n$]**, built with the alternation of RP(S)/RP(O) repeat units, and its characterization by ^{31}P NMR are described up to the fourth generation. The crystal structure of the first generation **1-[G$_1$]** is determined by X-ray diffraction.

dendrimer / layer-block / phosphorus / phosphorhydrazide / hydrazone

Résumé — Premier dendrimère de type 'layer-block' construit par l'alternance régulière de deux types d'unités répétitives jusqu'à la quatrième génération. La synthèse du premier dendrimère de type 'layer-block' **1-[G$_n$]**, construit avec une alternance régulière et répétitive de groupements RP(S) et RP(O), ainsi que sa caractérisation par RMN ^{31}P, sont décrites jusqu'à la quatrième génération. La structure cristalline de la première génération **1-[G$_1$]** a été déterminée par diffraction des rayons X.

dendrimère / layer-block / phosphore / phosphorhydrazide / hydrazone

A substantial body of work has been devoted to the synthesis of dendrimers built with identical functional units for all generations [1]. In contrast, very few work dealt with the synthesis of 'layer-block' dendrimers, ie, dendrimers which have at least two types of repeat units within the cascade structure such as [ether]/[ester] [2], [ruthenium]/[osmium] complexes [3], [N-N-P(S)]/[P=N-P(S)] fragments [4], or polyacetylene chains of different length [5], and organised as layers. Furthermore, none of these compounds has a regular alternation of two types of layers for several generations. We report here the synthesis of the first regular 'layer-block' dendrimer (**1-[G$_4$]**, fourth generation) built with the alternation of [RPS]/[RPO]/[RPS]/[RPO]/[RPS] units, as well as the X-ray structure determination of the first generation **1-[G$_1$]**.

The synthesis of these 'layer-block' dendrimers is derived from the one we have already described for dendrimers which incorporate only one type of repeat unit [6, 7]. It implies, besides hydroxybenzaldehyde sodium salt **3**, the alternative use of $H_2N-N(Me)P(O)Cl_2$ **2a** and $H_2N-N(Me)P(S)Cl_2$ **2b** (scheme 1).

The first generation **1-[G$_1$]** is obtained by condensation of three equivalents of **2a** with the trialdehyde **1-[G$'_0$]** at room temperature. Single crystals of **1-[G$_1$]** are grown in dichloromethane and characterised by X-ray diffraction. The CAMERON drawing of this compound is depicted in figure 1. Crystal data, data collection and refinement data, atomic coordinates with isotropic thermal parameters, bond lengths, and bond angles are gathered in tables I, II, III, and IV, respectively.

The most striking feature of this structure is that each $O-C_6H_4-CH=N-N(Me)P$ arm is flat (maximal deviation: 0.092, −0.276, and 0.064 Å depending on the arm considered). The mean arm length is 9.6 Å, from the core phosphorus P1 to phosphorus P2, P3, or P4. To the best of our knowledge, this value is by far the largest found for arms of dendrimers. Indeed, few structures of first generation of dendrimers have been determined by X-ray diffraction, and in all cases the number of bonds of each arm is small: one [8a], two [8b], three [8c], five [8d], or six [8e], whereas the arms of compound **1-[G$_1$]** are constituted by nine bonds. In fact, this compound is even larger than all second generation dendrimers whose structures were also determined by X-ray diffraction, and which possess only two [9a] or three [9b] bonds for each arm. Dendrimer **1-[G$_1$]** as a whole looks like a three-blade propeller when examined in the direction of the P=S bond. The distance between each phosphoryl group is also very large ($d_{P2\cdots P3} \cong d_{P3\cdots P4} \cong d_{P2\cdots P4} \cong 17$ Å) so chlorine atoms are readily available for further reactions. This is confirmed by the easy synthesis of dendrimer **1-[G$'_1$]**, obtained after substitution of chlorine atoms of **1-[G$_1$]** with hydroxybenzaldehyde sodium salt at room temperature (scheme 1).

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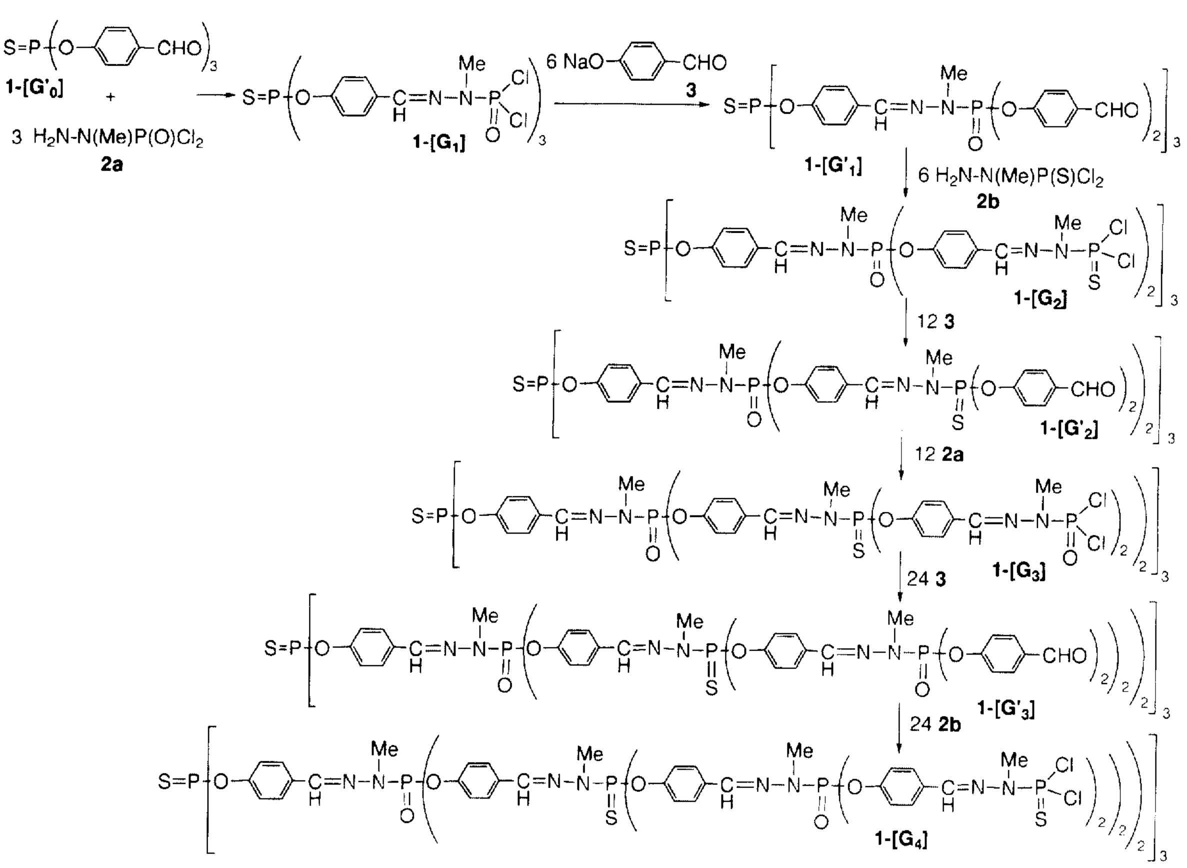
* Correspondence and reprints



Scheme 1

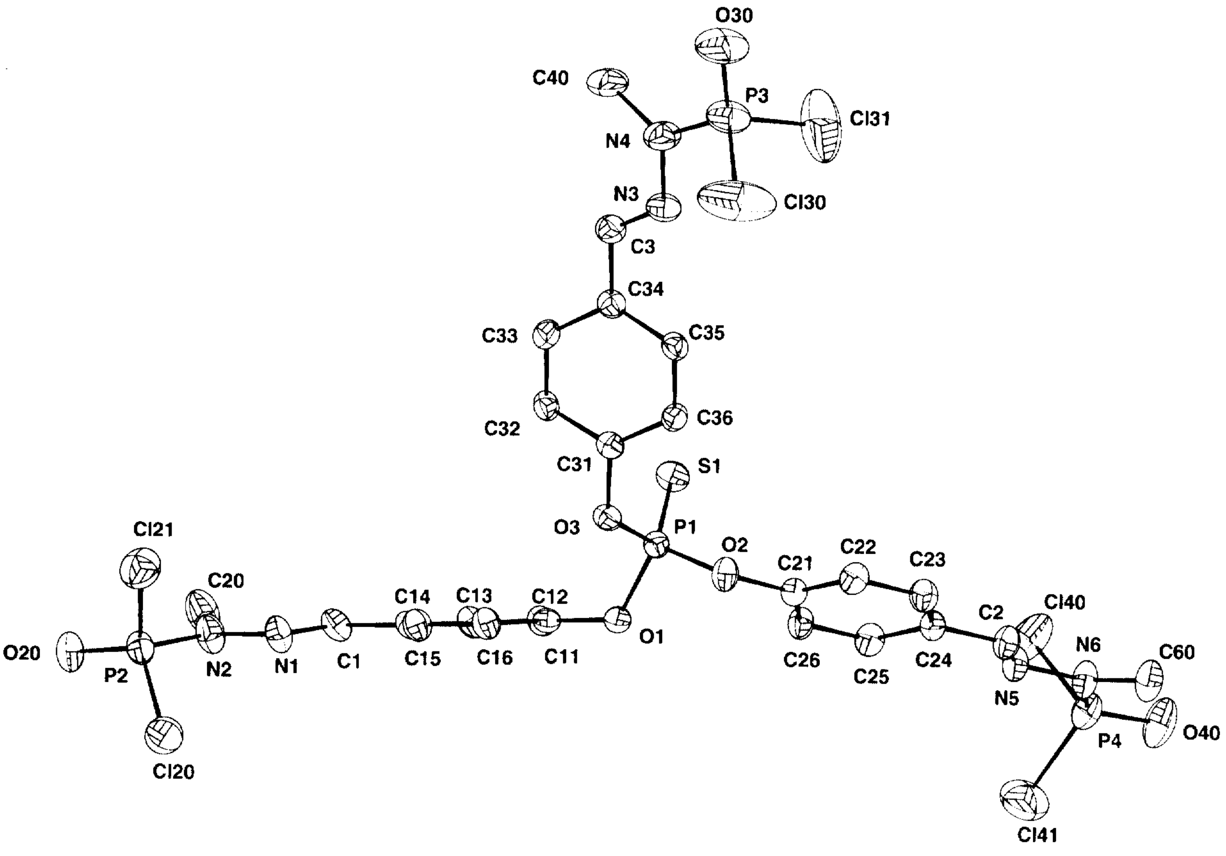


Fig 1. CAMERON drawing of compound 1-$[G_1]$.

Table I. Crystal data, data collection, and refinement data.

Crystal data	
Chemical formula	$C_{24}H_{24}N_6O_6P_4S_1Cl_6,CH_2Cl_2$
Molecular weight	946.1
Crystal system	Triclinic
Space group	P-1
a (Å)	11.694 (2)
b (Å)	14.239 (2)
c (Å)	14.777 (5)
α (°)	117.73 (2)
β (°)	93.11 (2)
γ (°)	105.45 (1)
V (Å^3)	2052.8 (9)
Z	2
μ (cm^{-1})	7.98
$F(000)$	955.2
ρ (calc) (g cm^{-3})	1.53
Crystal color	yellow
Crystal size (mm)	0.06 – 0.05 – 0.04
Crystal form	Block
Data collection	
Diffractometer	Enraf-Nonius CAD4-F
Data collection method	$\omega/2\theta$
Radiation type	MoKα
Wavelength (Å)	0.71073
Scan range θ (°)	$0.8 + 0.35\ \mathrm{tg}\theta$
Monochromator	graphite
θ range for cell parameters (°)	12–14
No of reflections for cell parameters	25
Temperature (K)	293
No of measured reflections	8393
No of independent reflections (R_{av})	8061 (0.03)
$2\theta_{max}$ (°)	52
$-h \rightarrow h$	$-12 \rightarrow 12$
$-k \rightarrow k$	$-16 \rightarrow 16$
$0 \rightarrow l$	$0 \rightarrow 17$
Refinement	
Refinement on	F_{obs}
Hydrogen atoms	calculated and not refined
R^a	0.049
Rw^b	0.058
GOF (S)^c	1.2
$\Delta\rho_{min}\Delta\rho_{max}$	0.47–0.42
Abs corr	none
Weighting scheme^d	$\{w = w'[1 - (\Delta F)/6\sigma(F_o)^2]^2\}$
No of reflections used with the criterion $[I > 3\sigma(I)]$	3296
No of parameters used	453

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [b] $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(|F_o|)^2]^{1/2}$; [c] Goodness of Fit $= [\Sigma(|F_o - F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$; [d] $w' = 1/\Sigma(r = 1,3)\mathrm{ArTr}(x)$, where Ar are the coefficients for the Chebyshev polynomial Tr(x) with $x = F_c/F_c(\max)$.

Table II. Fractional atomic coordinates and equivalent thermal parameters. Estimated standard deviations are in parentheses. U_{eq} is defined as the cube root of the product of the principal axes: $U_{eq} = [U_{11} * U_{22} * U_{33}]^{1/3}$.

Atom	x/a	y/b	z/c	U_{eq} (A^2)
S(1)	0.3186(1)	0.8379(1)	0.2039(1)	0.0558
P(1)	0.1765(1)	0.7445(1)	0.2152(1)	0.0398
P(2)	0.5425(2)	0.6611(2)	0.7655(1)	0.0629
P(3)	0.2307(2)	0.2074(2)	−0.4685(1)	0.0794
P(4)	−0.0373(2)	1.3526(1)	0.2427(2)	0.0658
Cl(20)	0.3716(2)	0.6177(2)	0.7779(2)	0.0917
Cl(21)	0.5414(2)	0.5281(2)	0.6324(2)	0.0986
Cl(30)	0.0680(3)	0.1453(3)	−0.4546(2)	0.1898
Cl(31)	0.2155(4)	0.3333(3)	−0.4838(3)	0.1850
Cl(40)	0.1390(2)	1.3804(2)	0.2667(2)	0.1110
Cl(41)	−0.0790(3)	1.3554(2)	0.3711(2)	0.1337
O(1)	0.1497(3)	0.7791(3)	0.3279(3)	0.0458
O(2)	0.0510(3)	0.7286(3)	0.1566(3)	0.0499
O(3)	0.1676(3)	0.6180(3)	0.1733(3)	0.0443
O(20)	0.6302(4)	0.6832(4)	0.8525(4)	0.0824
O(30)	0.2680(5)	0.1299(5)	−0.5556(4)	0.1144
O(40)	−0.0706(5)	1.4322(4)	0.2222(5)	0.1000
N(1)	0.4769(4)	0.7490(4)	0.6658(4)	0.0594
N(2)	0.5650(4)	0.7668(4)	0.7449(4)	0.0667
N(3)	0.2788(5)	0.3267(4)	−0.2708(4)	0.0612
N(4)	0.3205(5)	0.2611(5)	−0.3571(4)	0.0700
N(5)	−0.0573(5)	1.1474(4)	0.1655(4)	0.0585
N(6)	−0.0954(5)	1.2231(4)	0.1484(4)	0.0645
C(1)	0.4870(5)	0.8281(5)	0.6465(4)	0.0543
C(2)	−0.1008(5)	1.0429(5)	0.0992(5)	0.0534
C(3)	0.3377(6)	0.3639(5)	−0.1804(5)	0.0553
C(11)	0.2351(5)	0.7912(4)	0.4074(4)	0.0433
C(12)	0.3196(5)	0.8948(4)	0.4727(4)	0.0495
C(13)	0.4018(5)	0.9051(4)	0.5507(4)	0.0508
C(14)	0.3960(5)	0.8136(5)	0.5638(4)	0.0467
C(15)	0.3080(5)	0.7102(5)	0.4961(5)	0.0551
C(16)	0.2260(5)	0.6986(4)	0.4181(4)	0.0499
C(20)	0.6747(7)	0.8623(7)	0.7925(6)	0.0855
C(21)	0.0168(5)	0.8111(4)	0.1465(4)	0.0423
C(22)	−0.0594(5)	0.7741(4)	0.0545(4)	0.0487
C(23)	−0.0980(5)	0.8511(5)	0.0399(4)	0.0519
C(24)	−0.0597(5)	0.9638(5)	0.1166(4)	0.0460
C(25)	0.0171(5)	0.9976(4)	0.2105(4)	0.0524
C(26)	0.0541(5)	0.9214(5)	0.2250(4)	0.0496
C(31)	0.2106(5)	0.5569(4)	0.0838(4)	0.0419
C(32)	0.2977(5)	0.5135(4)	0.0958(4)	0.0469
C(33)	0.3401(5)	0.4509(5)	0.0090(4)	0.0519
C(34)	0.2934(5)	0.4319(4)	−0.0892(4)	0.0458
C(35)	0.2041(5)	0.4757(4)	−0.0987(4)	0.0449
C(36)	0.1620(5)	0.5387(4)	−0.0124(4)	0.0453
C(40)	0.4354(8)	0.2451(7)	−0.3479(6)	0.0892
C(60)	−0.1944(6)	1.1869(6)	0.0626(6)	0.0751

All reactions are easily monitored by ^{31}P NMR, which shows in all cases the total disappearance of the signal of phosphorus groups implied in the reaction, on behalf of the appearance of a new signal (fig 2). The presence of both phosphoryl and thiophosphoryl groups gives clearer spectra compared with the corresponding fully thiophosphorylated dendrimer [6]. This is mainly due to the occurence of signals corresponding to P=S and P=O type phosphorus in two very different areas ($63.1 \geqslant \delta(P{=}S) \geqslant 60.4$ and $18.8 \geqslant \delta(P{=}O) \geqslant -6.8$). Furthermore, the difference between the chemical shift of $P(X)Cl_2$ and $P(X)(OC_6H_4{-}CHO)_2$ groups is much larger for X = O ($\Delta\delta \cong 25$ ppm) than for X = S ($\Delta\delta \cong 3$ ppm).

We have carried out the synthesis up to the fourth generation (compound **1-[G$_4$]**, fig 3), by repeating the condensation and substitution reactions. All these reactions afford quantitatively dendrimers **1-[G$_n$]** and **1-[G$'_n$]** (n = 1–4) as crude products, and each compound is isolated in good yield after work up (60–88% yield). Dendrimer **1-[G$_4$]** possess 1 P=S/3 P=O/6 P=S/12 P=O/24 P=S groups at the core and at the

Table III. Full list of interatomic distances (Å). esd's in parentheses refer to the last significant digit.

S(1)–P(1)	1.902(2)	N(5)–N(6)	1.386(6)
P(1)–O(1)	1.577(4)	N(5)–C(2)	1.273(7)
P(1)–O(2)	1.568(4)	N(6)–C(60)	1.459(8)
P(1)–O(3)	1.579(3)	C(1)–C(14)	1.475(8)
P(2)–Cl(20)	1.974(3)	C(2)–C(24)	1.452(8)
P(2)–Cl(21)	1.993(3)	C(3)–C(34)	1.467(8)
P(2)–O(20)	1.452(5)	C(11)–C(12)	1.370(7)
P(2)–N(2)	1.629(5)	C(11)–C(16)	1.377(7)
P(3)–Cl(30)	1.940(3)	C(12)–C(13)	1.386(8)
P(3)–Cl(31)	1.959(4)	C(13)–C(14)	1.388(7)
P(3)–O(30)	1.435(5)	C(14)–C(15)	1.392(8)
P(3)–N(4)	1.616(6)	C(15)–C(16)	1.377(8)
P(4)–Cl(40)	1.972(3)	C(21)–C(22)	1.367(7)
P(4)–Cl(41)	1.969(3)	C(21)–C(26)	1.374(7)
P(4)–O(40)	1.440(5)	C(22)–C(23)	1.390(8)
P(4)–N(6)	1.625(5)	C(23)–C(24)	1.389(8)
O(1)–C(11)	1.414(6)	C(24)–C(25)	1.406(7)
O(2)–C(21)	1.403(6)	C(25)–C(26)	1.367(8)
O(3)–C(31)	1.411(6)	C(31)–C(32)	1.366(7)
N(1)–N(2)	1.394(6)	C(31)–C(36)	1.379(7)
N(1)–C(1)	1.263(7)	C(32)–C(33)	1.388(7)
N(2)–C(20)	1.440(8)	C(33)–C(34)	1.396(8)
N(3)–N(4)	1.392(6)	C(34)–C(35)	1.382(7)
N(3)–C(3)	1.260(7)	C(35)–C(36)	1.383(7)
N(4)–C(40)	1.431(9)		

Molecule of solvent: C(100)–Cl(101), 1.74(1); C(100)–Cl(102), 1.75(1).

Table IV. Full list of bond angles (°). esd's in parentheses refer to the last significant digit.

S(1)–P(1)–O(1)	117.8(2)	P(4)–N(6)–N(5)	114.0(4)
S(1)–P(1)–O(2)	117.7(2)	P(4)–N(6)–C(60)	122.8(4)
O(1)–P(1)–O(2)	100.0(2)	N(5)–N(6)–C(60)	122.3(5)
S(1)–P(1)–O(3)	116.3(2)	N(1)–C(1)–C(14)	119.6(5)
O(1)–P(1)–O(3)	101.3(2)	N(5)–C(2)–C(24)	119.7(5)
O(2)–P(1)–O(3)	100.7(2)	N(3)–C(3)–C(34)	119.3(5)
Cl(20)–P(2)–Cl(21)	101.6(1)	O(1)–C(11)–C(12)	119.0(5)
Cl(20)–P(2)–O(20)	114.7(2)	O(1)–C(11)–C(16)	118.0(5)
Cl(21)–P(2)–O(20)	112.1(2)	C(12)–C(11)–C(16)	123.0(5)
Cl(20)–P(2)–N(2)	106.6(2)	C(11)–C(12)–C(13)	118.0(5)
Cl(21)–P(2)–N(2)	107.6(2)	C(12)–C(13)–C(14)	120.7(5)
O(20)–P(2)–N(2)	113.4(3)	C(1)–C(14)–C(13)	118.8(5)
Cl(30)–P(3)–Cl(31)	100.8(2)	C(1)–C(14)–C(15)	122.0(5)
Cl(30)–P(3)–O(30)	114.1(3)	C(13)–C(14)–C(15)	119.2(5)
Cl(31)–P(3)–O(30)	112.5(3)	C(14)–C(15)–C(16)	120.7(5)
Cl(30)–P(3)–N(4)	107.4(2)	C(11)–C(16)–C(15)	118.3(5)
Cl(31)–P(3)–N(4)	106.9(2)	O(2)–C(21)–C(22)	115.7(4)
O(30)–P(3)–N(4)	114.1(3)	O(2)–C(21)–C(26)	122.3(5)
Cl(40)–P(4)–Cl(41)	102.6(2)	C(22)–C(21)–C(26)	122.0(5)
Cl(40)–P(4)–O(40)	113.5(3)	C(21)–C(22)–C(23)	118.7(5)
Cl(41)–P(4)–O(40)	113.9(3)	C(22)–C(23)–C(24)	120.9(5)
Cl(40)–P(4)–N(6)	104.6(2)	C(2)–C(24)–C(23)	119.9(5)
Cl(41)–P(4)–N(6)	107.0(2)	C(2)–C(24)–C(25)	121.7(5)
O(40)–P(4)–N(6)	114.1(3)	C(23)–C(24)–C(25)	118.4(5)
P(1)–O(1)–C(11)	120.7(3)	C(24)–C(25)–C(26)	120.6(5)
P(1)–O(2)–C(21)	126.7(3)	C(21)–C(26)–C(25)	119.5(5)
P(1)–O(3)–C(31)	122.6(3)	O(3)–C(31)–C(32)	117.6(4)
N(2)–N(1)–C(1)	117.5(5)	O(3)–C(31)–C(36)	120.4(4)
P(2)–N(2)–N(1)	113.8(4)	C(32)–C(31)–C(36)	121.9(5)
P(2)–N(2)–C(20)	122.8(4)	C(31)–C(32)–C(33)	119.2(5)
N(1)–N(2)–C(20)	122.7(5)	C(32)–C(33)–C(34)	120.2(5)
N(4)–N(3)–C(3)	119.1(5)	C(3)–C(34)–C(33)	119.5(5)
P(3)–N(4)–N(3)	114.7(4)	C(3)–C(34)–C(35)	121.4(5)
P(3)–N(4)–C(40)	122.7(4)	C(33)–C(34)–C(35)	119.1(5)
N(3)–N(4)–C(40)	122.6(5)	C(34)–C(35)–C(36)	120.9(5)
N(6)–N(5)–C(2)	119.8(5)	C(31)–C(36)–C(35)	118.7(5)

Molecule of solvent: Cl(101)–C(100)–Cl(102), 110.1(6).

junctions of the first, second, third, and fourth layers, respectively. It is fully characterised, as all other **1-[G$_n$]** and **1-[G$'_n$]** compounds, by elemental analysis and ^{31}P, ^{1}H, and ^{13}C NMR. It can be seen on figure 2 that the ^{31}P NMR spectrum of the fourth generation **1-[G$_4$]** consists of five singlets in an approximate intensity ratio of 1/3/6/12/24. Furthermore, the signals appear in the expected area for the core ($\delta(P_0) = 56.2$), for the phosphoryl groups ($\delta(P_1) = -5.2$; $\delta(P_3) = -5.9$) and for the thiophosphoryl groups ($\delta(P_2) = 62.4$; $\delta(P_4) = 63.1$) (see scheme 2 for the numbering used).

The synthesis could be carried out up to higher generations, but we decided to stop the synthesis at this step, as it demonstrates the feasability of the synthesis of regular 'layer-block' dendrimers, and the usefulness of this type of compounds to improve characterization. Preliminary experiments have shown that dendrimers with phosphoryl groups only on the surface and thiophosphoryl groups for all the internal layers are more reactive than all-thiophosphorylated dendrimers [7e]. Work is in progress to test the reactivity of the new 'layer-block' dendrimers **1-[G$_n$]** and **1-[G$'_n$]**, and particularly to check the influence of the presence of P=O groups compared with P=S groups.

Experimental section

General

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. Compound **1-[G$'_0$]** was prepared according to a literature procedure [7a].

IR: Perkin-Elmer FT 1725x.

NMR: Bruker AC 200 (200.13 MHz, 81.01 MHz and 50.32 MHz, for ^{1}H, ^{31}P and ^{13}C, respectively). For ^{1}H and ^{13}C NMR, CDCl$_3$ as solvent, TMS as external standard; for ^{31}P NMR, CDCl$_3$ as solvent, 85% H$_3$PO$_4$ as external standard (see scheme 2 for the numbering used).

MS: Finnigann MAT TSQ 700 (FAB).

X-ray crystallographic study [10]

The data were collected on an Enraf-Nonius CAD4-F diffractometer at room temperature, using a graphite monochromated Mo-Kα radiation. The $\omega/2\theta$ scan mode was used. The structure was solved by direct methods using SHELXS86 [11] and subsequent difference Fourrier maps, and refined by least-squares procedures on F_{obs}. All hydrogen atoms were located by difference Fourrier maps, but they were introduced in calculation in idealized positions ($d(\mathrm{C–H}) = 0.96$ Å), and their fractional coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the carbon atom to which they were attached. Least squares refinements were carried out by minimizing the function $\Sigma\omega(||F_o| - ||F_c|)^2$ where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $\{w = w'[1-(\Delta F)/6\sigma(F_o)^2]^2\}$ where $w' = 1/\Sigma(r = 1,n)\mathrm{ArTr}(x)$, with 3 coefficients Ar for the Chebyshev polynomial ArTr(x) where x was F_c/F_c (max) [12]. Models reached convergence with $R = \Sigma(||F_o| - ||F_c|)/\Sigma|F_o|$, and $Rw = [\Sigma\omega(||F_o| - ||F_c|)^2/\Sigma(|F_o|)^2]^{1/2}$.

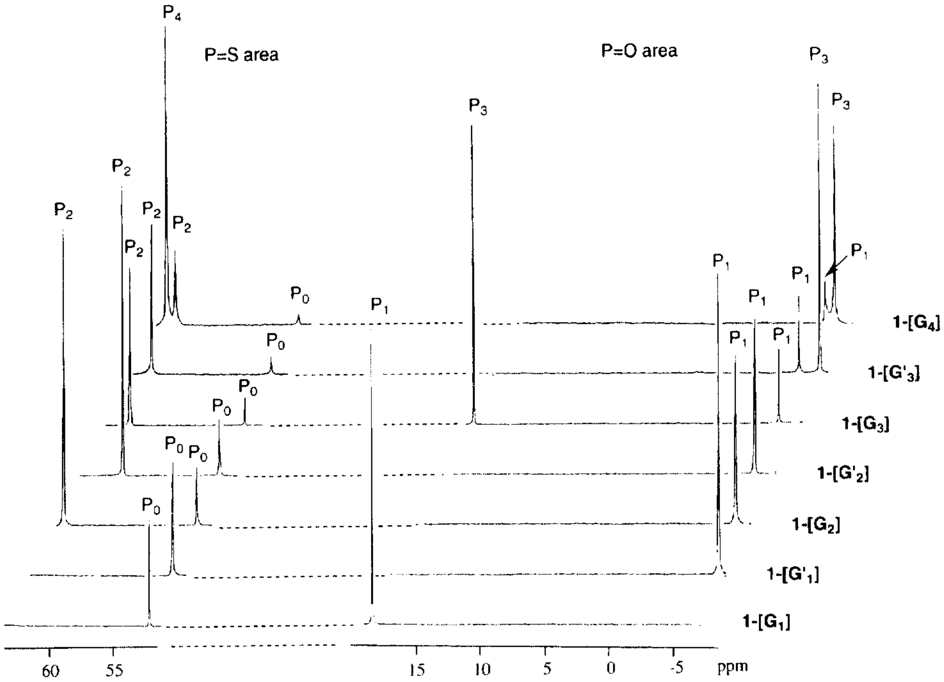
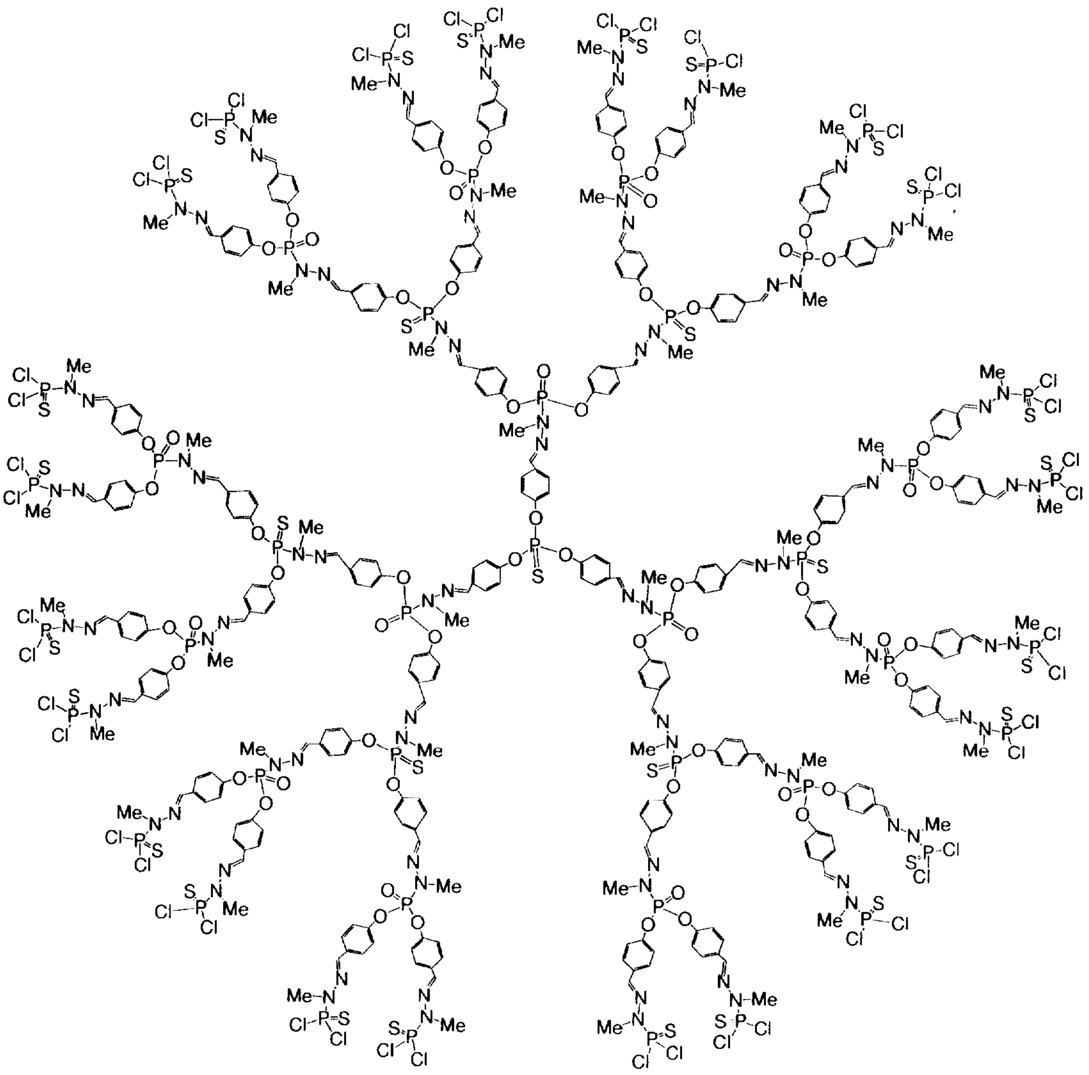
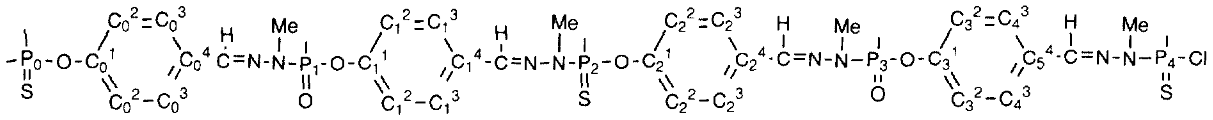


Fig 2. ^{31}P NMR spectra of dendrimers **1-[G$_1$]** – **1-[G$_4$]** and **1-[G$'_1$]** – **1-[G$'_3$]**.



1-[G$_4$]

Fig 3. Fourth generation of the dendrimer.



Scheme 2

Details of data collection and refinement are given in table I. The calculations were performed with the aid of the CRYSTALS package programs [13] running on a PC. The drawing of the molecule was realized with the help of the soft CAMERON [14]. The scattering factors were taken from International Tables for X-ray Crystallography [15].

Dichlorophosphorhydrazides ***2a*** *and* ***2b***

To a solution of trichlorophosphine oxide (3.26 mL, 3.5 × 10^{-2} mol) or sulfide (3.55 mL, 3.5 × 10^{-2} mol) in 100 mL of chloroform was slowly added methylhydrazine (3.72 mL, 7.0 × 10^{-2} mol) in solution in 50 mL of chloroform at −60 °C, and under stirring. The mixture was left overnight under stirring while the temperature raise slowly to room temperature. Then methylhydrazine hydrochloride was eliminated by filtration and centrifugation. Compound **2a** and **2b** were left in solution and used in situ.

- *Dichlorophosphorhydrazide* ***2a***

^{31}P {^{1}H} NMR ($CHCl_3$): δ 23.0 (s).

- *Dichlorophosphorhydrazide* ***2b***

^{31}P {^{1}H} NMR ($CHCl_3$): δ 70.0 (s).

First generation (3 P(O)Cl$_2$ end groups) ***1-[G$_1$]***

To a solution of 7.1 × 10^{-3} mol of compound **2a** in chloroform obtained as described above, was added compound **1-[G$'_0$]** (1.00 g, 2.35 × 10^{-3} mol) in solution in 20 mL of chloroform, at room temperature. The mixture was stirred for 2 h, then filtered, centrifuged and evaporated to dryness. The resulting powder was washed with ether to give 1.58 g of dendrimer **1-[G$_1$]** (78%), pale yellow powder.

^{31}P {^{1}H} NMR ($CDCl_3$): δ 18.8 (s, P_1), 52.3 (s, P_0).

^{1}H NMR ($CDCl_3$): δ 3.3 (d, $^3J_{HP1}$ = 10.9 Hz, 9H, P_1–N–CH_3), 7.3 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HP0}$ = 1.5 Hz, 6H, C_0^2–H), 7.7 (d, $^4J_{HP1}$ = 3.1 Hz, 3H, CH=N), 7.7 (d, $^3J_{HH}$ = 8.3 Hz, 6H, C_0^3–H).

^{13}C {^{1}H} NMR ($CDCl_3$): δ 30.6 (d, $^2J_{CP1}$ = 10.9 Hz, P_1–N–CH_3), 120.9 (d, $^3J_{CP0}$ = 5.1 Hz, C_0^2), 128.1 (s, C_0^3), 131.1 (s, C_0^4), 139.9 (d, $^3J_{CP1}$ = 20.7 Hz, CH=N), 151.0 (d, $^2J_{CP0}$ = 7.6 Hz, C_0^1).

MS (FAB$^+$): m/z (%): 859 $[M + 1]^+$ (for Cl = 35) and isotopic repartition: 861 (100%).

Anal calc for $C_{24}H_{24}Cl_6N_6O_6P_4S$: C, 33.47; H, 2.81; N, 9.76. Found: C, 33.38; H, 2.73; N, 9.63.

First generation (6 CHO end groups) ***1-[G$'_1$]***

To a suspension of hydroxybenzaldehyde sodium salt (1.53 g, 1.05 × 10^{-2} mol) in 15 mL of THF was added a solution of dendrimer **1-[G$_1$]** (1.50 g, 1.74 × 10^{-3} mol) in 15 mL of THF, at room temperature. The mixture was stirred for 2 h, then filtered, centrifuged and evaporated to dryness. The resulting powder was washed with ether to give 1.58 g of dendrimer **1-[G$'_1$]** (66%), yellow powder.

IR (KBr): ν 1 704 cm^{-1} (CHO).

^{31}P {^{1}H} NMR ($CDCl_3$): δ −6.8 (s, P_1), 52.5 (s, P_0).

^{1}H ($CDCl_3$): δ 3.2 (d, $^3J_{HP1}$ = 12.3 Hz, 9H, P_1–N–CH_3), 7.3 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HP0}$ = 1.6 Hz, 6H, C_0^2–H), 7.4 (d, $^3J_{HH}$ = 8.5 Hz, 12H, C_1^2–H), 7.6 (s, 3H, CH=N), 7.6 (d, $^3J_{HH}$ = 8.3 Hz, 6H, C_0^3–H), 7.9 (d, $^3J_{HH}$ = 8.5 Hz, 12H, C_1^3–H), 9.9 (s, 6 H, CHO).

^{13}C {^{1}H} NMR ($CDCl_3$): δ 31.6 (d, $^2J_{CP1}$ = 10.7 Hz, P_1–N–CH_3), 120.5 (d, $^3J_{CP1}$ = 4.7 Hz, C_1^2), 120.9 (d, $^3J_{CP0}$ = 4.6 Hz, C_0^2), 127.7 (s, C_0^3), 131.0 (s, C_1^3), 131.5 (s, C_0^4), 133.1 (s, C_1^4), 138.3 (d, $^3J_{CP1}$ = 15.5 Hz, CH=N), 150.6 (d, $^2J_{CP0}$ = 7.4 Hz, C_0^1), 154.2 (d, $^2J_{CP1}$ = 7.1 Hz, C_1^1), 190.0 (s, CHO).

MS (FAB$^+$); m/z (%): 1375 $[M + 1]^+$ (100%).

Anal calc for $C_{66}H_{54}N_6O_{18}P_4S$: C, 57.64; H, 3.96; N, 6.11. Found: C, 57.38; H, 3.66; N, 5.93.

Second generation (6 P(S)Cl$_2$ end groups) ***1-[G$_2$]***

To a solution of 6.9 × 10^{-3} mol of compound **2b** in chloroform obtained as described above, was added dendrimer **1-[G$'_1$]** (1.50 g, 1.09 × 10^{-3} mol) in solution in 30 mL of chloroform, at room temperature. The mixture was stirred overnight, then filtered, centrifuged and evaporated to dryness. The resulting powder was washed with ether to give 2.17 g of dendrimer **1-[G$_2$]** (85%), yellow powder.

^{31}P {^{1}H} NMR ($CDCl_3$): δ −6.0 (s, P_1), 52.6 (s, P_0), 63.1 (s, P_2).

^{1}H NMR ($CDCl_3$): δ 3.2 (d, $^3J_{HP1}$ = 8.0 Hz, 9H, P_1–N–CH_3), 3.4 (d, $^3J_{HP2}$ = 13.9 Hz, 18H, P_2–N–CH_3), 7.2–7.3 (m, 18H, C_0^2–H, C_1^2–H), 7.55 (s, 3H, C_0^4–CH=N), 7.6–7.7 (m, 18H, C_0^3–H, C_1^3–H), 7.7 (s, 6H, C_1^4–CH=N).

^{13}C {^{1}H} NMR ($CDCl_3$): δ 31.2 (d, $^2J_{CP2}$ = 13.1 Hz, P_2–N–CH_3), 31.8 (d, $^2J_{CP1}$ = 10.4 Hz, P_1–N–CH_3), 120.5 (d, $^3J_{CP0}$ = 4.5 Hz, C_0^2), 120.8 (d, $^3J_{CP1}$ = 5.2 Hz, C_1^2), 127.7 (s, C_0^3), 128.2 (s, C_1^3), 130.9 (s, C_1^4), 131.8 (s, C_0^4), 137.9 (d, $^3J_{CP1}$ = 15.3 Hz, C_0^4–*C*H=N), 139.9 (d, $^3J_{CP2}$ = 18.6 Hz, C_1^4–*C*H=N), 150.5 (d, $^2J_{CP0}$ = 8.7 Hz, C_0^1), 151.0 (d, $^2J_{CP1}$ = 7.3 Hz, C_1^1).

MS (FAB$^+$); m/z (%): 2335 $[M + 1]^+$ (for Cl = 35) and isotopic repartition: 2339 (100%).

Anal calc for $C_{72}H_{72}Cl_{12}N_{18}O_{12}P_{10}S_7$: C, 36.94; H, 3.10; N, 10.77. Found: C, 36.78; H, 3.01; N, 10.68.

Second generation (12 CHO end groups) ***1-[G$'_2$]***

To a suspension of hydroxybenzaldehyde sodium salt (1.50 g, 1.04 × 10^{-2} mol) in 20 mL of THF was added a solution of dendrimer **1-[G$_2$]** (2.00 g, 8.54 × 10^{-4} mol) in 20 mL of THF, at room temperature. The mixture was stirred overnight, then filtered, centrifuged and evaporated to dryness. The resulting powder was washed with ether to give 2.52 g of dendrimer **1-[G$'_2$]** (88%), pale yellow powder.

IR (KBr): ν 1 702 cm^{-1} (CHO).

^{31}P {^{1}H} NMR ($CDCl_3$): δ −5.6 (s, P_1), 52.8 (s, P_0), 60.4 (s, P_2).

^{1}H NMR ($CDCl_3$): δ 3.2 (d, $^3J_{HP1}$ = 8.1 Hz, 9H, P_1–N–CH_3), 3.4 (d, $^3J_{HP2}$ = 10.9 Hz, 18H, P_2–N–CH_3), 7.25–7.4 (m, 42H, C_0^2–H, C_1^2–H, C_2^2–H), 7.6–7.7 (m, 27H, C_0^3–H, C_1^3–H, CH=N), 7.8 (d, $^3J_{HH}$ = 8.6 Hz, 24H, C_2^3–H), 9.9 (s, 12H, CHO).

^{13}C {^{1}H} NMR (CDCl$_3$): δ 31.7 (d, $^2J_{CP1}$ = 8.7 Hz, P$_1$–N–CH$_3$), 32.2 (d, $^2J_{CP2}$ = 13.3 Hz, P$_2$–N–CH$_3$), 120.4 (d, $^3J_{CP1}$ = 4.8 Hz, C_1^2), 120.8 (d, $^3J_{CP0}$ = 4.8 Hz, C_0^2), 121.3 (d, $^3J_{CP2}$ = 5.1 Hz, C_2^2), 127.7 (s, C_0^3), 127.8 (s, C_1^3), 130.8 (s, C_2^3), 131.2 (s, C_1^4), 131.9 (s, C_0^4), 133.0 (s, C_2^4), 138,7 (d, $^3J_{CP1,2}$ = 13.5 Hz, CH=N), 150.6 (d, $^2J_{CP0,1}$ = 6.1 Hz, C_0^1, C_1^1), 154.4 (d, $^2J_{CP2}$ = 7.2 Hz, C_2^1), 190,0 (s, CHO).

MS (FAB$^+$); *m/z* (%): 3369 [M + 1]$^+$ (100%).

Anal calc for $C_{156}H_{132}N_{18}O_{36}P_{10}S_7$: C, 55.61; H, 3.95; N, 7.48. Found: C, 55.37; H, 3.82; N, 7.28.

Third generation (12 P(O)Cl$_2$ end groups) **1-[G$_3$]**

To a solution of 7.2 × 10^{-3} mol of compound **2a** in chloroform was added dendrimer **1-[G$'_2$]** (2.00 g, 5.94 × 10^{-4} mol) in solution in 30 mL of chloroform, at room temperature. The mixture was stirred for 2 h, then filtered, centrifuged and evaporated to dryness. The resulting powder was washed with ether to give 1.82 g of dendrimer **1-[G$_3$]** (60%), pale yellow powder.

^{31}P {^{1}H} NMR (CDCl$_3$): δ −5.5 (s, P$_1$), 18.8 (s, P$_3$), 52.8 (s, P$_0$), 62.0 (s, P$_2$).

^{1}H NMR (CDCl$_3$): δ 3.2 (d, $^3J_{HP1}$ = 9.0 Hz, 9H, P$_1$–N–CH$_3$), 3.3 (d, $^3J_{HP3}$ = 10.9 Hz, 36H, P$_3$–N–CH$_3$), 3.35 (d, $^3J_{HP2}$ = 9.0 Hz, 18H, P$_2$–N–CH$_3$), 7.2–7.3 (m, 42H, C_0^2–H, C_1^2–H, C_2^2–H), 7.6–7.7 (m, 63H, C_0^3–H, C_1^3–H, C_2^3–H, CH=N).

^{13}C {^{1}H} NMR (CDCl$_3$): δ 30.6 (d, $^2J_{CP3}$ = 10.4 Hz, P$_3$–N–CH$_3$), 31.8 (d, $^2J_{CP1}$ = 10.2 Hz, P$_1$–N–CH$_3$), 32.4 (d, $^2J_{CP2}$ = 13.0 Hz, P$_2$–N–CH$_3$), 120.3 (d, $^3J_{CP1}$ = 4.3 Hz, C_1^2), 120.8 (d, $^3J_{CP0}$ = 4.8 Hz, C_0^2), 121.2 (d, $^3J_{CP2}$ = 4.6 Hz, C_2^2), 127.7 (s, C_0^3), 127.8 (s, C_1^3), 127.9 (s, C_2^3), 130.5 (s, C_2^4), 131.4 (s, C_1^4), 131.9 (s, C_0^4), 137.0–139.0 (m, $C_{0,1}^4$–*C*H=N), 140.3 (d, $^3J_{CP3}$ = 20.2 Hz, C_2^4–*C*H=N), 150.5 (d, $^2J_{CP2}$ = 4.3 Hz, C_2^1), 151.2 (d, $^2J_{CP0,1}$ = 8.4 Hz, C_0^1, C_1^1).

Anal calc for $C_{168}H_{168}Cl_{24}N_{42}O_{36}P_{22}S_7$: C, 39.50; H, 3.31; N, 11.52. Found: C, 39.38; H, 3.19; N, 11.40.

Third generation (24 CHO end groups) **1-[G$'_3$]**

To a suspension of hydroxybenzaldehyde sodium salt (1.02 g, 7.1 × 10^{-3} mol) in 20 mL of THF was added a solution of dendrimer **1-[G$_3$]** (1.50 g, 2.94 × 10^{-4} mol) in 20 mL of THF, at room temperature. The mixture was stirred for 2 h, then filtered, centrifuged and evaporated to dryness. The resulting powder was washed with ether to give 1.33 g of dendrimer **1-[G$'_3$]** (63%), pale yellow powder.

IR (KBr): ν 1 704 cm^{-1} (CHO).

^{31}P {^{1}H} NMR (CDCl$_3$): δ −6.7 (s, P$_3$), −5.1 (s, P$_1$), 52.8 (s, P$_0$), 62.3 (s, P$_2$).

^{1}H NMR (CDCl$_3$): δ 3.2 (d, $^3J_{HP1,3}$ = 7.7 Hz, 45H, P$_{1,3}$–N–CH$_3$), 3.35 (d, $^3J_{HP2}$ = 10.2 Hz, 18H, P$_2$–N–CH$_3$), 7.1–7.9 (m, 201H, C$_6$H$_4$, CH=N), 9.9 (s, 24H, CHO).

^{13}C {^{1}H} NMR (CDCl$_3$): δ 31.6 (d, $^2J_{CP1,3}$ = 10.2 Hz, P$_{1,3}$–N–CH$_3$), 32.4 (d, $^2J_{CP2}$ = 13.1 Hz, P$_2$–N–CH$_3$), 120.5 (d, $^3J_{CP1,3}$ = 4.7 Hz, C_1^2, C_3^2), 120.8 (d, $^3J_{CP0}$ = 4.8 Hz, C_0^2), 121.1 (d, $^3J_{CP2}$ = 3.6 Hz, C_2^2), 127.5 (s, C_2^3), 127.6 (s, C_0^3), 127.9 (s, C_1^3), 131.0 (s, C_3^3), 131.6 (s, C_1^4, C_2^4), 131.8 (s, C_0^4), 133.0 (s, C_3^4), 137.0–139.0 (m, CH=N), 150.0–150.5 (m, C_0^1, C_1^1), 150.8 (d, $^2J_{CP2}$ = 8.7 Hz, C_2^1), 154.1 (d, $^2J_{CP3}$ = 5.6 Hz, C_3^1), 190.0 (s, CHO).

Anal calc for $C_{336}H_{288}N_{42}O_{84}P_{22}S_7$: C, 56.33; H, 4.05; N, 8.21. Found: C, 56.01; H, 3.88; N, 8.09.

Fourth generation (24 P(S)Cl$_2$ end groups) **1-[G$_4$]**

To a solution of 3.4 × 10^{-3} mol of compound **2b** in chloroform obtained as described above, was added dendrimer **1-[G$'_3$]** (1.00 g, 1.40 × 10^{-4} mol) in solution in 20 mL of chloroform, at room temperature. The mixture was stirred overnight, then filtered, centrifuged and evaporated to dryness. The resulting powder was washed with ether to give 1.36 g of dendrimer **1-[G$_4$]** (88%), yellow powder.

^{31}P {^{1}H} NMR (CDCl$_3$): δ −5.9 (s, P$_3$), −5.2 (s, P$_1$), 52.6 (s, P$_0$), 62.4 (s, P$_2$), 63.1 (s, P$_4$).

^{1}H NMR (CDCl$_3$): δ 3.2 (d, $^3J_{HP1,3}$ = 8.1 Hz, 45H, P$_{1,3}$–N–CH$_3$), 3.3 (d, $^3J_{HP2}$ = 10.0 Hz, 18H, P$_2$–N–CH$_3$), 3.4 (d, $^3J_{HP4}$ = 12.4 Hz, 72H, P$_4$–N–CH$_3$), 7.1–7.9 (m, 225H, C$_6$H$_4$, CH=N).

^{13}C {^{1}H} NMR (CDCl$_3$): δ 31.2 (d, $^2J_{CP4}$ = 13.1 Hz, P$_4$–N–CH$_3$), 31.6 (d, $^2J_{CP1,3}$ = 9.6 Hz, P$_{1,3}$–N–CH$_3$), 32.4 (d, $^2J_{CP2}$ = 11.6 Hz, P$_2$–N–CH$_3$), 120.4 (d, $^3J_{CP3}$ = 4.1 Hz, C_1^2, C_3^2), 120.8 (d, $^3J_{CP0}$ = 4.8 Hz, C_0^2), 121.1 (d, $^3J_{CP2}$ = 2.9 Hz, C_2^2), 127.5 (s, C_2^3), 127.7 (s, C_0^3), 127.8 (s, C_1^3), 128.2 (s, C_3^3), 130.8 (s, C_3^4), 131.3 (s, C_1^4, C_2^4), 131.5 (s, C_0^4), 138.0–138.5 (m, $C_{0,1,2}^4$-*C*H=N), 140.0 (d, $^3J_{CP4}$ = 18.9 Hz, C_3^4–*C*H=N), 150.9 (d, $^2J_{CP3}$ = 7.0 Hz, C_3^1), 150.0–151.0 (m, C_0^1, C_1^1, C_2^1).

Anal calc for $C_{360}H_{360}Cl_{48}N_{90}O_{60}P_{46}S_{31}$: C, 39.21; H, 3.29; N, 11.43. Found: C, 38.94; H, 3.12; N, 11.23.

Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK as supplementary publication No. SUP 90475 and is available on request from the Document Supply Center.

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