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Synthesis of bowl-shaped dendrimers from generation 1 to generation 8

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Abstract

The synthesis of functionalized phosphorus-containing dendrimers is described up to the eighth generation, starting from the hexachlorocyclotriphosphazene core. The dendrimer is built step by step by the repetition of two reactions: the substitution of chlorine atoms by 4-hydroxybenzaldehyde, and the condensation of aldehyde functions with $H_2N-N(Me)P(S)Cl_2$. The eighth generation of this new class of dendrimers bears up to 1536 aldehyde terminal functions and is one of the largest artificial molecules of defined structure ever described.

Keywords: Dendrimer; Cascade molecule; Cyclotriphosphazene; Phosphorhydrazide; Aldehyde; Group 15

1. Introduction

A new field of research in chemistry appeared a few years ago with the synthesis of a new class of macromolecules called "cascade molecules" [1] or "dendrimers" [2,3]. These names evoke the structure of the compounds, which are highly branched functional polymers of defined structure. Indeed, these macromolecules are polymers since they are based on the association of hundreds or thousands of repetitive units. However, dendrimers differ fundamentally from classical polymers since they have several striking features and properties due to their arborescent construction. The molecular weight and shape of dendrimers are precisely controlled, and all the functions are located on the surface where they are easily accessible. Dendrimers are built step by step by the repetition of a sequence of reactions, allowing multiplication of the number of repetitive units and terminal functions. Each sequence of reactions creates what is called a new "generation".

The first dendrimers were purely organic compounds [1–4], but main group elements containing dendrimers [5], mainly silicon [6] and phosphorus [7,8], have recently been synthesized. For our part, we described the first neutral phosphorus dendrimers [9] up to generation 7 [10] then 10 [11], starting from a trifunctional core ($P(X)Cl_3$, X = S, O). In this case, dendrimers are cauliflower-shaped for the first generations, and become bowl-shaped for high generations, as shown by electron microscopy for the tenth generation [11]. We thought that it could be interesting to synthesize a family of dendrimers whose shape would be the same for all generations. With this perspective, we have already described two three-step syntheses of dendrimers starting from the hexafunctional core $N_3P_3Cl_6$, but were obliged to stop the synthesis at the first generation in one case due to oxidation problems [12], and at the third generation in the second case due to insolubility problems [13]. Another type of bowl-shaped phosphorus dendrimer was recently described up to generation 5 [8]. We now report the synthesis of bowl-shaped dendrimers built upon $N_3P_3Cl_6$, from generation 1 (12 terminal functions) to generation 8 (1536 terminal functions), using the two-step procedure described for the trifunctional core [9–11].

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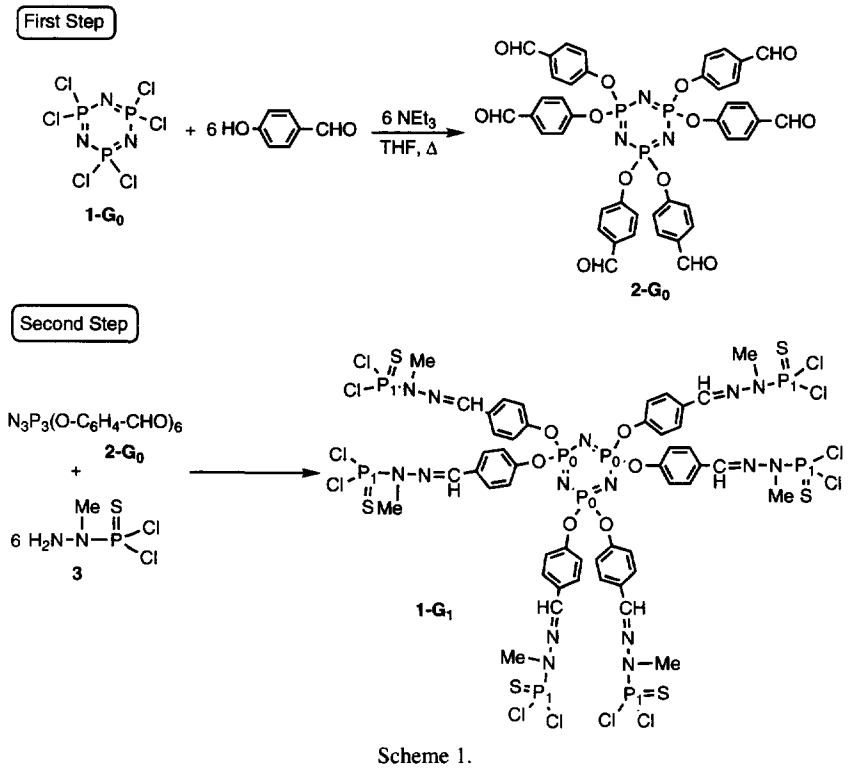
2. Results and discussion

The first reaction consists of the grafting of six hydroxybenzaldehyde groups onto the cyclotriphosphazene core **1-G$_0$**, in the presence of 6 equiv. of triethylamine (Scheme 1). This reaction needs 15 h in refluxing THF to go to completion. The reaction is monitored by ^{31}P NMR which shows the disappearance of the singlet corresponding to **1-G$_0$** ($\delta = 20.1$ ppm) followed by several multiplets due to the intermediates, then a singlet ($\delta = 7.3$ ppm) corresponding to the hexaaldehyde **2-G$_0$**. The second step consists of the condensation of 6 equiv. of dichlorophosphorhydrazide **3** with the aldehyde functions of **2-G$_0$** in chloroform for 48 h at 50 °C, and affords the first generation of the dendrimer **1-G$_1$** (Scheme 1). The condensation induces a slight deshielding of the singlet corresponding to N_3P_3 ($\delta = 8.4$ ppm) and a shielding of the signal corresponding to the $P(S)Cl_2$ moieties ($\delta = 70.6$ ppm for **3**; $\delta =$ 62.6 ppm for **1-G$_1$**) in the ^{31}P NMR spectra. The condensation was also confirmed by ^{1}H and ^{13}C NMR and IR spectroscopies, which show the disappearance of signals corresponding to the CH=O functions on behalf of signals corresponding to the CH=N functions. The presence of a unique set of signals ($m/z = 1822$ [M + 1]$^+$, Cl = 35) with the correct isotopic repartition for a compound containing 12 chlorine atoms ($m/z = 1828$: 100%) in mass spectrometry also proves the formation of **1-G$_1$**.

In order to obtain the second generation of the dendrimer, we first need to graft 12 hydroxybenzaldehyde groups onto the P–Cl functions of **1-G$_1$**. We can again use triethylamine as the base, but the reaction is slow (several days in refluxing THF) and we obtain better results with the sodium salt of hydroxybenzaldehyde, which induces the formation of the dendrimer **2-G$_1$** after stirring overnight at room temperature (Scheme 2). Here again, the reaction is monitored by ^{31}P NMR, as shown in Fig. 1. Almost no change occurs for the signal corresponding to the core, but we observe the total disappearance of the singlet at $\delta = 62.6$ ppm corresponding to the phosphorus P_1 in **1-G$_1$** on behalf of a new singlet at $\delta = 60.6$ ppm due to the phosphorus P_1 in **2-G$_1$**. The second generation of the dendrimer **2-G$_1$** is obtained by a process similar to the synthesis of the first generation **1-G$_1$**: the condensation of the dichlorophosphorhydrazide **3** with the aldehyde functions, which is performed in this case at room temperature. The ^{31}P NMR spectrum of **1-G$_2$** consists of three singlets in a 1:2:4 ratio ($\delta = 8.4$ ppm for the core, $\delta = 62.2$ ppm for P_1 and $\delta = 63.0$ ppm for the newly grafted phosphorus P_2) (Fig. 1).

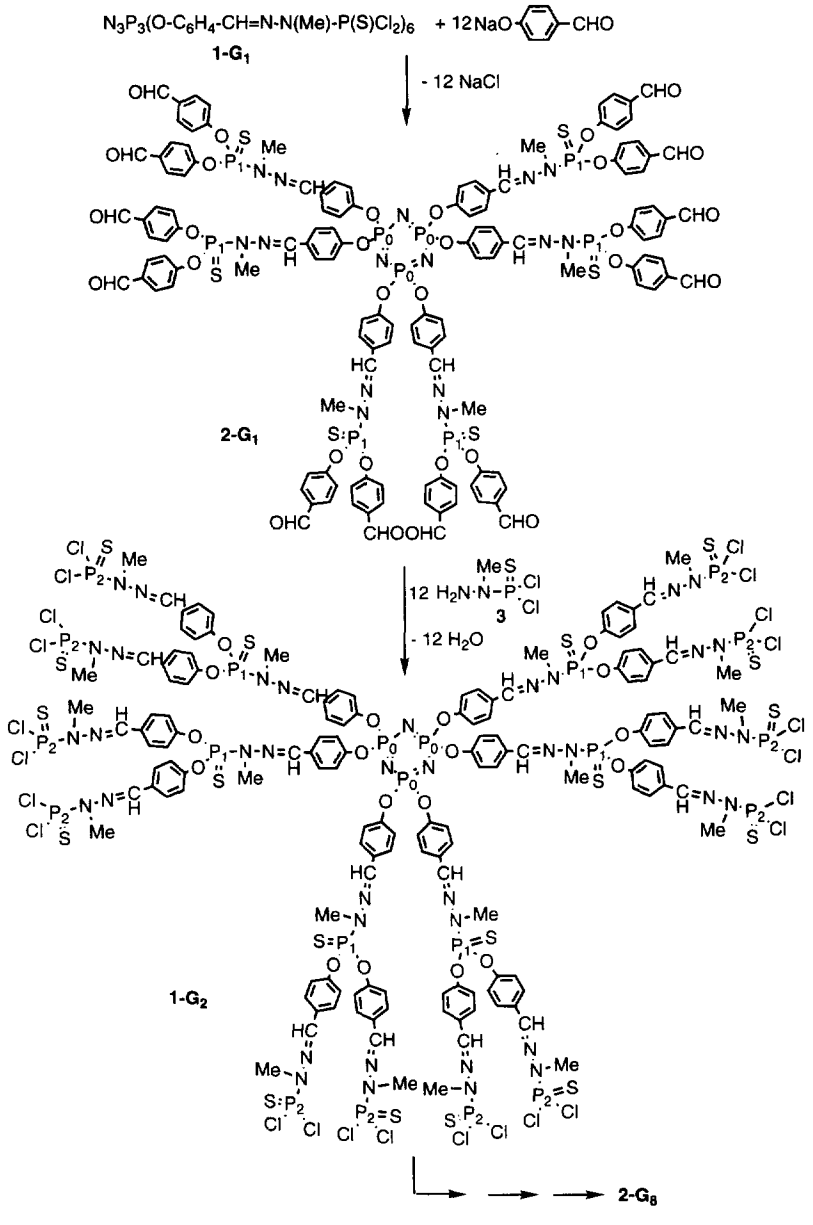
The repetition of these two steps, i.e. reaction with the sodium salt of hydroxybenzaldehyde and condensation with the dichlorophosphorhydrazide **3**, is effected up to the obtaining of the eighth generation of the dendrimer, with 1536 aldehyde terminal functions, **2-G$_8$** (Fig. 2).



Scheme 1.

All the steps of the synthesis are monitored by ^{31}P NMR (Fig. 1), which shows in all cases the disappearance of the signal corresponding to the phosphorus of the surface on behalf of a new singlet, slightly deshielded, during the transformation $P(S)Cl_2 \rightarrow P(S)[OC_6H_4\text{–}CHO]_2$ (**1-G**$_n$ → **2-G**$_n$). The signal corresponding to these phosphorus totally disappears during the next step (**2-G**$_n$ → **1-G**$_{n+1}$) on behalf of a new singlet, slightly deshielded. Furthermore, a singlet corresponding to the newly grafted phosphorus appears. All the signals of the different layers are distinguishable up to generation 4. An overlap occurs for the signals of phosphorus P_1 and P_2 of generation 5 (**1-G**$_5$), but the signal of the core is still distinguishable, and disappears only for generation 6. Thus, the precision of ^{31}P NMR to confirm the reaction of all the functions of the dendrimer at each step is 3% in this case, determined by the ratio P_0/P_5 (3:96) in **1-G**$_5$. In fact, to ascertain the full substitution or condensation, we use in all cases a slight excess of reagents (10% for **3**, 3% for $NaOC_6H_4$–CHO) which is easy to eliminate, and the reactions are left overnight, even though they are completed after 1 h.

The eighth generations of dendrimers, **1-G**$_8$ and **2-G**$_8$, are among the highest generations ever obtained in the chemistry of dendrimers; only two compounds of



Scheme 2.

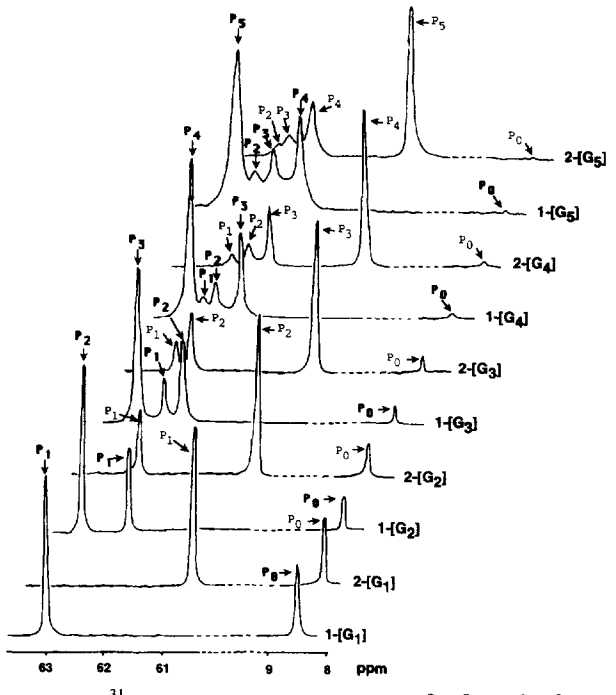


Fig. 1. ^{31}P NMR spectra of dendrimers **1-[G_1]** to **1-[G_5]**.

higher generation (tenth) have previously been described, by Tomalia et al. [2] and by us [11]. Despite their high theoretical molecular weight (377 733 g mol^{-1} for **1-G_8**, 509 313 g mol^{-1} for **2-G_8**) these compounds remain perfectly soluble in several organic solvents such as tetrahydrofuran, chloroform, dichloromethane, dioxane, etc. This means that we could go ahead with the synthesis of higher generations, but we decided to stop the synthesis at this step since our initial goal was achieved. Indeed, electron microscopy of gold derivatives of **2-G_3**, **2-G_4** and **2-G_5** shows a perfect bowl-shape structure for all these dendrimers [11].

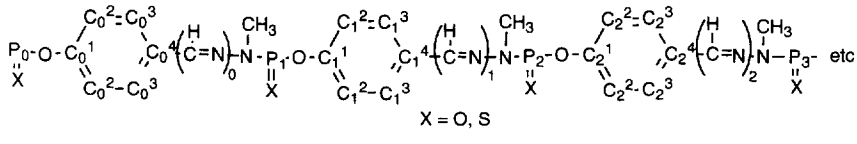
Work is in progress to study the chemical and physical properties of this new family of bowl-shaped dendrimers.

3. Experimental section

3.1. General

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer. ^{31}P NMR chemical shifts were reported in ppm relative to 85% H_3PO_4. Mass spectra were recorded on a Finniganmat TSQ 700 or 95 spectrometer (FAB).

The numbering used for ^{1}H, ^{13}C and ^{31}P NMR is as follows:



3.2. Synthesis of the hexaaldehyde 2-G_0

To a solution of hexachlorocyclotriphosphazene **1-G_0** (0.5 g, 1.438 mmol) in 10 ml of THF was added a solution of 4-hydroxybenzaldehyde (2.1 g, 17.26 mmol) and triethylamine (2.4 ml, 17.26 mmol) in THF (30 ml). This mixture was refluxed for 15 h. The precipitate of triethylamine hydrochloride was eliminated by filtration, and the solvent was evaporated to give an oil which was extracted with methanol (30 ml). Methanol was then evaporated to give **2-G_0** as a powder.

2-G_0. Pale yellow powder. M.p. 141–142 °C dec. 90% yield. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 7.3 (s) ppm. ^{1}H NMR ($CDCl_3$): δ 7.1 (d, $^{3}J_{HH}$ = 8.0 Hz, 12H, C^2–H), 7.7 (d, $^{3}J_{HH}$ = 8.0 Hz, 12H, C^3–H), 9.9 (s, 6H, CHO) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 120.5 (s, C^2), 130.7 (s, C^3), 133.2 (s, C^4), 154.0 (s, C^1), 189.7 (s, CHO) ppm. IR (KBr): 1704 (S, ν_{CHO}) cm^{-1}. MS: m/z 862 $[M+1]^+$. Anal. Found: C, 57.9; H, 3.88; N, 4.89. $C_{42}H_{30}N_3O_{12}P_3$ Calc.: C, 42.33; H, 3.23; N, 3.50%.

3.3. General procedure for the synthesis of dendrimers with terminal $P(S)Cl_2$ functions 1-[G_n] (n = 1–8)

To a solution of 1 equiv. of dendrimer **2-[G_n]** (n = 0–7, aldehyde terminal functions) in chloroform was added a solution of dichlorophosphonomethylhydrazide **3** in chloroform ((6×2^n) equiv. + 10% excess) at room temperature. The resulting solution was stirred for 48 h at 50 °C (for the first generation) or overnight at room temperature for the other generations. The solvent was then removed under vacuum to give a paste (for the first generation) or a powder of **1-[G_{n+1}]** (n = 1–7), which was washed twice with a pentane/ether (1:2) solution.

3.4. General procedure for the synthesis of dendrimers with terminal aldehyde functions 2-[G_n] (n = 1–8)

To a solution of 1 equiv. of dendrimer **1-[G_n]** (n = 1–8, $P(S)Cl_2$ terminal functions) in THF was added

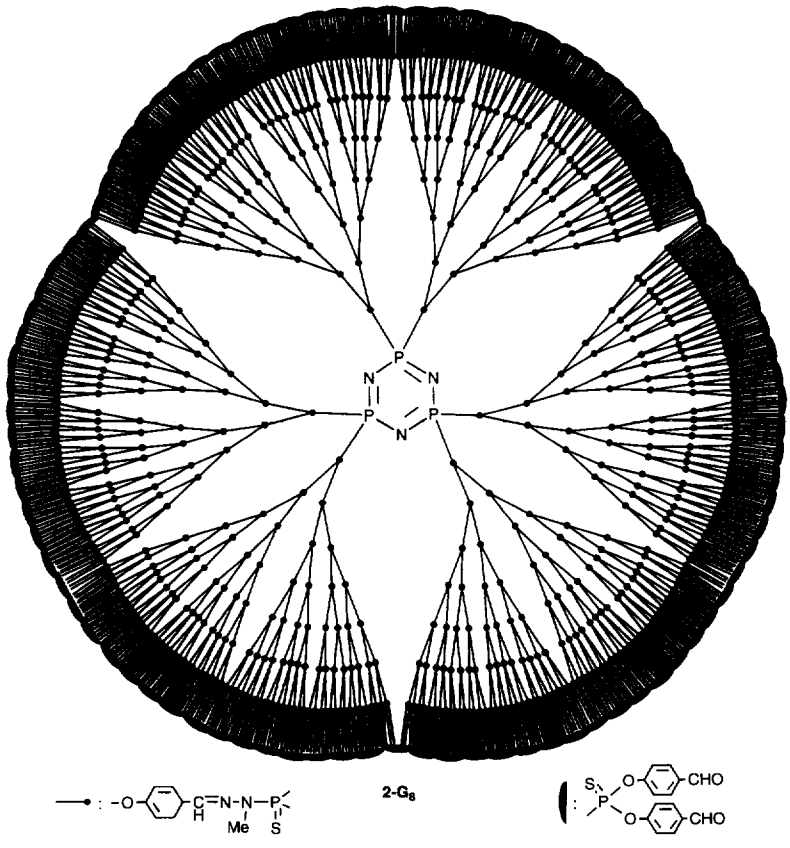


Fig. 2. Schematic drawing of the eighth generation of the dendrimer.

powdered 4-hydroxybenzaldehyde sodium salt ((6 × 2^n) equiv. + 3% excess). The resulting heterogeneous solution was stirred overnight at room temperature. After centrifugation and evaporation of the solvent, the resulting powder was washed twice with ether to give **2-[G$_n$]**.

1-[G$_1$]. Pale yellow powder. M.p. 98 °C dec. 95% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.4 (s, P_0), 62.6 (s, P_1) ppm. ^{1}H NMR ($CDCl_3$): δ 3.5 (d, $^3J_{HP1}$ = 14 Hz, 18H, P_1–N–CH_3), 7.0 (d, $^3J_{HH}$ = 8.4 Hz, 12H, C_0^2–H), 7.6 (d, $^3J_{HP1}$ = 2.0 Hz, 6H, CH=N), 7.6 (d, $^3J_{HH}$ = 8.4 Hz, 12H, C_0^3–H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 31.3 (d, $^2J_{CP1}$ = 13.0 Hz, P_1–N–CH_3), 120.7 (s, C_0^2), 128.0 (s, C_0^3), 130.6 (s, C_0^4), 139.9 (d, $^3J_{CP1}$ = 19.0 Hz, CH=N), 151.0 (s, C_0^1) ppm. MS: m/z 1822 [M + 1]$^+$ (Cl = 35) isotopic repartition (1828: 100%). Anal. Found: C, 31.39; H, 2.53; N, 11.37. $C_{48}H_{48}Cl_{12}N_{15}O_6P_9S_6$ Calc.: C, 31.54; H, 2.65; N, 11.50%.

2-[G$_1$]. Pale yellow powder. 92% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.2 (s, P_0), 60.6 (s, P_1) ppm. ^{1}H ($CDCl_3$): δ 3.3 (d, $^3J_{HP1}$ = 10.6 Hz, 18H, P_1–N–CH_3), 7.0 (d, $^3J_{HH}$ = 8.6 Hz, 12H, C_0^2–H), 7.3 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HP1}$ = 1.2 Hz, 24H, C_1^2–H), 7.6 (d, $^3J_{HH}$ = 8.6 Hz, 12H, C_0^3–H), 7.6 (d, $^3J_{HP1}$ = 1.5 Hz, 6H, CH=N), 7.8 (d, $^3J_{HH}$ = 8.5 Hz, 24H, C_1^3–H), 9.9 (s, 12H, CHO) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.2 (d, $^2J_{CP1}$ = 12.7 Hz, P_1–N–CH_3), 120.7 (s, C_0^2), 121.2 (d, $^3J_{CP1}$ = 5.2 Hz, C_1^2), 127.6 (s, C_0^3), 130.8 (s, C_1^3), 131.1 (s, C_0^4), 133.0 (s, C_1^4), 138.7 (d, $^3J_{CP1}$ = 14.4 Hz, CH=N), 150.6 (br s, C_0^1), 154.3 (d, $^2J_{CP1}$ = 6.9 Hz, C_1^1), 189.9 (s, CHO) ppm. MS: m/z 2855 [M + 1]$^+$. IR (KBr): 1704 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 55.38; H, 3.68; N, 7.21. $C_{132}H_{108}N_{15}O_{30}P_9S_6$ Calc.: C, 55.52; H, 3.81; N, 7.36%.

1-[G$_2$]. Pale yellow powder. M.p. 83 °C dec. 93% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.4 (s, P_0), 62.2 (s, P_1), 63.0 (s, P_2) ppm. ^{1}H NMR ($CDCl_3$): δ 3.3 (d, $^3J_{HP1}$ = 10.7 Hz, 18H, P_1–N–CH_3), 3.4 (d, $^3J_{HP2}$ = 14.4 Hz, 36H, P_2–N–CH_3), 7.0 (d, $^3J_{HH}$ = 8.5 Hz, 12H, C_0^2–H), 7.2 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HP2}$ = 1.2 Hz, 24H, C_1^2–H), 7.5–7.7 (m, 54H, C_0^3–H, C_1^3–H and $(CH{=}N)_{0\text{-}1}$) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 31.2 (d, $^2J_{CP2}$ = 13.2 Hz, P_2–N–CH_3), 32.4 (d, $^2J_{CP1}$ = 11.9 Hz, P_1–N–CH_3), 120.7 (s, C_0^2), 121.1 (d, $^3J_{CP1}$ = 4.2 Hz, C_1^2), 127.6 (s, C_0^3), 128.0 (s, C_1^3), 130.9 (s, C_1^4), 131.3 (s, C_0^4), 138.2 (d, $^3J_{CP1}$ = 14.5 Hz, $(CH{=}N)_0$), 139.9 (d, $^3J_{CP2}$ = 18.5 Hz, $(CH{=}N)_1$), 150.6 (d, $^2J_{CP0}$ = 7.3 Hz, C_0^1), 151.1 (d, $^2J_{CP1}$ = 7.1 Hz, C_1^1) ppm. Anal. Found: C, 35.94; H, 2.88; N, 11.25. $C_{144}H_{144}Cl_{24}N_{39}O_{18}P_{21}S_{18}$ Calc.: C, 36.12; H, 3.03; N, 11.41%.

2-[G$_2$]. Pale yellow powder. M.p. 81 °C dec. 93% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.4 (s, P_0), 62.5 (s, P_1), 60.5 (s, P_2) ppm. ^{1}H NMR ($CDCl_3$): δ 3.2 (d, $^3J_{HP1}$ = 10.4 Hz, 18H, P_1–N–CH_3), 3.3 (d, $^3J_{HP2}$ = 10.7

Hz, 36H, P_2–N–CH_3), 6.9 (d, $^3J_{HH}$ = 8.4 Hz, 12H, C_0^2–H), 7.1 (d, $^3J_{HH}$ = 8.1 Hz, 24H, C_1^2–H), 7.2–7.6 (m, 102H, C_2^2–H, C_0^3–H, C_1^3–H and (CH=N)$_{0\text{-}1}$), 7.8 (d, $^3J_{HH}$ = 8.4 Hz, 48H, C_2^3–H), 9.9 (s, 24H, CHO) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.2 (d, $^2J_{CP1\text{-}2}$ = 12.5 Hz, $P_{1\text{-}2}$–N–CH_3), 120.6 (br d, C_0^2), 121.2 (d, $^3J_{CP2}$ = 5.0 Hz, C_1^2, C_2^2), 127.5 (s, C_0^3), 127.6 (s, C_1^3), 130.7 (s, C_2^3), 131.2 (s, C_0, C_1^4), 132.9 (s, C_2^4), 138.0–139.0 (m, (CH=N)$_{0\text{-}1}$), 150.6 (m, C_0^1, C_1^1), 154.4 (d, $^2J_{CP2}$ = 7.0 Hz, C_2^1), 190.0 (s, CHO) ppm. IR (KBr): 1702 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 54.61; H, 3.71; N, 7.75. $C_{312}H_{264}N_{39}O_{66}P_{21}S_{18}$ Calc.: C, 54.76; H, 3.89; N, 7.98%.

1-[G$_3$]. Pale yellow powder. M.p. 155 °C dec. 90% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.5 (s, P_0), 62.2 (s, P_2), 62.5 (s, P_1), 63.0 (s, P_3) ppm. ^{1}H NMR ($CDCl_3$): δ 3.2 (d, $^3J_{HP1}$ = 10.3 Hz, 18H, P_1–N–CH_3), 3.3 (d, $^3J_{HP2}$ = 10.8 Hz, 36H, P_2–N–CH_3), 3.4 (d, $^3J_{HP3}$ = 13.9 Hz, 72H, P_3–N–CH_3), 6.9 (d, $^3J_{HH}$ = 7.9 Hz, 12H, C_0^2–H), 7.1–7.3 (m, 72H, C_1^2–H, C_2^2–H), 7.6–7.8 (m, 116H, C_0^3–H, C_1^3–H, C_2^3–H and (CH=N)$_{0\text{-}1\text{-}2}$) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 31.2 (d, $^2J_{CP3}$ = 13.1 Hz, P_3–N–CH_3), 32.4 (d, $^2J_{CP1\text{-}2}$ = 11.6 Hz, $P_{1\text{-}2}$–N–CH_3), 120.6 (br d, C_0^2), 121.2 (d, $^3J_{CP2}$ = 3.6 Hz, C_1^2, C_2^2), 127.5 (s, C_0^3, C_1^3), 128.1 (s, C_2^3), 130.8 (s, C_2^4), 131.5 (br s, C_0^4, C_1^4), 138.2 (m, (CH=N)$_{0\text{-}1}$), 140.0 (d, $^3J_{CP3}$ = 18.9 Hz, (CH=N)$_2$), 150.5 (m, C_0^1, C_1^1), 151.0 (d, $^2J_{CP2}$ = 7.2 Hz, C_2^1) ppm. Anal. Found: C, 37.58; H, 3.01; N, 11.14. $C_{336}H_{336}Cl_{48}N_{87}O_{42}P_{45}S_{42}$ Calc.: C, 37.70; H, 3.16; N, 11.38%.

2-[G$_3$]. Pale yellow powder. M.p. 131 °C dec. 95% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.4 (s, P_0), 60.4 (s, P_3), 62.5 (s, P_2), 62.7 (s, P_1) ppm. ^{1}H NMR ($CDCl_3$): δ 3.2 (d, $^3J_{HP1}$ = 10.8 Hz, 18H, P_1–N–CH_3), 3.25 (d, $^3J_{HP2}$ = 10.7 Hz, 36H, P_2–N–CH_3), 3.3 (d, $^3J_{HP3}$ = 10.7 Hz, 72H, P_3–N–CH_3), 6.9 (d, $^3J_{HH}$ = 7.7 Hz, 12H, C_0^2–H), 7.1–7.3 (m, 168H, C_1^2–H, C_2^2–H, C_3^2–H), 7.6–7.8 (m, 222H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H and (CH=N)$_{0\text{-}1\text{-}2}$), 9.8 (s, 48H, CHO) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.3 (d, $^2J_{CP1\text{-}2\text{-}3}$ = 13.2 Hz, $P_{1\text{-}2\text{-}3}$–N–CH_3), 120.6 (br d, C_0^2), 121.3 (d, $^3J_{CP0\text{-}1\text{-}2}$ = 3.6 Hz, C_1^2, C_2^2, C_3^2), 127.7 (s, C_0^3, C_1^3, C_2^3), 130.8 (s, C_3^3), 131.2 (br s, C_0^4, C_1^4, C_2^4), 132.9 (s, C_3^4), 138.0–138.8 (m, (CH=N)$_{0\text{-}1}$), 138.9 (d, $^3J_{CP3}$ = 13.8 Hz, (CH=N)$_2$), 150.0–150.6 (m, C_0^1, C_1^1), 150.7 (d, $^2J_{CP2}$ = 7.7 Hz, C_2^1), 154.4 (d, $^2J_{CP3}$ = 7.2 Hz, C_3^1), 190.1 (s, CHO) ppm. IR (KBr): 1702 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 54.21; H, 3.81; N, 8.09. $C_{672}H_{576}N_{87}O_{138}P_{45}S_{42}$ Calc.: C, 54.47; H, 3.92; N, 8.22%.

1-[G$_4$]. Pale yellow powder. M.p. 160 °C dec. 90% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.3 (s, P_0), 62.1 (s, P_3), 62.6 (s, P_2), 62.7 (s, P_1), 63.0 (s, P_4) ppm. ^{1}H NMR ($CDCl_3$): δ 3.1–3.5 (m, 270H, $P_{1\text{-}2\text{-}3\text{-}4}$–N–$CH_3$), 6.9–7.3 (m, 180H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H), 7.5–7.8 (m, 270H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H and (CH=N)$_{0\text{-}1\text{-}2\text{-}3}$) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 31.2 (d, $^2J_{CP4}$ = 13.1 Hz, P_4–N–CH_3), 32.4 (d, $^2J_{CP1\text{-}2\text{-}3}$ = 13.1 Hz, $P_{1\text{-}2\text{-}3}$–N–CH_3), 120.6 (br d, C_0^2), 121.1 (br s, C_1^2, C_2^2, C_3^2), 127.7 (s, C_0^3, C_1^3, C_2^3), 128.1 (s, C_3^3), 130.8 (s, C_3^4), 131.4 (br s, C_0^4, C_1^4, C_2^4), 138.0–138.8 (m, (CH=N)$_{0\text{-}1\text{-}2}$), 140.0 (d, $^3J_{CP4}$ = 18.6 Hz, (CH=N)$_3$), 150.0–150.5 (m, C_0^1, C_1^1), 150.6 (d, $^2J_{CP2}$ = 6.0 Hz, C_2^1), 151.1 (d, $^2J_{CP3}$ = 6.8 Hz, C_3^1) ppm. Anal. Found: C, 38.01; H, 3.12; N, 11.27. $C_{720}H_{720}Cl_{96}N_{183}O_{90}P_{93}S_{90}$ Calc.: C, 38.36; H, 3.22; N, 11.37%.

2-[G$_4$]. Pale yellow powder. M.p. 140 °C dec. 93% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 8.3 (s, P_0), 60.4 (s, P_4), 62.4 (s, P_3), 62.7 (s, P_2), 63.1 (s, P_1) ppm. ^{1}H NMR ($CDCl_3$): δ 3.2–3.25 (m, 126H, $P_{1\text{-}2\text{-}3}$–N–CH_3), 3.3 (d, $^3J_{HP4}$ = 9.9 Hz, 144H, P_4–N–CH_3), 7.0–7.3 (m, 372H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H), 7.5–7.8 (m, 462H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H and (CH=N)$_{0\text{-}1\text{-}2\text{-}3}$), 9.8 (s, 96H, CHO) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.3 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4}$ = 13.7 Hz, $P_{1\text{-}2\text{-}3\text{-}4}$–N–$CH_3$), 120.6 (br d, C_0^2), 121.2 (d, $^3J_{CP0\text{-}1\text{-}2\text{-}3}$ = 3.7 Hz, C_1^2, C_2^2, C_3^2, C_4^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3), 130.8 (s, C_4^3), 131.1 (br s, C_0^4, C_1^4, C_2^4, C_3^4), 132.9 (s, C_4^4), 138.0–139.1 (m, (CH=N)$_{0\text{-}1\text{-}2\text{-}3}$), 150.0–150.6 (m, C_0^1, C_1^1, C_2^1), 150.7 (d, $^2J_{CP3}$ = 7.3 Hz, C_3^1), 154.4 (d, $^2J_{CP4}$ = 7.3 Hz, C_4^1), 190.1 (s, CHO) ppm. IR (KBr): 1702 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 54.23; H, 3.81; N, 8.18. $C_{1392}H_{1200}N_{183}O_{282}P_{93}S_{90}$ Calc.: C, 54.33; H, 3.93; N, 8.33%.

1-[G$_5$]. Pale yellow powder. M.p. 154 °C dec. 95% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 62.0 (s, P_4), 62.4 (s, P_3), 62.8 (br s, P_1, P_2), 63.0 (s, P_5) ppm. ^{1}H NMR ($CDCl_3$): δ 3.1–3.5 (m, 558H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 6.9–7.3 (m, 372H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H), 7.5–7.8 (m, 558H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H (CH=N)$_{0\text{-}1\text{-}2\text{-}3\text{-}4}$) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 31.2 (d, $^2J_{CP5}$ = 13.1 Hz, P_5–N–CH_3), 32.4 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4}$ = 13.0 Hz, $P_{1\text{-}2\text{-}3\text{-}4}$–N–$CH_3$), 121.1 (br s, C_1^2, C_2^2, C_3^2, C_4^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3), 128.1 (s, C_4^3), 130.8 (s, C_4^4), 131.4 (br s, C_0^4, C_1^4, C_2^4, C_3^4), 138.0–138.8 (m, (CH=N)$_{0\text{-}1\text{-}2\text{-}3}$), 140.1 (d, $^3J_{CP5}$ = 19.0 Hz, (CH=N)$_4$), 150.0–150.6 (m, C_0^1, C_1^1, C_2^1, C_3^1), 151.1 (d, $^2J_{CP4}$ = 7.0 Hz, C_4^1) ppm. Anal. Found: C, 38.51; H, 3.18; N, 11.22. $C_{1488}H_{1488}Cl_{192}N_{375}O_{186}P_{189}S_{186}$ Calc.: C, 38.66; H, 3.24; N, 11.36%.

2-[G$_5$]. Pale yellow powder. M.p. 129 °C dec. 80% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 60.4 (s, P_5), 62.3 (s, P_4), 62.7 (s, P_3), 62.9 (br s, P_1, P_2) ppm. ^{1}H NMR ($CDCl_3$): δ 3.2–3.5 (m, 558H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 7.0–7.3 (m, 756H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H, C_5^2–H), 7.5–7.8 (m, 942H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H, C_5^3–H and (CH=N)$_{0\text{-}1\text{-}2\text{-}3\text{-}4}$), 9.8 (s, 192H, CHO) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.3 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5}$ = 13.0 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 121.3 (br s, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 130.8 (s, C_5^3), 131.1 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4), 132.9 (s, C_5^4), 138.0–139.2 (m, (CH=N)$_{0\text{-}1\text{-}2\text{-}3\text{-}4}$), 150.0–150.7 (m, C_0^1,

C_1^1, C_2^1, C_3^1, C_4^1), 154.5 (d, $^2J_{CP5}$ = 6.7 Hz, C_5^1), 190.2 (s, CHO) ppm. IR (KBr): 1702 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 54.09; H, 3.81; N, 8.28. $C_{2832}H_{2448}N_{375}O_{570}P_{189}S_{186}$ Calc.: C, 54.27; H, 3.94; N, 8.38%.

1-[G_6]. Pale yellow powder. M.p. 155 °C dec. 97% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.0 (s, P_5), 62.4 (s, P_4), 62.5 (s, P_3), 63.0 (br s, P_1, P_2, P_6) ppm. ^1H NMR ($CDCl_3$): δ 3.1–3.5 (m, 1134H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$–N–$CH_3$), 6.9–7.3 (m, 756H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H, C_5^2–H), 7.5–7.8 (m, 1134H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H, C_5^3–H and $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.2 (d, $^2J_{CP6}$ = 12.5 Hz, P_6–N–CH_3), 32.4 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5}$ = 12.9 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 121.3 (br s, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 128.1 (s, C_5^3), 130.8 (s, C_5^4), 131.4 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4), 138.0–138.8 (m, $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4}$), 140.2 (d, $^3J_{CP6}$ = 19.0 Hz, $(CH{=}N)_5$), 150.0–150.6 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1), 151.2 (d, $^2J_{CP5}$ = 3.9 Hz, C_5^1) ppm. Anal. Found: C, 38.69; H, 3.15; N, 11.32. $C_{3024}H_{3024}Cl_{384}N_{759}O_{378}P_{381}S_{378}$ Calc.: C, 38.81; H, 3.26; N, 11.36%.

2-[G_6]. Pale yellow powder. M.p. 135 °C dec. 73% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.4 (s, P_6), 62.3 (s, P_5), 62.7 (s, P_4), 62.9 (br s, P_1, P_2, P_3) ppm. ^1H NMR ($CDCl_3$): δ 3.2–3.5 (m, 1134H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$–N–$CH_3$), 7.0–7.3 (m, 1524H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H, C_5^2–H, C_6^2–H), 7.5–7.8 (m, 1902H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H, C_5^3–H, C_6^3–H and $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5}$), 9.8 (br s, 384H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.3 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$ = 13.1 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$–N–$CH_3$), 121.3 (br s, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3), 130.8 (s, C_6^3), 131.1 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4), 132.9 (s, C_6^4), 138.0–139.2 (m, $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5}$), 150.0–150.7 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1), 154.5 (br s, C_6^1), 190.1 (s, CHO) ppm. IR (KBr): 1702 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 54.19; H, 3.89; N, 8.35. $C_{5712}H_{4944}N_{759}O_{1146}P_{381}S_{378}$ Calc.: C, 54.24; H, 3.94; N, 8.41%.

1-[G_7]. Pale yellow powder. M.p. 159 °C dec. 98% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.0 (s, P_6), 62.4 (s, P_5), 62.6 (s, P_4), 63.1 (br s, P_1, P_2, P_3, P_7) ppm. ^1H NMR ($CDCl_3$): δ 3.1–3.5 (m, 2286H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$–N–$CH_3$), 6.9–7.3 (m, 1524H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H, C_5^2–H, C_6^2–H), 7.5–7.8 (m, 2286H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H, C_5^3–H, C_6^3–H and $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.3 (d, $^2J_{CP7}$ = 13.0 Hz, P_7–N–CH_3), 32.5 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$ = 12.7 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$–N–$CH_3$), 121.3 (br s, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3), 128.1 (s, C_6^3), 130.9 (s, C_6^4), 131.4 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4), 138.0–138.8 (m, $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5}$), 140.2 (d, $^3J_{CP7}$ = 18.7 Hz, $(CH{=}N)_6$), 150.0–150.6 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1), 151.0–151.2 (m, C_6^1) ppm. Anal. Found: C, 38.83; H, 3.20; N, 11.32. $C_{6096}H_{6096}Cl_{768}N_{1527}O_{762}P_{765}S_{762}$ Calc.: C, 38.88; H, 3.26; N, 11.36%.

2-[G_7]. Pale yellow powder. M.p. 130 °C dec. 69% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.4 (s, P_7), 62.3 (s, P_6), 62.7 (s, P_5), 63.0 (br s, P_1, P_2, P_3, P_4) ppm. ^1H NMR ($CDCl_3$): δ 3.2–3.5 (m, 2286H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$–N–$CH_3$), 7.0–7.3 (m, 3060H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H, C_5^2–H, C_6^2–H, C_7^2–H), 7.5–7.8 (m, 3822H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H, C_5^3–H, C_6^3–H, C_7^3–H and $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$), 9.7–10.0 (m, 768H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.3 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$ = 13.3 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$–N–$CH_3$), 121.3 (br s, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2, C_7^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3, C_6^3), 130.8 (s, C_7^3), 131.2 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4, C_6^4), 132.9 (s, C_7^4), 138.0–139.3 (m, $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$), 150.0–150.7 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1, C_6^1), 154.3–154.6 (m, C_7^1), 190.2 (s, CHO) ppm. IR (KBr): 1702 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 54.11; H, 3.88; N, 8.38. $C_{11472}H_{9936}N_{1527}O_{2298}P_{765}S_{762}$ Calc.: C, 54.23; H, 3.94; N, 8.42%.

1-[G_8]. Pale yellow powder. M.p. 145 °C dec. 97% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.1 (s, P_7), 62.3 (s, P_6), 62.6 (s, P_5), 63.1 (br s, P_1, P_2, P_3, P_4, P_8) ppm. ^1H NMR ($CDCl_3$): δ 3.1–3.5 (m, 4590H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$–N–$CH_3$), 6.9–7.3 (m, 3060H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H, C_5^2–H, C_6^2–H, C_7^2–H), 7.5–7.8 (m, 4590H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H, C_5^3–H, C_6^3–H, C_7^3–H and $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.3 (d, $^2J_{CP8}$ = 12.9 Hz, P_8–N–CH_3), 32.5 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$ = 12.8 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$–N–$CH_3$), 121.3 (br s, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2, C_7^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3, C_6^3), 128.1 (s, C_7^3), 130.9 (s, C_7^4), 131.4 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4, C_6^4), 138.0–138.7 (m, $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$), 140.2 (d, $^3J_{CP8}$ = 17.8 Hz, $(CH{=}N)_7$), 150.0–150.7 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1, C_6^1), 151.0–151.2 (m, C_7^1) ppm. Anal. Found: C, 38.85; H, 3.20; N, 11.28. $C_{12240}H_{12240}Cl_{1536}N_{3063}O_{1530}P_{1533}S_{1530}$ Calc.: C, 38.92; H, 3.27; N, 11.36%.

2-[G_8]. Pale yellow powder. M.p. 121 °C dec. 68% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.4 (s, P_8), 62.3 (s, P_7), 62.7 (s, P_6), 62.9 (br s, P_1, P_2, P_3, P_4, P_5) ppm. ^1H NMR ($CDCl_3$): δ 3.1–3.6 (m, 4590H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$–N–$CH_3$), 7.0–7.4 (m, 6132H, C_0^2–H, C_1^2–H, C_2^2–H, C_3^2–H, C_4^2–H, C_5^2–H, C_6^2–H, C_7^2–H, C_8^2–H), 7.5–7.9 (m, 7662H, C_0^3–H, C_1^3–H, C_2^3–H, C_3^3–H, C_4^3–H, C_5^3–H, C_6^3–H, C_7^3–H, C_8^3–H and $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$), 9.7–10.0 (m, 1536H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.3 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$ = 13.2 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$–N–$CH_3$), 121.3 (br s, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2, C_7^2, C_8^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3, C_6^3, C_7^3), 130.8 (s, C_8^3), 131.2 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4, C_6^4, C_7^4), 133.0 (s, C_8^4), 138.0–139.4 (m, $(CH{=}N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7}$), 150.0–150.6 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1, C_6^1, C_7^1), 154.2–154.6 (m, C_8^1), 190.1 (s, CHO) ppm. IR (KBr): 1701 (S, ν_{CHO}) cm^{-1}. Anal. Found: C, 54.12; H, 3.89;

N, 4.35. $C_{22992}H_{19920}N_{3063}O_{4602}P_{1533}S_{1530}$ Calc.: C, 54.22; H, 3.94; N, 8.42%.

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