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Synthesis of dendrimers with phosphine end groups at each generation

Anna Balueva [1], Sonia Merino [2], Anne-Marie Caminade *, Jean-Pierre Majoral *

Laboratoire de Chimie de Coordination, CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

The synthesis of new phenoxydiphenylphosphino derivatives allows the formation of dendrimers having phosphine end groups at each generation. The dendrimers are grown up to the fourth generation (32 phosphine terminal groups) using Staudinger reactions with azides and deprotection of borane–phosphine complexes by amines. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dendrimers; Phosphines; Borane; Staudinger reaction

1. Introduction

Dendrimers are hyperbranched regular macromolecular trees characterized by the presence of a large number of functional groups on the surface, which opens the way to a versatile reactivity [1]. Recent emphasis in this topic concerns the study of properties of these intriguing macromolecules [2], but the search for other methods of synthesis remains an active area. We have reported several ways of synthesis of phosphorus-containing dendrimers possessing various functional end groups at each step of the synthesis, mainly chlorine and aldehyde, which allowed us to carry out miscellaneous reactions [3] and to develop various applications [4]. We [5] and others [6] have also demonstrated that phosphine end groups are particularly interesting functions, due to their complexation ability, leading in particular to new catalysts. The grafting of phosphine end groups can be accomplished at the end of the synthesis of the dendrimer, or can occur at each generation during the synthesis. Our previous investigations concerning the latter case used the Staudinger reaction which creates P=N–P=S linkages within the dendritic structure. Furthermore, these linkages were demonstrated to possess a very interesting reactivity [7], but necessitated three steps at each generation to be created and to multiply by two the number of phosphine end groups. Thus, it appeared interesting to find straighter ways of synthesis, which could multiply more rapidly the number of phosphine end groups and P=N–P=S linkages with a smaller number of reactions. We recently proposed two ways to fulfill these requirements by synthesizing new building blocks, i.e. $N_3P(S)(OC_6H_4PPh_2BH_3)_2$, which allows to multiply by two the number of phosphine end groups every two steps [8], and $H_2NN(Me)P(S)(OC_6H_4PPh_2)_2$, which allows to multiply by four the number of phosphine end groups every two steps [9].

We report here the synthesis of (phenoxydiphenyl)phosphines and their use as functional building blocks for the synthesis of new di- and tetra-phosphine monomers, and of dendrimers up to the fourth generation (32 $RPPh_2$ end groups).

* Corresponding authors. Tel.: +33-561-333-123; fax: +33-561-553-003.

E-mail addresses: caminade@lcc-toulouse.fr (A.-M. Caminade), majoral@lcc-toulouse.fr (J.-P. Majoral).

[1] Present address: A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan Scientific Centre, Arbuzov Street 8, Kazan 42088, Russia.

[2] Present address: Area de Quimica Organica, Facultad de Quimicas, Av. Camilo Jose Cela s/n, 13071 Ciudad Real, Spain.

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2. Results and discussion

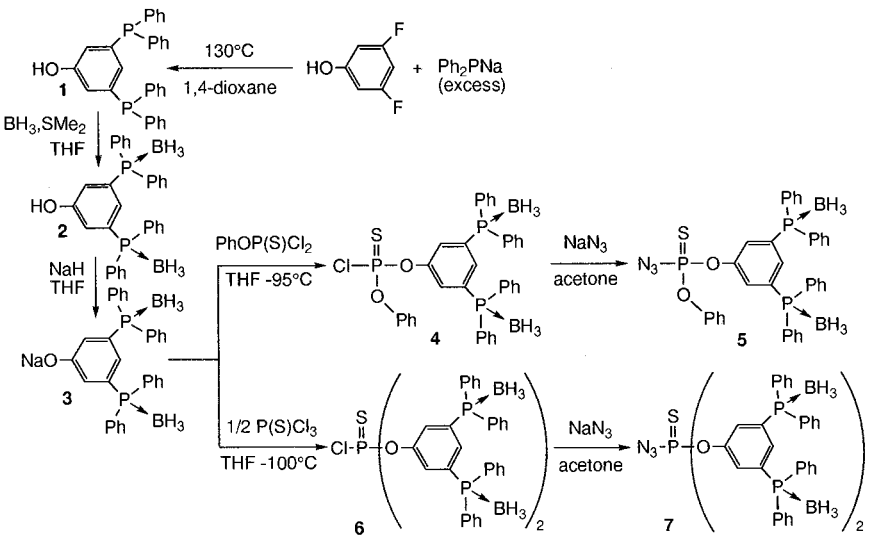
In order to rapidly multiply the number of phosphine end groups, we decided to synthesize the new functionalized diphosphine 1,3-$(PPh_2)_2$-5-HO–(C_6H_3) (**1**) (Scheme 1). For this purpose, we used a method analogous to the one described for the synthesis of 1,2-$(PPh_2)_2$-4-$HOCH_2$–(C_6H_3) [10]. The reaction of Ph_2PNa with 3,5-difluorophenol occurs very slowly at 130 °C in 1,4-dioxane and needs 12 days to go to completion. After purification on silicagel, compound **1** is isolated, and characterized in ^{31}P-NMR by a singlet at $\delta = -4.8$ ppm. The phosphino groups are not very sensitive to oxidation, however, we decided to protect them by BH_3 from this step. The reaction with $BH_3{\cdot}SMe_2$ affords cleanly the protected derivative **2**, characterized in ^{31}P-NMR by a broad singlet at $\delta =$ 21.4 ppm.

The phenolate derivative **3** is readily obtained from **2**, by reaction with NaH. This compound is the precursor of diphosphino and tetraphosphino derivatives usable for the synthesis of dendrimers. For this purpose, the sodium salt **3** is reacted with chlorothiophosphine derivatives. Reaction of one equivalent of **3** with one equivalent of $PhOP(S)Cl_2$ at -95 °C gives derivative **4**, possessing one chlorine and two protected phosphines. No attempt was made to perfectly purify this compound, and it was directly used to react with NaN_3 to yield the azide **5** (Scheme 1). Column chromatography on silicagel affords pure **5**, characterized by the presence of two singlets in ^{31}P-NMR ($\delta = 59.5$ (P=S) and 22.3 ppm (P→BH_3)) and a strong band in IR spectroscopy ($\bar{\nu}_{N_3} = 2189\ cm^{-1}$).

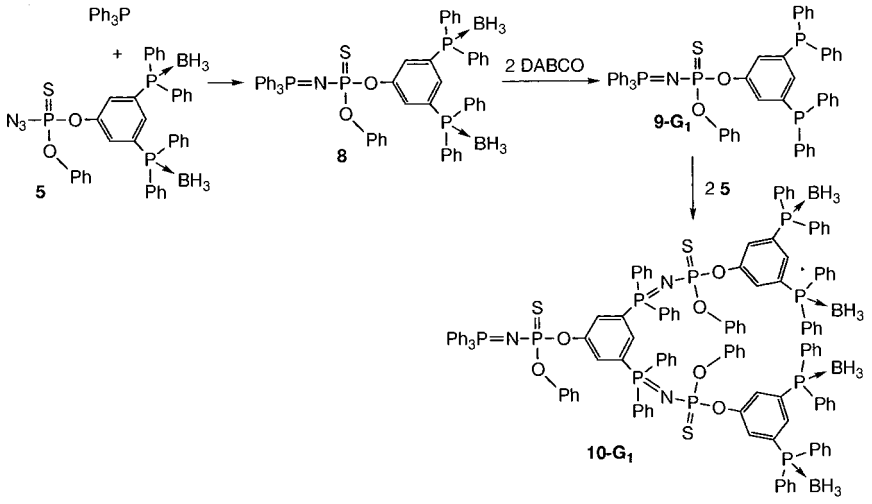
Two equivalents of the sodium salt **3** react with one equivalent of $P(S)Cl_3$ at -100 °C to afford compound **6**, characterized in ^{31}P-NMR by the presence of two singlets at $\delta = 58.4$ (P=S) and 22.4 ppm (P→BH_3) (Scheme 1). This compound also was not perfectly purified, but used to react with NaN_3. The azide **7** thus obtained is purified by column chromatography and characterized in ^{31}P-NMR by the presence of two singlets ($\delta = 59.4$ (P=S) and 22.4 ppm (P→BH_3), and by IR spectroscopy ($\bar{\nu}_{N_3} = 2189\ cm^{-1}$).

We intended to use compounds **5** and **7** for the synthesis of dendrimers. In this perspective, we reacted first the azide **5** with Ph_3P (Scheme 2). The reaction affords compound **8**, which is purified by column chromatography. The ^{31}P-NMR spectrum of **8** consists of three signals: two doublets at $\delta = 14.4$ (P=N) and 52.6 ppm (P=S) with $^3J_{PP} = 28.8$ Hz, and one broad singlet at $\delta = 21.7$ ppm (P→BH_3). IR spectroscopy indicates the disappearance of the signal corresponding to N_3. The second step of the synthesis necessitates to deprotect both phosphino groups of **8**. This is achieved by using 1,4-diazabicyclo-[2,2,2]-octane (DABCO). Compound **9-G$_1$** is purified by chromatography, in spite of the presence of two free phosphino groups. The ^{31}P-NMR spectrum confirms that the deprotection occurred, characterized by the presence of a singlet at $\delta = -4.8$ ppm, corresponding to the free PPh_2 groups. Compound **9-G$_1$** can be considered as the first generation of the dendrimer, since it possesses two phosphino groups whereas the core (PPh_3) had only one.

The next step to grow the dendrimer obviously consists in reacting the azide **5** with the diphosphine **9-G$_1$**. However, we had to face some problems in this case. Indeed, the steric hindrance of both PPh_2 groups in 1,3 position slackens the Staudinger reaction of the azide **5**, and side reactions are observed. In particular a migration of some BH_3 groups from the phosphino group of compound **5** to the phosphino group of compound **9-G$_1$** occurs. In spite of this problem, compound **10-G$_1$**



Scheme 1. Synthesis of various phenoxydiphenylphosphino derivatives usable for the synthesis of dendrimers.

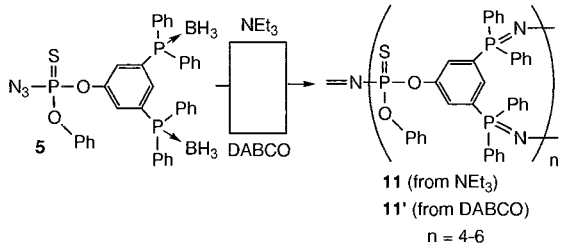


Scheme 2. Synthesis of the first generation of the dendrimer **10-G$_1$**.

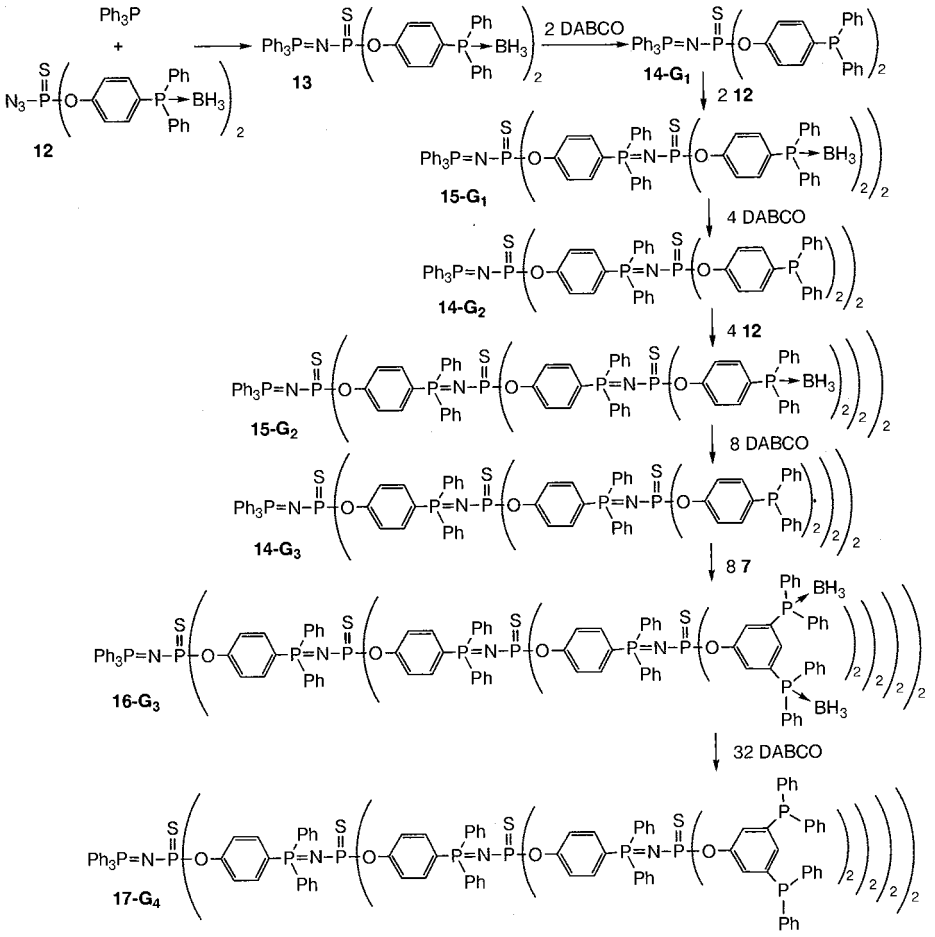
is isolated by column chromatography, but in low yield (22%). The ^{31}P-NMR spectrum of **10-G$_1$** consists of five signals: two sets of two doublets in a 2:1 ratio at $\delta = 13.5$ (Ph_2P=N) and 52.7 ppm (P=S) with $^2J_{PP} = 29.4$ Hz, $\delta = 14.6$ (Ph_3P=N) and 52.6 ppm (P=S) with $^2J_{PP} = 28.2$ Hz, and a broad singlet at $\delta = 21.7$ ppm (P→BH_3). The presence of two sets of two doublets confirms that the Staudinger reaction occurred, but we decided to stop the synthetic process at this step, because the phenomenon of exchange of BH_3 observed during the synthesis of **10-G$_1$** should occur at each step and hamper the synthesis and purification of further generations.

However, we thought that this exchange phenomenon would not be a constraint for the synthesis of hyperbranched polymers issued from compound **5**. For this purpose, we treated compound **5** with an amine, either NEt_3 or DABCO (Scheme 3). Such treatment should result in a polymerization, the deprotected phosphines reacting with the azide. The end of the reaction is characterized by the disappearance of both the signal corresponding to the P→BH_3 groups in ^{31}P-NMR and the signal of the N_3 groups in IR. The ^{31}P-NMR spectrum of compound **11** displays large signals at $\delta = 13$ (Ph_2P=N) and 52 ppm (P=S) and two relatively thin singlets at $\delta = -4.7$ and -4.8 ppm corresponding to free PPh_2. The presence of two signals is presumably due to 'terminal' and 'linear' groups, corresponding, respectively, to two phosphino groups linked to one aromatic group, and one phosphino group linked to one aromatic group bearing also a phosphazene group. Size exclusion chromatography (SEC) and laser light scattering (LLS) give an average value for the molecular weight of the hyperbranched polymer **11**: 3000 for the sample obtained with NEt_3, and 3800 for the sample obtained with DABCO. Considering that the molecular weight of the monomeric unit NP(S)(OC_6H_5)(OC_6H_3(PPh_2)$_2$) is 631, these values indicate that only four to six monomeric units are linked. On the other hand, both ^{31}P-NMR and IR spectroscopies indicate the total disappearance of the N_3 groups. The only way to explain both phenomena is to consider that macrocycles are formed in most cases, instead of hyperbranched polymers. Indeed, the *meta* position should favour the formation of such macrocycles instead of the growing of the chain.

This problem, in addition to the steric constraints induced by the presence of both phosphino groups in *meta* position should prevent the use of these 1,3 diphosphino compounds to build dendrimers, and we did not tried to use the tetraphosphine **7** in such a way. However, compound **7** could be grafted on the surface of dendrimers. Thus, we decided to built the dendrimer using the same sequence of reactions, but with a less hindered building block, $N_3P(S)(OC_6H_4PPh_2BH_3)_2$ (**12**) [8]. The reaction with PPh_3 affords compound **13** which is deprotected with DABCO, leading to compound **14-G$_1$** (Scheme 4). The presence of the phosphino group in *para* position in **14-G$_1$** compared to the bis(*meta*) position in **10-G$_1$** induces a higher reactivity, and we do not observe transfer reactions of BH_3 when **14-G$_1$** is reacted with the azide **12**. Compound **15-G$_1$** is isolated



Scheme 3. One-step synthesis of the hyperbranched polymers **11** and **11′**.



Scheme 4. Step-by-step synthesis of dendrimers **14-G$_n$**, **15-G$_n$**, **16-G$_3$**, and **17-G$_4$**.

in good yield, then deprotected with DABCO, to give the second generation of the dendrimer **14-G$_2$**. This compound is characterized in ^{31}P-NMR by the presence of two sets of doublets at $\delta = 14.8$ and 49.9 ppm (Ph_3P=N–P=S) with $^2J_{PP} = 28.9$ Hz, and $\delta = 13.2$ and 50.8 ppm (Ph_2P=N–P=S) with $^2J_{PP} = 29.4$ Hz, and one singlet at $\delta = -6.4$ ppm (free Ph_2P). Dendrimer **14-G$_2$** reacts with the azide **12** to give compound **15-G$_2$**, which is deprotected with DABCO, leading to the third generation **14-G$_3$**, whose ^{31}P-NMR spectrum is depicted Fig. 1.

Starting from the third generation **14-G$_3$**, we could use again the azide **12**, but we preferred to multiply more rapidly the number of terminal phosphino groups. Thus, the azide **7** was used instead of **12**. The reaction occurs easily, leading to dendrimer **16-G$_3$**, whose protected phosphino groups are deprotected with DABCO (Scheme 4). The fourth generation dendrimer **17-G$_4$** possesses 32 PPh_2 groups, that is to say four times the number of phosphino groups of the preceding generation (Fig. 2). The ^{31}P-NMR spectrum confirms the obtaining of dendrimer **17-G$_4$**, with the presence of one singlet ($\delta = -4.9$ ppm, free PPh_2) and four sets of two doublets ($\delta = 14.9$ and 50.0, Ph_3P=N–P=S; 14.5 and 49.8, Ph_2P=N–P=S of the first generation; 14.3 and 49.6, Ph_2P=N–P=S group of the second generation; 13.5 and 52.7, Ph_2P=N–P=S groups of the third generation). Fig. 1 displays all the ^{31}P-NMR spectra of dendrimers from **15-G$_1$** to **17-G$_4$**. It is important to note that all the signals corresponding to each type of phosphorus are detected, even for **17-G$_4$** (17 peaks corresponding to eight types of phosphorus).

Beside ^{31}P-NMR, all these compounds are analyzed by ^{1}H-, and ^{13}C-NMR, IR, and elemental analyses, but in all cases, ^{31}P-NMR appears as the best tool to characterize each step of the synthesis. During the construction of the skeleton of the dendrimer, the Staudinger reaction induces a deshielding of the signal of the PPh_2 group from $\delta \approx -6$ for **14-G$_n$** to ≈ 14 ppm for **15-G$_n$**, and the shielding of the signal of the P=S group from 57.8 for **12** to ≈ 51 ppm for **15-G$_n$**. The deprotection reaction induces a shielding of the signal of the PPh_2 group from ≈ 20 for **15-G$_n$** to ≈ -6 ppm for **14-G$_{n+1}$**. Analogous phenomena are observed in the last step, with the grafting of the azide **7** (Fig. 1).

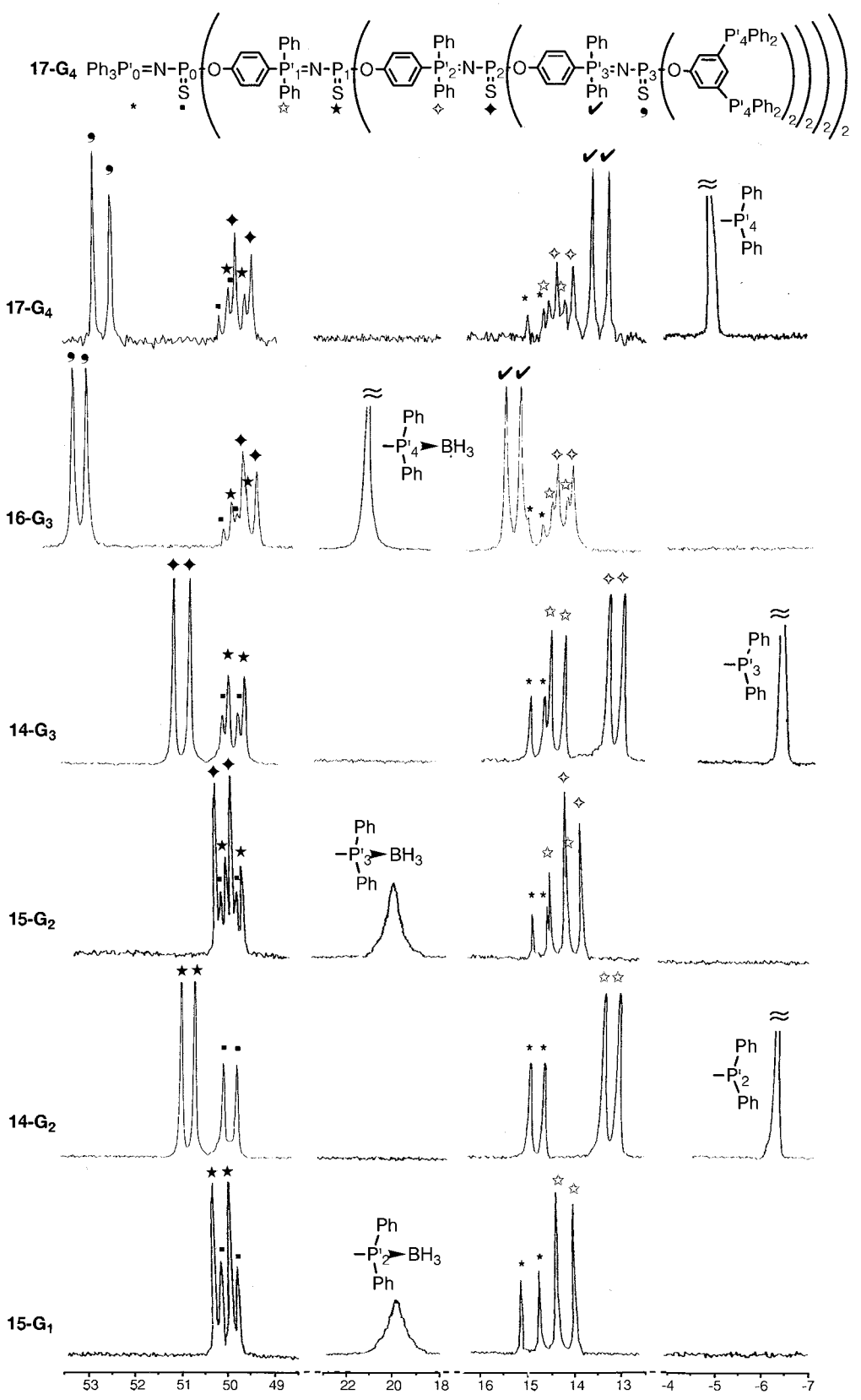


Fig. 1. ^{31}P-NMR spectra of all dendrimers from **15-G$_1$** to **17-G$_4$**.

3. Conclusions

The functionalized 1,3-diphosphines that we have obtained are difficult to use as building blocks for the synthesis of dendrimers, but it is interesting to graft them on the surface of dendrimers, in order to multiply rapidly the number of phosphino end groups in the last step. We have shown in particular that the grafting of $N_3P(S)[OC_6H_3(PPh_2BH_3)_2]_2$ allows to multiply by four the number of end groups when going from the third to the fourth generation. The largest compound synthesized possesses 32 PPh_2 end groups and 15 P=N–P=S groups. Since, we have previously demonstrated with other dendrimers that both types of functions display a versatile reactivity, work is in progress to study the reactivity and the complexation properties of this new series of dendrimers.

4. Experimental

General. All reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-

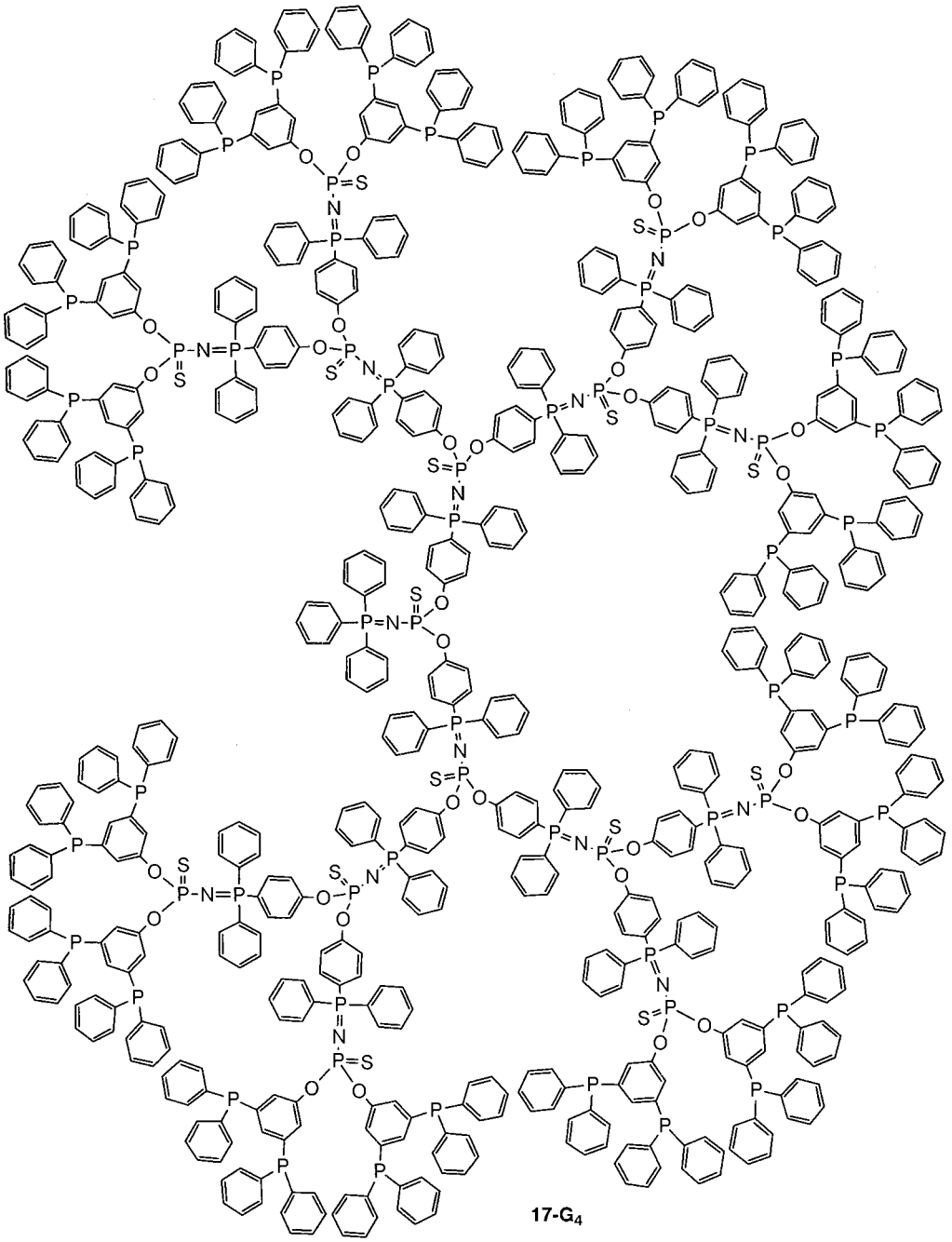


Fig. 2. Chemical structure of dendrimer **17-G$_4$**.

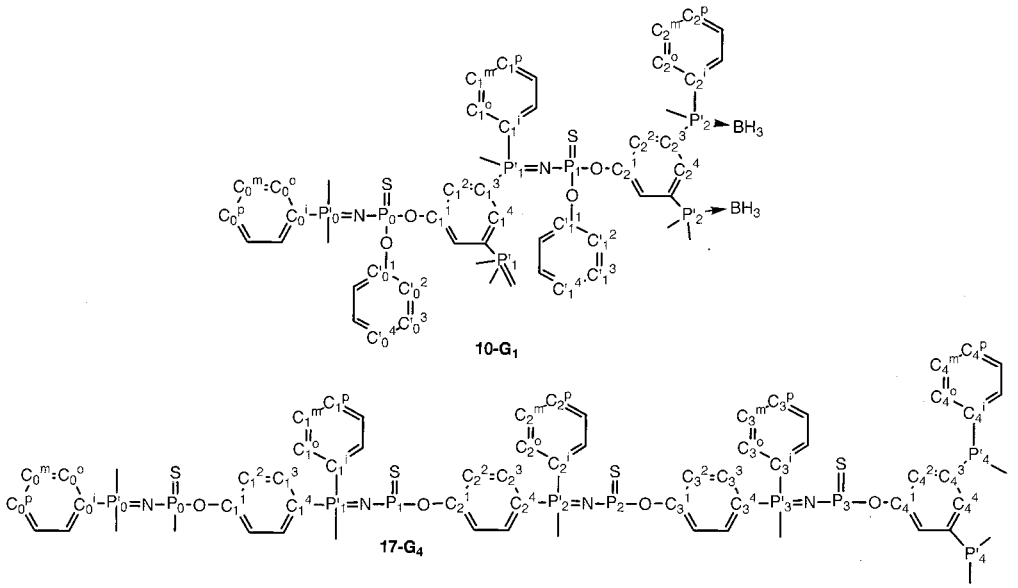


Fig. 3. Numbering used for NMR.

line manipulations. All solvents were dried, distilled and degassed before use. Instrumentation: Bruker AC80, AC200, or AM250 (^{1}H-, ^{13}C-, ^{31}P-NMR), Perkin–Elmer 1725X (FT-IR). The numbering used for NMR assignment is depicted in Fig. 3. Elemental analyses were performed by the Service d'Analyse du Laboratoire de Chimie de Coordination, Toulouse (France). Compound **12** was prepared according to a published procedure [8]. The actual molar masses were calculated from the response of a multi-angle Laser-Light-Scattering detector (Wyatt Technology) ASTRA software version 4.20, which was connected to the size exclusion chromatography (MALLS/SEC) line.

4.1. Synthesis of 3,5-bis(diphenylphosphino)phenol (*1*)

Ph_2PCl (9 ml, 50 mmol) was added dropwise under reflux to a stirred mixture of Na chips (2.6 g, 113 mmol) and dry 1,4-dioxane (6.5 ml). The mixture was refluxed for a further 4 h and stirred overnight at room temperature (r.t.). The suspension of Ph_2PNa was added to 3,5-difluorophenol (1.05 g, 8 mmol). The mixture was stirred at 130–135 °C in a sealed Schlenk flask for 12 days, then cooled. EtOH (15–20 ml) was added to remove the residual Na metal and the mixture was stirred for 0.5 h. The solution was evaporated to dryness and the residue was extracted by CH_2Cl_2 (60 ml) for 1 h. The resulting suspension was centrifugated and the precipitate was removed by a careful decantation. The solvent was removed in vacuo, and the most part of the side-product Ph_2PH was distilled off under vacuum (0.5 mm, 130–150 °C). Compound **1** was isolated by column chromatography of the residue on silica gel (THF–pentane 15:85 as eluent). Compound **1** was obtained as a white powder (yield 2.4 g, 65%).

*Compound **1**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −4.8 (s). ^{1}H-NMR ($CDCl_3$): δ 5.76 (br Δ, 1H, OH), 6.66 (ddd, $^3J_{HP} = 7.64$ Hz, $^4J_{HH} = 1.27$ Hz, $^5J_{HP} = 2.5$ Hz, 2H, C^2–H), 6.88 (tt, $^3J_{HP} = 7.65$ Hz, $^4J_{HH} = 1.27$ Hz, 1H, C^4–H), 7.19–7.35 (m, 20H, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 120.36 (d, $^2J_{CP} = 18.8$ Hz, C^2), 128.33 (d, $^3J_{CP} = 7.2$ Hz, C^m), 128.66 (s, C^p), 130.89 (t, $^2J_{CP} = 21.1$ Hz, C^4), 133.56 (d, $^2J_{CP} = 19.1$ Hz, C^o), 136.38 (d, $^1J_{CP} = 10.2$ Hz, C^i), 139.12 (dd, $^1J_{CP} = 13.0$ Hz, $^3J_{CP} = 7.2$ Hz, C^3), 155.72 (t, $^3J_{CP} = 7.3$ Hz, C^1). Calc. for $C_{30}H_{24}OP_2$ (462.46): C, 77.91; H, 5.23. Anal. Found: C, 78.14; H, 5.28%.

4.2. Synthesis of 3,5 bis(borane-diphenylphosphino)phenol (*2*)

$BH_3{\cdot}SMe_2$ (2 M solution in toluene, 2.7 ml, 5.4 mmol) was added to a solution of **1** (0.95 g, 2.05 mmol) in degassed THF (7 ml) at 0 °C. The reaction mixture was stirred overnight at r.t., then evaporated to dryness. Compound **2** was isolated by chromatography on silica gel (ether–pentane (2:1) as eluent). Compound **2** was obtained as colorless crystals (yield 0.9 g, 89%). M.p.: 77 °C (dec.).

*Compound **2**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 21.4 (br s). ^{1}H-NMR ($CDCl_3$): δ 1.1 (br s, 6H, BH_3), 6.96 (tt, $^3J_{HP} = 10.04$ Hz, $^4J_{HH} = 1.25$ Hz, 1H, C^4–H), 7.27 (ddd, $^3J_{HP} = 11.74$ Hz, $^4J_{HH} = 1.25$ Hz, $^5J_{HP} = 2.4$ Hz, 2H, C^2–H), 7.31–7.54 (m, 20H, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 122.60 (d,$^2J_{CP} = 12.2$ Hz, C^2), 128.13 (d, $^1J_{CP} = 58$ Hz, C^i), 128.67 (d, $^3J_{CP} = 9.5$ Hz, C^m), 131.29 (s, C^p), 131.75 (dd, $^1J_{CP} = 54.5$ Hz, $^3J_{CP} = 10.7$ Hz, C^3), 132.84 (d, $^2J_{CP} = 10.2$ Hz, C^o), 133.30 (t, $^2J_{CP} = 12$ Hz, C^4), 156.75 (t, $^3J_{CP} = 13.6$ Hz, C^1). Calc. for

$C_{30}H_{30}B_2OP_2$ (490.13): C, 73.51; H, 6.16. Anal. Found: C, 73.40; H, 6.25%.

4.3. Synthesis of the sodium salt of 3,5-bis(borane-diphenylphosphino)phenol (3)

A solution of **2** (0.9 g, 1.84 mmol) in THF (6 ml) was added dropwise to a stirred suspension of NaH (0.05 g, 2.08 mmol) in THF (3 ml). The reaction mixture was stirred at r.t. for 2.5 h, the residual NaH was removed by filtration under Ar and the filtrate was evaporated to dryness overnight to give [**3**·2 THF] as a yellow powder (yield 0.88 g, 73%).

Compound ***3****:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 19.8 (br s). ^{1}H-NMR ($CDCl_3$): δ 1.1 (br s, 6H, BH_3), 1.66 (m, 8H, CH_2), 3.55 (m, 8H, –CH_2–O–), 6.25 (t, $^3J_{HP} = 10.1$ Hz, 1H, C^4–H), 6.79 (d, $^3J_{HP} = 13.26$ Hz, 2H, C^2–H), 7.16–7.44 (m, 20H, C_6H_5).

4.4. Synthesis of azido (3,5-bis(borane-diphenylphosphino)phenoxy)(phenoxy)thiophosphate (5)

A solution of [**3**·2 THF] (2.49 g, 3.96 mmol) in THF (60 ml) was added dropwise very slowly to a solution of dichloro(phenoxy)thiophosphate (0.9 g, 3.96 mmol) in THF (15 ml) between −90 and −100 °C under stirring. The reaction mixture was allowed to reach slowly the r.t. and was stirred overnight. The reaction mixture was partially concentrated in vacuo, the precipitate was removed by centrifugation and filtration under Ar. Evaporation of the filtrate gave chloro(3,5-bis(borane-diphenylphosphino)phenoxy)(phenoxy) thiophosphate **4** (yield 2.63 g, 98%) as a yellow oil which was not further purified.

Compound ***4****:* $^{31}P\{^1H\}$-NMR: δ 58.7 (s, P_0), 22.4 (br s, P_1).

Previously dried in vacuo NaN_3 (0.25 g, 4.38 mmol) was added to the stirred solution of unpurified **4** (2.63 g, 3.86 mmol) in acetone (16 ml). The reaction mixture was stirred overnight at r.t., and the precipitate of NaCl was removed by centrifugation and filtration. The solution was evaporated to dryness and **5** was isolated by chromatography of the residue on silica gel (pentane–ether (1:1) as eluent) as a very viscous colorless oil (yield 1.2 g, 45%).

Compound ***5****:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 22.3 (br s, P_1), 59.5 (s, P'_0). ^{1}H-NMR ($CDCl_3$): δ 1.2 (br s, 6H, BH_3) 7.09–7.67 (m, 28H, C_6H_3, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 120.84 (d, $^3J_{CP'0} = 4.4$ Hz, C'^2), 126.22 (d, $^5J_{CP'0} = 2.3$ Hz, C'^4), 127.37 (d, $^1J_{CP1} = 58.8$ Hz, C^i), 128.14 (dd, $^2J_{CP1} = 11.5$ Hz, $^3J_{CP'0} = 6$ Hz, C^2), 128.89 (d, $^3J_{CP1} = 10.2$ Hz, C^m), 129.76 (s, C'^3), 131.64 (s, C^p), 132.91 (d, $^2J_{CP1} = 10.1$ Hz, C^o), 133.41 (dd, $^1J_{CP1} = 52$ Hz, $^3J_{CP1} = 10.3$ Hz, C^3), 134.38 (t, $^2J_{CP1} = 8.9$ Hz, C^4), 149.46 (d, $^2J_{CP'0} = 8.3$ Hz, C'^1), 150.08 (dt, $^2J_{CP'0} = 8.7$ Hz, $^3J_{CP1} = 13.08$ Hz, C^1). IR (KBr): 2189 cm^{-1} ($\bar{\nu}_{N3}$). Calc. for $C_{36}H_{34}B_2N_3O_2P_3S$ (687.29): C, 62.91; H, 4.98; N, 6.11. Anal. Found: C, 62.79; H, 4.85; N, 6.03%.

4.5. Synthesis of azido bis(3,5-bis(borane-diphenylphosphino)phenoxy)thiophosphate (7)

A solution of [**3**·2 THF] (2.24 g, 3.4 mmol) in THF (60 ml) was added dropwise very slowly to a stirred solution of $P(S)Cl_3$ (0.164 ml, 1.62 mmol) in THF (15 ml) between −95 and −100 °C. Then, the reaction mixture was allowed to reach the r.t. very slowly and was stirred overnight. The reaction mixture was partially concentrated in vacuo, centrifugated and filtered to remove NaCl. Evaporation of the filtrate in vacuo gave chloro bis(3,5-bis(borane-diphenylphosphino)-phenoxy)thiophosphate (**6**) (yield 1.7 g, 97.5%) as a very viscous yellow oil, which was not further purified.

Compound ***6****:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 22.4 (br s, P_1), 58.4 (s, P_0).

Previously dried in vacuo NaN_3 (0.12 g, 1.85 mmol) was added to a stirred solution of unpurified **6** (1.70 g, 1.58 mmol) in acetone (10 ml) and the reaction mixture was stirred overnight at r.t., then centrifugated and filtered to remove NaCl. The filtrate was evaporated to dryness. Compound **7** was isolated by chromatography of the residue on silicagel (eluent: $CHCl_3$) as a white powder (yield 0.62 g, 33%). M.p.: 78–81 °C.

Compound ***7****:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 22.4 (br s, P_1), 59.4 (s, P_0). ^{1}H-NMR ($CDCl_3$): δ 7.17–7.78 (m, C_6H_3, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 127.49 (d, $^1J_{CP1} = 58.1$ Hz, C^i), 128.16 (dd, $^2J_{CP1} = 11.4$ Hz, $^3J_{CP0} = 3.6$ Hz, C^2), 129.09 (d, $^3J_{CP1} = 10.0$ Hz, C^m), 131.84 (s, C^p), 133.06 (d, $^2J_{CP1} = 9.8$ Hz, C^o), 133.82 (dd, $^1J_{CP1} = 54.2$ Hz, $^3J_{CP1} = 9.8$ Hz, C^3), 134.86 (t, $^2J_{CP1} = 7.9$ Hz, C^4), 149.82 (dt, $^2J_{CP0} = 8.5$ Hz, $^3J_{CP1} = 12.8$ Hz, C^1). IR (KBr): 2189 cm^{-1} ($\bar{\nu}_{N3}$). Calc. for $C_{60}H_{58}B_4N_3O_2P_5S$ (1083.3): C, 66.52; H, 5.39; N, 3.87. Anal. Found: C, 66.58; H, 5.45; N, 3.78%.

4.6. Synthesis of compound 8

A solution of triphenylphosphine (0.203 g, 0.774 mmol) in CH_2Cl_2 (17 ml) was added dropwise slowly to a stirred solution of **5** (0.532 g, 0.774 mmol) in CH_2Cl_2 (6 ml) at r.t. The reaction mixture was stirred overnight and the solvent was removed in vacuo. Compound **8** was isolated by chromatography of the residue on silica gel (pentane–ether as eluent, the ratio was changed gradually from (1:1) to (1:3)) as a very viscous colorless oil (yield 0.547 g, 76.7%).

Compound ***8****:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.4 (d, $^2J_{P0P'0} = 28.8$ Hz, P_0), 21.7 (br s, P_1), 52.6 (d, $^2J_{P'0P0} = 28.8$ Hz, P'_0). ^{1}H-NMR ($CDCl_3$): δ 1.2 (br s, 6H, BH_3), 7.55–6.98 (m, 43H, C_6H_3, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.41 (d, $^3J_{CP'0} = 5.1$ Hz, C'^3_0), 124.25 (s, C^4_0), 127.93 (d, $^1J_{CP1} = 57.8$ Hz, C^i_1), 128.14 (dd, $^2J_{CP1} =$

11.3 Hz, $^3J_{CP'0} = 4.9$ Hz, C_1^2), 128.4 (dd, $^1J_{CP0} = 106$ Hz, $^3J_{CP'0} = 4$ Hz, C_0^i), 128.57 (d, $^3J_{CP0} = 12.1$ Hz, C_0^m), 128.81 (s, $C_0'^3$), 128.86 (d,$^2J_{CP1} = 10.0$ Hz, C_1^m), 131.52 (s, C_0^p), 131.85 (dd, $^1J_{CP1} = 53.2$ Hz, $^3J_{CP1} = 9.8$ Hz, C_1^3), 132.51 (s, C_0^p), 132.61 (d, $^2J_{CP0} = 10.9$ Hz, C_0^o), 133.01 (d, $^2J_{CP1} = 9.9$ Hz, C_1^o), 134.41 (t, $^2J_{CP1} = 8.3$ Hz, C_1^4), 151.51 (d, $^2J_{CP'0} = 8.4$ Hz, C'^4), 152.5 (dt, $^2J_{CP'0} = 8.5$ Hz, $^3J_{CP1} = 13.1$ Hz, C_1^1). Calc. for $C_{54}H_{49}B_2NO_2P_4S$ (921.6): C, 70.38; H, 5.35; N, 1.52. Anal. Found: C, 70.53; H, 5.44; N, 1.43%.′

4.7. Synthesis of compound **9-G$_1$**

A solution of 1,4-diazabicyclo-[2,2,2]-octane (DABCO) (0.130 g, 1.20 mmol) in toluene (2 ml) was added to a stirred solution of **8** (0.521 g, 0.566 mmol) in toluene (5 ml). The reaction mixture was stirred overnight at r.t. and the solvent was removed in vacuo. Compound **9-G$_1$** was isolated by chromatography on silicagel (ether–pentane (1:1) as eluent) as a very viscous colorless oil (yield 0.27 g, 53%).

*Compound **9-G$_1$**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −4.8 (s, P_1), 13.6 (d, $^2J_{P0P'0} = 29$ Hz, P_0), 52.3 (d, $^2J_{P'0P0} = 29$ Hz, P'_0). ^{1}H-NMR ($CDCl_3$): δ 6.93–7.57 (m, C_6H_5, C_6H_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.41 (d, $^3J_{CP'0} =$ 5.2 Hz, C'^2_0), 123.7 (br s, C'^4_0), 126.87 (dd, $^2J_{CP1} = 18.7$ Hz, $^3J_{CP'0} = 4.6$ Hz, C_1^2), 128.26 (d, $^3J_{CP1} = 7.2$, H_2, C_1^m), 128.38 (d, $^3J_{CP0} = 13.7$ Hz, C_0^m), 128.5 (dd, $^1J_{CP0} = 106.7$ Hz, $^3J_{CP'0} = 4.4$ Hz, C_0^i), 128.52 (s, C_1^p), 128.74 (s, C'^3_0), 132.25 (d, $^4J_{CPO} = 2.4$ Hz, C_0^p), 132.59 (d, $^2J_{CP0} = 10.8$ Hz, C_0^o), 133.52 (d, $^2J_{CP1} = 19.8$ Hz, C_1^o), 134.35 (t, $^2J_{CP1} = 20.6$ Hz, C_1^4), 136.44 (d, $^1J_{CP1} = 10.9$ Hz, C_1^i), 138.74 (dd, $^1J_{CP1} = 12.3$ Hz, $^3J_{CP1} = 4.2$ Hz, C_1^3), 151.49 (d, $^2J_{CP'0} = 8.2$ Hz, C'^1_0), 152.23 (dt, $^2J_{CP'0} = 7.6$ Hz, $^3J_{CP1} = 9.6$ Hz, C_1^1). Calc. for $C_{54}H_{43}NO_2P_4S$ (893.9): C, 72.55; H, 4.84; N, 1.56. Anal. Found: C, 72.32; H, 4.65; N, 1.45%.

4.8. Synthesis of dendrimer **10-G$_1$**

A solution of **9-G$_1$** (0.27 g, 0.3 mmol) in CH_2Cl_2 (17 ml) was added dropwise very slowly to a stirred solution of azide **5** (0.44 g, 0.64 mmol) in CH_2Cl_2 (6 ml). The reaction mixture was stirred overnight. An additional portion of **5** (0.066 g) in CH_2Cl_2 (2 ml) was added to accelerate and complete the reaction; the reaction mixture was stirred for 1 day. The solvent was removed in vacuo. Chromatography on silica gel with the gradual increase of the eluent's polarity from $CHCl_3$–CH_2Cl_2 mixture (9:1) to pure CH_2Cl_2 gave **10-G$_1$** (yield 0.15 g, 22%) as a very viscous colorless oil.

*Compound **10-G$_1$**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 13.5 (d, $^2J_{P1P'1} = 29.4$ Hz, P_1), 14.6 (d, $^2J_{P0P'0} = 28.2$ Hz, P_0). 21.7 (br s, P_2), 52.6 (d, $^2J_{P'0P0} = 28.2$ Hz, P'_0), 52.7 (d, $^2J_{P'1P1} = 29.4$ Hz, P'_1). ^{1}H-NMR ($CDCl_3$): δ 1.2 (br s, 12H, BH_3), 6.81–7.82 (m, 99H, C_6H_5, C_6H_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.36 (d, $^3J_{CP'1} = 5.1$ Hz, C'^2_1), 121.52 (d, $^3J_{CP'0} = 5.3$ Hz, C'^2_0), 124.15 (br s, C'^4_1), 124.23 (br s, C'^4_0), 127.21 (br d, $^1J_{CP1} = 107.2$ Hz, C_1^3), 128.14 (d, $^1J_{CP2} = 54.4$ Hz, C_2^i), 128.30 (dd, $^1J_{CP0} = 106.7$ Hz, $^3J_{CP'0} = 3.3$ Hz, C_0^i), 128.67 (d, $^3J_{CP0} = 11.6$ Hz, C_0^m), 128.8 (br s, C'^3_0, C'^3_1), 128.84 (d, $^3J_{CP2} = 9.6$ Hz, C_2^m), 128.98 (br d, $^1J_{CP1} = 103.1$ Hz, C_1^i), 128.99 (d, $^3C_{CP1} =$ 9.8 Hz, C_1^m), 131.41 (s, C_2^p), 131.76 (dd, $^1J_{CP2} = 55.3$ Hz, $^3J_{CP2} = 10.2$ Hz, C_2^3), 132.66 (br d, $^2J_{CP} = 11.8$ Hz, C_0^o), 132.69 (br s, C_0^p, C_1^p), 132.98 (d, $^2J_{CP1} = 9.8$ Hz, C_1^o), 133.06 (d, $^2J_{CP2} = 9.7$ Hz, C_2^o), 134.5 (br m, C_1^4, C_2^4), 151.55 (d, $^2J_{CP'1} = 8.5$ Hz, C'^1_1), 151.68 (d, $^2J_{CP'0} = 7.4$ Hz, C'^1_0), 152.42 (dt, $^3J_{CP1} = 16$ Hz, $^2J_{CP'0} = 8$ Hz, C_1^1), 152.44 (dt, $^3J_{CP2} = 13.5$ Hz, $^2J_{CP'1} = 7.6$ Hz, C_2^1), (C_1^2 and C_2^2 not detected). Calc. for $C_{126}H_{111}B_4N_3O_6P_{10}S_3$ (2212.4): C, 68.40; H, 5.05; N, 1.89. Anal. Found: C, 68.03; H, 4.86; N, 1.75%.

4.9. Synthesis of polymer **11**

NEt_3 (0.23 ml, 1.66 mmol) was added to a stirred solution of the azide **5** (0.275 g, 0.4 mmol) in THF (15 ml). The reaction was monitored by ^{31}P-NMR spectroscopy. After 2 days the signal at 58.46 ppm (N_3P=S group) disappeared and 2.3 ml of NEt_3 were added to achieve the deprotection of the phosphino groups. The reaction mixture was stirred for 6 days up to the complete disappearance of the signal of protected phosphino groups at 21.6 ppm. The volatile components were carefully removed in vacuo, and the residue was washed first with Et_2O, then with a mixture THF–pentane and with ether. Compound **11** was obtained as a very viscous colorless oil (yield 0.137 g, 54%).

*Compound **11**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −4.9 (s, P_1), −4.7 (s, P_1), 13 (m, P), 52 (m, P′). ^{1}H-NMR ($CDCl_3$): δ 6.8–8.5 (m, C_6H_5, C_6H_3). MW: 3000.

4.10. Synthesis of polymer **11**′

A solution of DABCO (0.251 g, 2.24 mmol) in toluene (2 ml) was added to the solution of the azide **5** (0.717 g, 1.044 mmol) in toluene (20 ml) and the reaction mixture was stirred overnight at r.t. The reaction mixture was filtrated, and the solvent was removed in vacuo. The residue was washed three times by reprecipitation with pentane from toluene and two times by MeCN and was dried in vacuo to give polymer **11**′ as a very viscous colorless oil (yield 0.26 g, 43%).

*Compound **11**′:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −4.9 (20%) and −4.7 (80%) (2s, P_1), 13 (m, P), 52 (m, P′). ^{1}H-NMR ($CDCl_3$): δ 6.5-8.6 (m, C_6H_5, C_6H_3). MW: 3800.

4.11. Synthesis of compound **13**

A solution of Ph_3P (0.187 g, 0.729 mmol) in CH_2Cl_2 (6 ml) was added dropwise very slowly to a stirred

solution of azidobis(4-borane-diphenylphosphinophenoxy)thiophosphate (**12**) (0.501 g, 0.729 mmol) in CH_2Cl_2 (6 ml) at r.t. The reaction mixture was stirred overnight, then filtrated and evaporated to dryness. The residue was washed twice with pentane–THF. Compound **13** was obtained as a white powder (yield 0.657 g, 98%). M.p.: 107 °C (dec.).

*Compound **13**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.4 (d, $^2J_{P0P'0} = 29.1$ Hz, P_0), 19.9 (br s, P_1), 50.1 (d, $^2J_{P'0P0} = 29.1$ Hz, P'_0). ^{1}H-NMR ($CDCl_3$): δ 1.5 (br s, 6H, BH_3), 7.19–7.61 (m, 43H, C_6H_5, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.93 (dd, $^3J_{CP1} = 10.8$ Hz, $^3J_{CP'0} = 5$ Hz, C_1^2), 124.07 (d, $^1J_{CP'0} = 60.2$ Hz, C_1^4), 128.3 (dd, $^1J_{CP0} = 108.8$ Hz, $^3J_{CP0} = 3.5$ Hz, C_0^i), 128.74 (d, $^3J_{CP0} = 13.5$ Hz, C_0^m), 128.77 (d, $^3J_{CP1} = 9.7$ Hz, C_1^m), 129.3 (d, $^1J_{CP1} = 55.3$ Hz, C_1^i), 131.25 (s, C_1^p), 132.73 (d, $^2J_{CP0} = 11.07$ Hz, C_0^o), 132.82 (s, C_0^p), 133.1 (d, $^2J_{CP1} = 9.8$ Hz, C_1^o), 134.49 (d, $^2J_{CP1} = 10.9$ Hz, C_1^3), 154.57 (d, $^2J_{CP'0} = 7.1$ Hz, C_1^1). Calc. for $C_{54}H_{49}B_2NO_2P_4S$ (921.57): C, 70.38; H, 5.35; N, 1.52. Anal. Found: C, 70.25; H, 5.28; N, 1.48%.

4.12. Synthesis of dendrimer *14-G$_1$*

A solution of DABCO (0.182 g, 1.62 mmol) in toluene (2 ml) was added to a stirred solution of **13** (0.677 g, 0.735 mmol) in toluene (7 ml). The reaction mixture was stirred for 2 days, then the solvent was removed in vacuo. Column chromatography of the residue on silica gel with toluene as eluent gave **14-G$_1$** (yield 0.45 g, 69%) as a white powder. M.p.: 59–62 °C.

*Compound **14-G$_1$**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −6.2 (s, P_1), 13.6 (d, $^2J_{P0P'0} = 29.5$ Hz, P_0). 50.9 (d, $^2J_{P'0P0} = 29.5$ Hz, P'_0). ^{1}H-NMR ($CDCl_3$): δ 7.14–7.67 (m, C_6H_4, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.64 (dd, $^3J_{CP1} = 7$ Hz, $^3J_{CP'0} = 5.9$ Hz, C_1^2), 128.35 (d, $^3J_{CP1} = 7$ Hz, C_1^m), 128.45 (dd, $^3J_{CP0} = 106.6$ Hz, $^3J_{CP'0} = 3$ Hz, C_0^i), 128.49 (d, $^3J_{CP0} = 12.7$ Hz, C_0^m), 128.56 (s, C_1^p), 131.77 (d, $^1J_{CP1} = 10.4$ Hz, C_1^4), 132.49 (s, C_0^p), 132.66 (d, $^3J_{CP0} = 11.2$ Hz, C_0^o), 133.46 (d, $^2J_{CP1} = 19.1$ Hz, C_1^o), 133.73 (d, $^2J_{CP1} = 20.8$ Hz, C_1^3), 137.16 (d, $^1J_{CP1} = 10.3$ Hz, C_1^i), 152.72 (d, $^2J_{CP'0} = 10$ Hz, C_1^1). Calc. for $C_{54}H_{43}NO_2P_4S$ (893.90): C, 72.55; H, 4.84; N, 1.56. Anal. Found: C, 72.48; H, 4.73; N, 1.49%.

4.13. Synthesis of dendrimer *15-G$_1$*

Compound **15-G$_1$** was obtained from **14-G$_1$** (0.439 g, 0.492 mmol) and **12** (0.7 g, 1.02 mmol) in CH_2Cl_2, analogously to **13**. Compound **15-G$_1$** was purified by two-time reprecipitation with ether from THF. Compound **15-G$_1$** was isolated as a white powder (yield 0.72 g, 67%). M.p.: 124–130 °C (dec.).

*Compound **15-G$_1$**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.1 (d, $^2J_{P1P'1} = 29.1$ Hz, P_1), 14.9 (d, $^2J_{P0P'0} = 28.7$ Hz, P_0), 19.8 (br s, P_2), 49.9 (d, $^2J_{P'0P0} = 28.7$ Hz, P'_0), 50.1 (d, $^2J_{P'1P1} = 29.1$ Hz, P'_1). ^{1}H-NMR ($CDCl_3$): δ 1.3 (br s, 12H, BH_3), 7.18–7.65 (m, 99H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.89 (br dd, $^3J_{CP'} = 5$ Hz, $^3J_{CP} = 10.4$ Hz, C_1^2, C_2^2), 123.33 (br d, $^1J_{CP1} = 110.2$ Hz, C_1^4), 124.11 (d, $^1J_{CP2} = 60.2$ Hz, C_2^4), 128.15 (dd, $^1J_{CP0} = 108$ Hz, $^3J_{CP'0} = 3.7$ Hz, C_0^i), 128.43 (dd, $^1J_{CP1} = 107.9$ Hz, $^3J_{CP'1} = 3.1$ Hz, C_1^i), 128.82 (br d, $^3J_{CP} = 10.9$ Hz, C_0^m, C_1^m, C_2^m), 129.3 (d, $^1J_{CP2} = 49.6$ Hz, C_2^i), 131.31 (br s, C_2^p), 132.72 (d, $^2J_{CP} = 10.7$ Hz, C_0^o, C_1^o), 132.81 (s, C_0^p, C_1^p), 133.09 (d, $^2J_{CP2} = 9.7$ Hz, C_2^o), 134.33 (d, $^2J_{CP1} = 15.8$ Hz, C_1^3), 134.54 (d, $^2J_{CP2} = 10.56$ Hz, C_2^3), 154.61 (d, $^2J_{CP'1} = 8.1$ Hz, C_1^1), 155.65 (dd, $^2J_{CP'0} = 8.4$ Hz, $^4J_{CP1} = 2.1$ Hz, C_2^1). Calc. for $C_{126}H_{111}B_4N_3O_6P_{10}S_3$ (2212.4): C, 68.40; H, 5.05; N, 1.89. Anal. Found: C, 68.28; H, 4.97; N, 1.78%.

4.14. Synthesis of dendrimer *14-G$_2$*

Compound **14-G$_2$** was obtained from **15-G$_1$** (0.728 g, 0.329 mmol) and DABCO (0.162 g, 1.44 mmol) in toluene (10 ml), analogously to **14-G$_1$**. Compound **14-G$_2$** was purified by two-time reprecipitation with ether from toluene. An additional portion of **14-G$_2$** was obtained by chromatography on silicagel of the concentrated filtrate from washings (toluene–ether (9:1)). Compound **14-G$_2$** was obtained as a white powder (yield 0.48 g, 67.7%). M.p.: 102–106 °C.

*Compound **14-G$_2$**:* $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −6.4 (s, P_2), 13.2 (d, $^2J_{P1P'1} = 29.4$ Hz, P_1), 14.8 (d, $^2J_{P'0P0} = 28.9$ Hz, P_0) 49.9 (d, $^2J_{P'0P0} = 28.9$ Hz, P'_0), 50.8 (d, $^2J_{P'1P1} = 29.4$ Hz, P'_1). ^{1}H-NMR ($CDCl_3$): δ 6.95–7.65 (m, C_6H_4, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.77 (br dd, $^3J_{CP'} = 5.5$ Hz, $^3J_{CP} = 7.4$ Hz, C_1^2, C_2^2), 123.64 (dd, $^1J_{CP1} = 110.9$ Hz, $^3J_{CP'1} = 3.8$ Hz, C_1^4), 128.16 (dd, $^1J_{CP0} = 105.8$ Hz, $^3J_{CP'0} = 3.5$ Hz, C_0^i), 128.53 (d, $^3J_{CP2} = 7$ Hz, C_2^m), 128.73 (s, C_2^p), 128.76 (dd, $^1J_{CP1} = 105.9$ Hz, $^3J_{CP'1} = 3.6$ Hz, C_1^i), 128.84 (d, $^3J_{CP} = 13.4$ Hz, C_0^m, C_1^m), 132.05 (d, $^1J_{CP2} = 9.9$ Hz, C_2^4), 132.60 (s, C_0^p, C_1^p), 132.78 (br d, $^2J_{CP} = 11.8$ Hz, C_0^o, C_1^o), 133.61 (d, $^2J_{CP2} = 19.5$ Hz, C_2^o), 134.36 (d, $^2J_{CP1} = 12.1$ Hz, C_1^3), 134.92 (d, $^2J_{CP2} = 20.6$ Hz, C_2^3), 137.38 (d, $^1J_{CP2} = 10$Hz, C_2^i), 152.88 (d, $^2J_{CP'1} = 9.6$ Hz, C_2^1), 155.54 (dd, $^2J_{CP'0} = 10.2$ Hz, $^4J_{CP1} = 3.7$ Hz, C_1^1). Calc. for $C_{126}H_{99}N_3O_6P_{10}S_3$ (2157.1): C, 70.15; H, 4.62; N, 1.94. Anal. Found: C, 69.98; H, 4.75; N, 1.88%.

4.15. Synthesis of dendrimer *15-G$_2$*

Compound **15-G$_2$** was obtained from **14-G$_2$** (0.284 g, 0.126 mmol) and **12** (0.362 g, 0.527 mmol) in degassed CH_2Cl_2, analogously to **15-G$_1$**. Compound **15-G$_2$** was purified by two-time reprecipitation with ether from THF. Compound **15-G$_2$** was obtained as a white powder (yield 0.42 g, 69%). M.p. 154–160 °C.

Compound ***15-G$_2$***: $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.0 (d, $^2J_{P2P'2} = 29.6$ Hz, P_2), 14.4 (d, $^2J_{P1P'1} = 29.0$ Hz, P_1), 14.8 (d, $^2J_{P0P'0} = 29.1$ Hz, P_0), 19.8 (br s, P_3), 49.8 (d, $^2J_{P'1P1} = 29$ Hz, P'_1), 49.9 (d,$^2J_{P'0P0} = 29.1$ Hz, P'_0) 50.1 (d, $^2J_{P'2P2} = 29.6$ Hz, P'_2). ^{1}H-NMR ($CDCl_3$): δ 1.2 (br s, 24H, BH_3), 7.16–7.61 (m, 211H, C_6H_5, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.56–121.97 (m, C_1^2, C_2^2, C_3^2), 123.15 (br d, $^1J_{CP1} = 110.1$ Hz, C_1^4), 123.28 (dd, $^1J_{CP2} = 110.3$ Hz, $^3J_{CP'2} = 3.5$ Hz, C_2^4), 124.05 (d, $^1J_{CP3} = 60.3$ Hz, C_3^4), 128.02 (dd, $^1J_{CP0} = 108$ Hz, $^3J_{CP'0} = 3.5$ Hz, C_0^i), 128.21 (dd, $^1J_{CP1} = 108.2$ Hz, $^3J_{CP'1} = 3.5$ Hz, C_1^i), 128.36 (dd, $^1J_{CP2} = 108$ Hz, $^3J_{CP'2} = 3.3$ Hz, C_2^i), 128.74 (d, $^3J_{CP} = 13.5$ Hz, C_0^m, C_1^m, C_2^m), 128.80 (d, $^3J_{CP3} = 10.3$ Hz, C_3^m), 129.26 (d, $^1J_{CP3} = 47.2$ Hz, C_3^i), 131.28 (s, C_3^p), 132.67 (d, $^2J_{CP} = 11.7$ Hz, C_0^o, C_1^o, C_2^o), 132.90 (s, C_0^p, C_1^p, C_2^p), 133.06 (d, $^2J_{CP3} = 9.9$ Hz, C_3^o), 134.30 (d, $^2J_{CP} = 14$ Hz, C_1^3, C_2^3), 134.51 (d, $^2J_{CP3} = 11.4$ Hz, C_3^3), 154.53 (d, $^2J_{CP'2} = 8.3$ Hz, C_3^1), 155.57 (dd, $^2J_{CP} = 9.7$ Hz, $^4J_{CP} = 3.2$ Hz, C_1^1, C_2^1). Calc. for $C_{270}H_{235}B_8N_7O_{14}P_{22}S_7$ (4794.2): C, 67.64; H, 4.94; N, 2.04. Anal. Found: C, 67.55; H, 4.89; N, 1.98%.

4.16. Synthesis of dendrimer *14-G$_3$*

Compound **14-G$_3$** was obtained from **15-G$_2$** (0.42 g, 0.0876 mmol) and DABCO (0.122 g, 1.09 mmol) in toluene for 3 days, analogously to **14-G$_1$**. Compound **14-G$_3$** was purified by two-time reprecipitation with ether from toluene and dried in vacuo. Compound **14-G$_3$** was obtained as a white powder (yield 0.4 g, 97%). M.p.: 118–120 °C.

Compound ***14-G$_3$***: $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −6.3 (s, P_3), 13.0 (d, $^2J_{P2P'2} = 29.5$ Hz, P_2), 14.3 (d, $^2J_{P1P'1} = 29.2$ Hz, P_1), 14.7 (d, $^2J_{P0P'0} = 28.7$ Hz, P_0), 49.8 (d, $^2J_{P'1P1} = 29.2$ Hz, P'_1), 49.9 (d, $^2J_{P'0P0} = 28.7$ Hz, P'_0), 50.9 (d, $^2J_{P'2P2} = 29.5$ Hz, P'_2). ^{1}H-NMR ($CDCl_3$): δ 7.14–7.59 (m, C_6H_5, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.25–121.8 (m, C_1^2, C_2^2, C_3^2), 123.41 (br d, $^1J_{CP} = 111.7$ Hz, C_1^4, C_2^4), 127.86 (dd, $^1J_{CP0} = 106.7$ Hz, $^3J_{CP'0} = 3.5$ Hz, C_0^i), 128.10 (dd, $^1J_{CP1} = 105.7$ Hz, $^3J_{CP'1} = 3.5$ Hz, C_1^i), 128.34 (d, $^3J_{CP3} = 6.3$ Hz, C_3^m), 128.42 (d, $^3J_{CP} = 9.8$ Hz, C_1^m, C_2^m), 128.52 (dd, $^1J_{CP2} = 109.6$ Hz, $^3J_{CP'2} = 3.5$ Hz, C_2^i), 128.53 (s, C_3^p), 128.65 (d, $^3J_{CP0} = 12.4$ Hz, C_0^m), 131.84 (d, $^1J_{CP3} = 9.6$ Hz, C_3^4), 132.57 (br d, $^2J_{CP} = 12$ Hz, C_0^o, C_1^o, C_2^o, C_0^p, C_1^p, C_2^p), 133.41 (d, $^2J_{CP3} = 19.6$ Hz, C_3^o), 134.18 (d, $^2J_{CP} = 12.5$ Hz, C_1^3, C_2^3), 134.72 (d, $^2J_{CP3} = 20.7$ Hz, C_3^3), 137.17 (d, $^1J_{CP3} = 11.1$ Hz, C_3^i), 152.67 (d, $^2J_{CP'2} = 9$ Hz, C_3^1), 155.28 (d, $^2J_{CP'1} = 7.2$ Hz, $^4J_{CP1} = 3$ Hz, C_2^1), 155.45 (dd, $^2J_{CP'0} = 7.2$ Hz, $^4J_{CP0} = 3$ Hz, C_1^1). Calc. for $C_{270}H_{211}N_7O_{14}P_{22}S_7$ (4683.5): C, 69.24; H, 4.54; N, 2.09. Anal. Found: C, 69.15; H, 4.48; N, 2.00%.

4.17. Synthesis of dendrimer *16-G$_3$*

A solution of **14-G$_3$** (0.230 g, 0.049 mmol) in CH_2Cl_2 (6 ml) was added dropwise very slowly to a stirred solution of the azide **7** (0.472 g, 0.436 mmol) in CH_2Cl_2 (6 ml) at r.t. The reaction mixture was stirred overnight at r.t., filtrated and the solvent was removed in vacuo. The residue was washed twice by reprecipitation with ether from THF and dried overnight in vacuo to give **16-G$_3$** as a white powder (yield 0.61 g, 95%). M.p.: 142–146 °C (dec.).

Compound ***16-G$_3$***: $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.1 (d, $^2J_{P2P'2} = 29.0$ Hz, P_2), 14.2 (d, $^2J_{P1P'1} = 28.6$ Hz, P_1), 14.8 (d, $^2J_{P0P'0} = 27.2$ Hz, P_0), 15.2 (d, $^2J_{P3P'3} = 28.1$ Hz, P_3), 21.0 (br s, P_4), 49.4 (d, $^2J_{P'2P2} = 29.0$ Hz, P'_2), 49.7 (d, $^2J_{P'1P1} = 28.6$ Hz, P'_1), 49.9 (d, $^2J_{P'0P0} = 27.2$ Hz, P'_0), 53.1 (d, $^2J_{P'3P3} = 28.1$ Hz, P'_3). ^{1}H-NMR ($CDCl_3$): δ 1.2 (br s, 96H, BH_3), 7.00–7.60 (m, 579H, C_6H_5, C_6H_4, C_6H_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.57–121.88 (m, C_1^2, C_2^2, C_3^2), 123.0 (br d, $^1J_{CP3} = 108$ Hz, C_3^4), 123.27 (br d, $^1J_{CP} = 110.1$ Hz, C_1^4, C_2^4), 128.06 (d, $^1J_{CP4} = 57.7$ Hz, C_4^i), 128.10 (dd, $^1J_{CP3} = 108$ Hz, $^3J_{CP'3} = 3$ Hz, C_3^i), 128.3 (br m, C_4^2), 128.40 (dd, $^1J_{CP} = 110$ Hz, $^3J_{CP'} = 3$ Hz, C_1^i, C_2^i), 128.70 (d, $^3J_{CP} = 11.4$ Hz, C_0^m, C_1^m, C_2^m, C_3^m), 128.87 (d, $^3J_{CP4} = 9.9$ Hz, C_4^m), 131.48 (s, C_4^p), 131.95 (br d, $^1J_{CP4} = 50$ Hz, C_4^3), 132.57 (br d, $^2J_{CP} = 9.9$ Hz, C_0^o, C_1^o, C_2^o, C_3^o, C_0^p, C_1^p, C_2^p, C_3^p), 133.00 (d, $^2J_{CP4} = 9.7$ Hz, C_4^o), 134.06 (d, $^2J_{CP3} = 12.1$ Hz, C_3^3), 134.25 (t, $^2J_{CP4} = 12.0$ Hz, C_4^4), 134.34 (d, $^2J_{CP} = 11.4$ Hz, C_1^3, C_2^3), 152.09 (dt, $^3J_{CP4} = 11.9$ Hz, $^3J_{CP'3} = 10.1$ Hz, C_4^1), 155.52–155.65 (m, C_1^1, C_2^1, C_3^1), (C_0^i not detected). Calc. for $C_{750}H_{675}B_{32}N_{15}O_{30}P_{62}S_{15}$ (13 126): C, 68.62; H, 5.18; N, 1.60. Anal. Found: C, 68.54; H, 5.12; N, 1.52%.

4.18. Synthesis of dendrimer *17-G$_4$*

DABCO (0.147 g, 1.31 mmol) was added to a solution of **16-G$_3$** (0.359 g, 0.027 mmol) in a toluene–CH_2Cl_2 mixture (5:1) (7 ml). The solution was stirred overnight at r.t. and evaporated. Degassed toluene (4 ml) was added to the residue and the precipitate was removed by filtration. Compound **17-G$_4$** was isolated by reprecipitation with ether from the filtrate and additionally washed by reprecipitation with ether from toluene. Compound **17-G$_4$** was obtained as a white powder (yield 0.28 g, 80%). M.p. 125–128 °C.

Compound ***17-G$_4$***: $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −4.9 (s, P_4), 13.4 (d, $^2J_{P3P'3} = 29.7$ Hz, P_3), 14.2 (d, $^2J_{P2P'2} = 29.1$ Hz, P_2), 14.3 (d, $^2J_{P1P'1} = 28.9$ Hz, P_1), 14.8 (d, $^2J_{P0P'0} = 28.8$ Hz, P_0), 49.5 (d, $^2J_{P'2P2} = 29.1$ Hz, P'_2), 49.7 (d, $^2J_{P'1P1} = 28.9$ Hz, P'_1), 49.9 (d, $^2J_{P'0P0} = 28.8$ Hz, P'_0), 52.6 (d, $^2J_{P'3P3} = 29.7$ Hz, P'_3). ^{1}H-NMR ($CDCl_3$): δ 6.97–7.54 (m, C_6H_5, C_6H_4, C_6H_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 121.3–122.15 (m, C_1^2, C_2^2, C_3^2), 123.30 (br d, $^1J_{CP} = 113$ Hz, C_1^4, C_2^4), 123.48 (br d, $^1J_{CP3} = 114.7$ Hz, C_3^4), 126.95 (br d, $^2J_{CP4} = 21$ Hz, C_4^2), 128.40 (br d, $^1J_{CP} = 110$ Hz, C_1^i, C_2^i), 128.43 (d, $^3J_{CP4} = 6.1$ Hz, C_4^m), 128.63 (dd, $^1J_{CP3} = 106.1$ Hz, $^3J_{CP'3} = 3.6$ Hz, C_3^i),

128.79 (br d, $^3J_{CP} = 12.3$ Hz, C_0^m, C_1^m, C_2^m, C_3^m, C_4^p), 132.64 (br d, $^2J_{CP} = 11$ Hz, C_0^o, C_1^o, C_2^o, C_3^o, C_0^p, C_1^p, C_2^p, C_3^p), 133.61 (d, $^2J_{CP4} = 19.7$ Hz, C_4^o), 134.10 (t, $^2J_{CP4} = 20$ Hz, C_4^4), 134.22 (d, $^2J_{CP3} = 10.4$ Hz, C_3^3), 134.40 (br d, $^2J_{CP} = 12.5$ Hz, C_1^3, C_2^3), 136.67 (d, $^1J_{CP4} = 11$ Hz, C_4^i), 138.79 (dd, $^1J_{CP4} = 9.3$ Hz, $^3J_{CP4} = 5.7$ Hz, C_4^3), 152.09 (dt, $^2J_{CP'3} = 8.6$ Hz, $^3J_{CP4} = 6.3$ Hz, C_4^1), 155.2–155.9 (m, C_1^1, C_2^1, C_3^1), (C_0^i not detected). Calc. for $C_{750}H_{579}N_{15}O_{30}P_{62}S_{15}$ (12 683): C, 71.02; H, 4.60; N, 1.65. Anal. Found: C, 70.89; H, 4.54; N, 1.57%.

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