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Review

Accelerated methods of synthesis of phosphorus-containing dendrimers

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Abstract

In order to shorten the long and tedious synthesis of dendrimers, several improvements have been proposed. This paper is a review of the improved methods recently published concerning the synthesis of phosphorus-containing dendrimers. It describes first the synthesis of hyperbranched polymers and their comparison with real dendrimers obtained from the same monomer. Then, the influence of the modification of the core of dendrimers is shown. In a third part, the use of dendrons is illustrated by several examples; they allow for instance to built a generation 8 directly from a generation 3 dendrimer. The last part describes the use of branched monomers of types AB_2 and CD_2, in which A reacts only with D and B reacts only with C. These reactions do not need any protecting groups, and the only by-products are H_2O and N_2. Using these monomers, the 4th generation is obtained in only four steps, instead of 8 for classical methods. This method has been improved by using more branched monomers AB_5 and CD_5, built from the cyclotriphosphazene. In this case, a dendrimer having 750 end groups is obtained in only three steps. The A (NH_2), B (PPh_2), C (N_3) and D (CHO) functions are identical in all cases, and they allow a real "Lego" chemistry, as shown by the synthesis of CA_2 and DB_2 monomers, also used for the accelerated synthesis of dendrimers.

Keywords: Dendrimers; Phosphorus; Hyperbranched polymers; Branched monomers; Cyclotriphosphazene

1. Introduction

Dendrimers and dendritic macromolecules [1] met an enormous success with more than 7000 references indexed, 97% of them having been published within the last ten years. This success is certainly related to their pleasant aesthetic, but above all, it is due to their very unique properties in various fields such as chemistry, physics or biology. However, these macromolecules suffer from a drawback that is their lengthy and tedious step-by-step synthesis. In order to remedy this inconvenience, several ways have been already proposed to accelerate the synthesis of dendrimers. The first one consists in grafting dendrons to the surface of small dendrimers ("hypercores"). In this method, often called "double-stage" [2], a dramatic increase of the number of end groups is obtained, but the total number of reactions used to synthesize the hypercore and the dendron is the same as for the classical step-by-step synthesis of the final dendrimer. A second method, called "double exponential growth" [3] consists in growing a dendron bidirectionally, at the periphery and the focal point which would be of interest for the rapid synthesis of high generation dendrimers. A third method uses "hypermonomers" [4] for instance of type AB_4 or AB_8 instead of the classical AB_2 monomers; this strategy rapidly increases the number of end groups.

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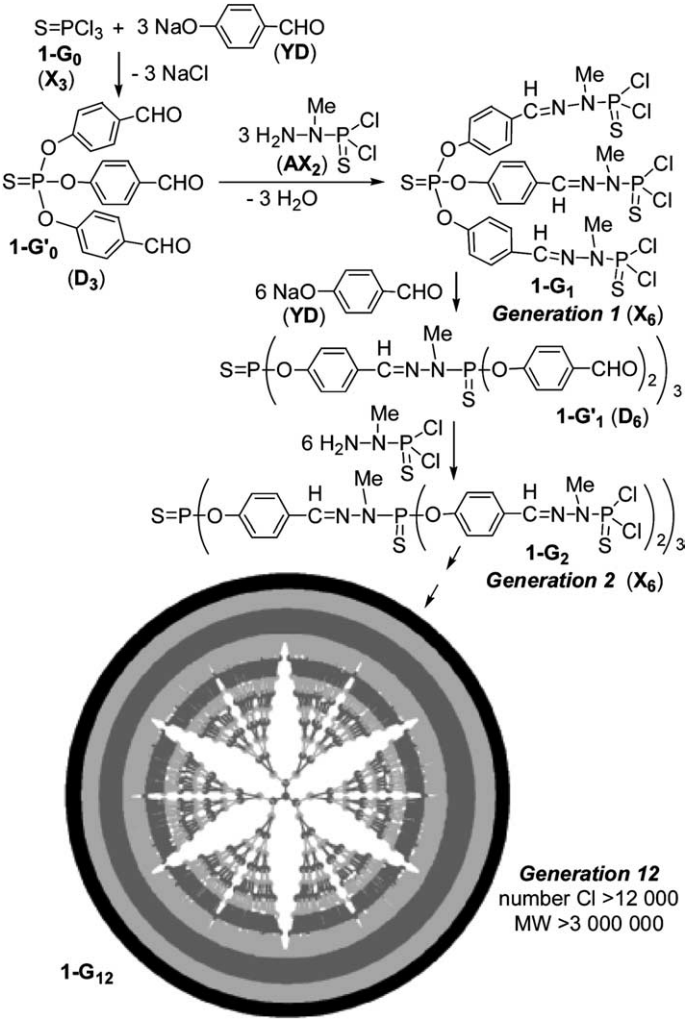
A fourth method called "orthogonal coupling strategy" [5] uses two types of AB_2 units containing two pairs of complementary coupling functionalities; it implies a set of completely independent class of protecting groups and generates by-products, but each monomer gives a new generation. Finally, in contrast to the lengthy process used to obtain dendrimers, the synthesis of hyperbranched polymers [6] is carried out one-pot and is much less time-consuming. However, the properties of dendrimers compared to that of hyperbranched polymers may be largely different.

This was the state of the art when we got interested in finding improved methods of synthesis of dendrimers, and more precisely of dendrimers having one phosphorus atom at each branching point [7]. Our classical method of synthesis is powerful, since it allowed us to obtain the highest generation known for any type of dendrimer (**1-G$_{12}$**, generation 12). It uses a branched (**AX$_2$**) and a linear (**YD**) monomer, for condensation reactions between the **A** (NH_2) and **D** (CHO) functions, and nucleophilic substitutions between the **X** (Cl) and **Y** (NaO) functions; both reactions are quantitative (Scheme 1) [8]. This method necessitates two steps to grow one generation and to multiply by two the number of end groups; thus, obtaining the 12th generation is really a lengthy and multistep process (24 steps). In this paper, we will describe diverse strategies to accelerate the synthesis of phosphorus-containing dendrimers. All these methods, despite their diversity, use two very simple and quantitative reactions: condensation between NH_2 (**A**) and CHO (**D**) functions, and Staudinger reactions between PPh_2 (**B**) and N_3 (**C**) functions. The **A**, **B**, **C** and **D** functions have been chosen because they give a set of totally independent reactions, since neither **A** nor **D** are able to react with **B** or **C**.

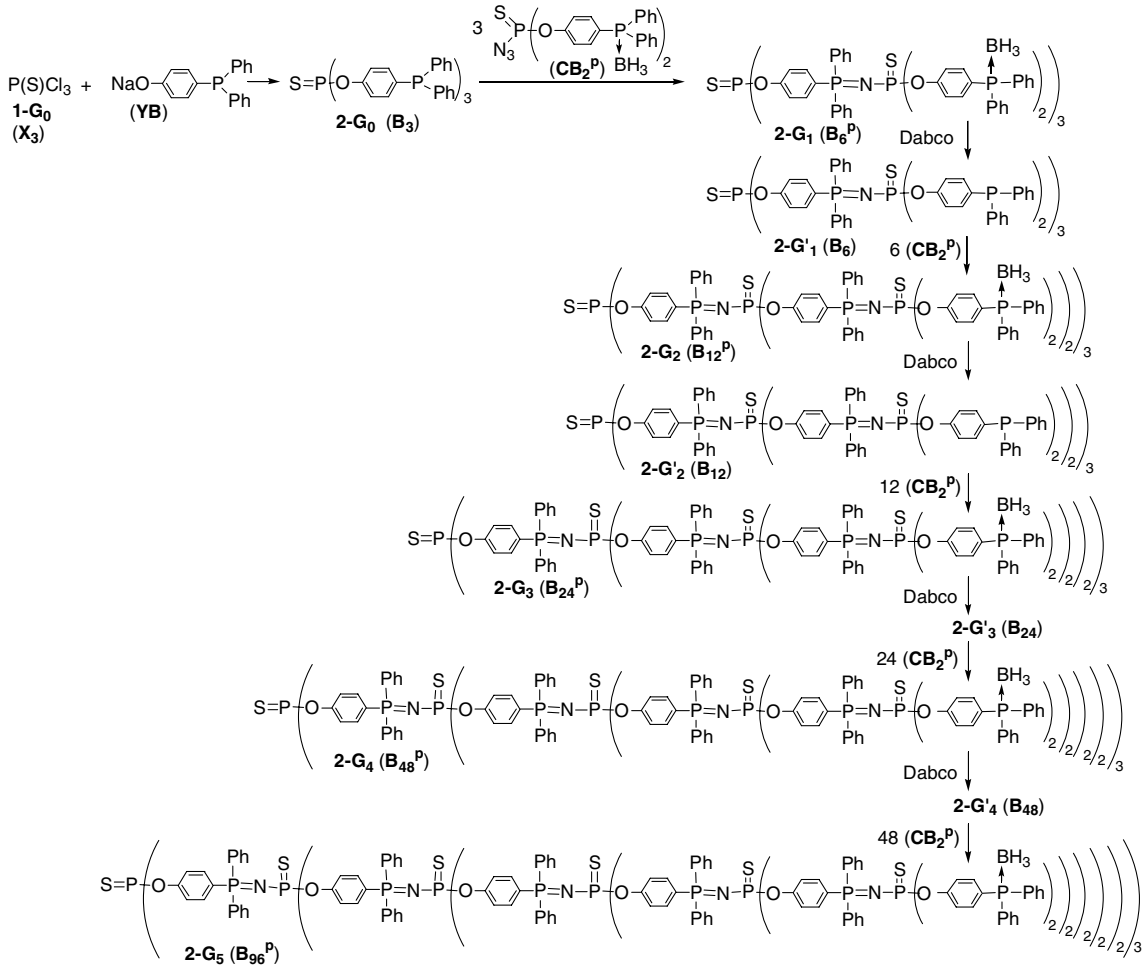
2. Results and discussion

2.1. Polymerization reactions

In view of the very short time necessitated by the one-pot synthesis of hyperbranched polymers, it seemed

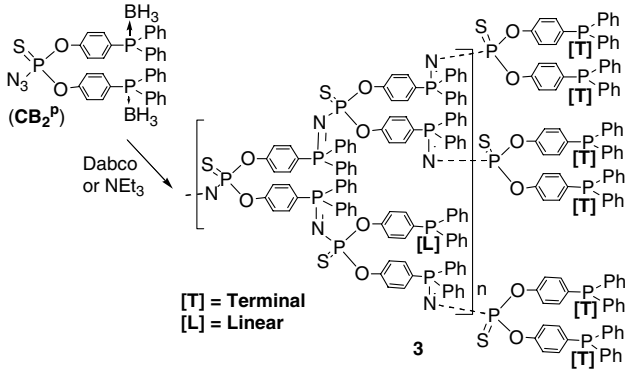


Scheme 1.



Scheme 2.

tempting at first glance to replace dendrimers by them. In order to determine to which extent this replacement could be acceptable, we designed a branched protected monomer ($\mathbf{CB_2^p}$) (Scheme 2), usable both for the synthesis of a new family of phosphorus-containing dendrimers and of hyperbranched polymers [9]. The synthesis of the dendrimer $\mathbf{2\text{-}G_n}$ necessitates two steps for each generation, a Staudinger reaction between the **C** (N_3) and **B** (PPh_2) functions, followed by the deprotection of the phosphino borane $\mathbf{B^p}$ by DABCO. In this case also both reactions are quantitative, and the experiment was carried out up to the 5th generation, obtained after 10 synthetic steps. In contrast, the hyperbranched polymer **3** is obtained in one step, by the deprotection of ($\mathbf{CB_2^p}$), which induces a "polyStaudinger" reaction (Scheme 3). Depending on the temperature, the reaction time, the concentration, the solvent, and the amine used for the deprotection, various hyperbranched polymers were obtained, in which the molar masses and their distribution varied. However, the degree of branching is essentially the same for all polymers of this series, irrespective of the conditions used. It was found particularly high (0.83–0.85), higher than most of the values reported in the literature for hyperbranched polymers obtained by polycondensations (0.5–0.6). Do these unusually high values mean that polymers **3** could replace dendrimers $\mathbf{2\text{-}G_n}$, in which the degree of branching is one? To answer this question, the physical properties of both types of compounds were studied. The first difference concerns the polydispersity, which was found very low for



Scheme 3.

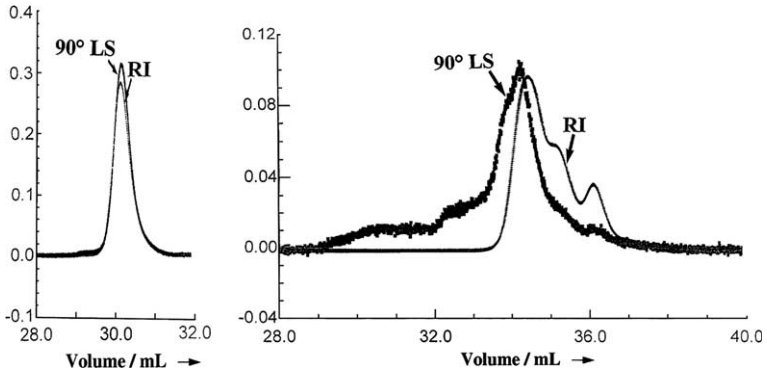


Fig. 1. Traces obtained by size exclusion chromatography (SEC) equipped with a multi angle laser light scattering detector (MALLS), and a refractive index detector: left, dendrimer **2-G$_3$**; right, polymer **3**.

dendrimers (the highest value is 1.029 for **2-G$_5$**), and very high for the hyperbranched polymers **3** (from 1.5 to 8, depending on the conditions used to synthesize the sample) (see Fig. 1 for the comparison of the MALLS/SEC traces). The second difference concerns the intrinsic viscosity. The [η] values for the hyperbranched polymers **3** increase slightly when the molar mass increases, whereas the [η] values for dendrimers **2-G$_n$** give a bell-shaped curve, with a maximum between 3rd and 4th generation. These results are in accordance with results found previously for other types of hyperbranched polymers and dendrimers [10]. It can be inferred from these results that dendrimers and hyperbranched polymers constituted of the same repeating units have marked differences in their respective behaviour; the replacement of the former by the latter does not appear to be an acceptable alternative, excepted in some particular cases. Thus the challenge of improving the methods of syntheses of dendrimers remains valuable.

2.2. Modification of the core

Obviously, for a given method of synthesis, the number of end groups for a given generation depends only on the number of functional groups of the core. In the methods shown in Schemes 1 and 2, the core is

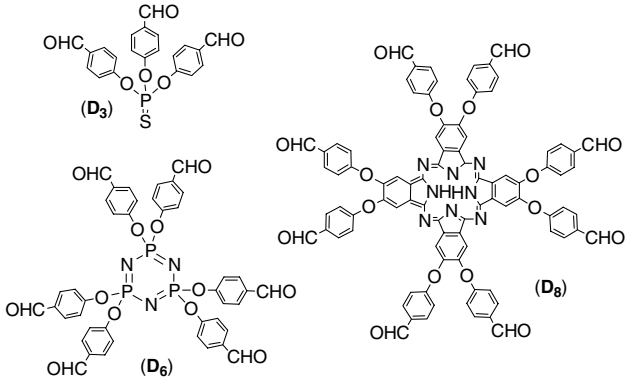
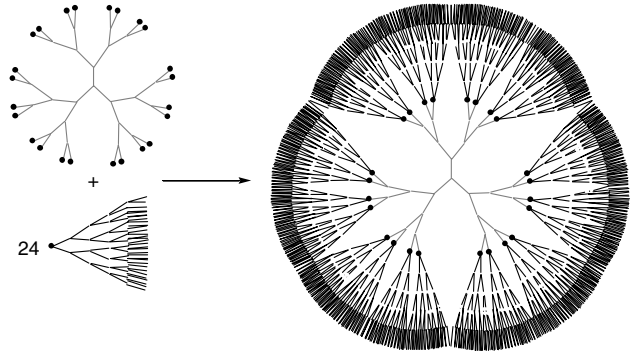
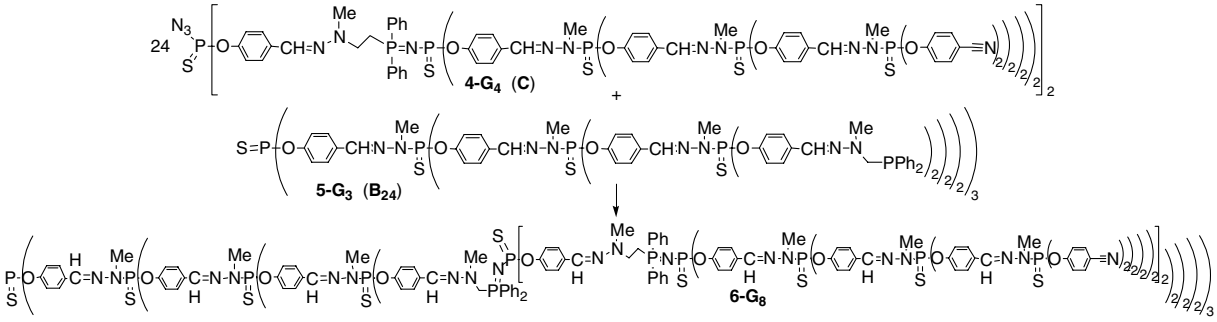


Chart 1.



Scheme 4.

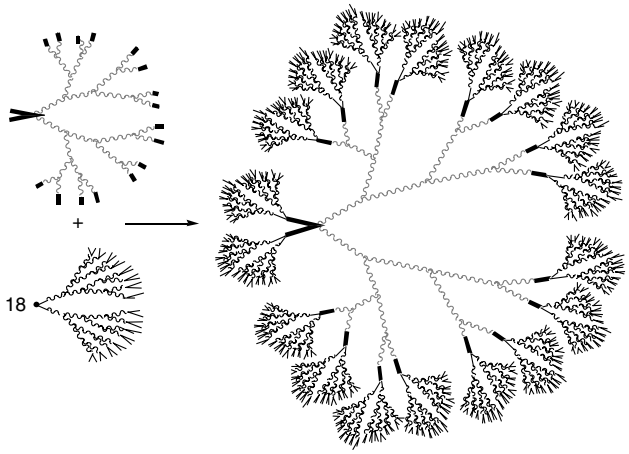


Scheme 5.

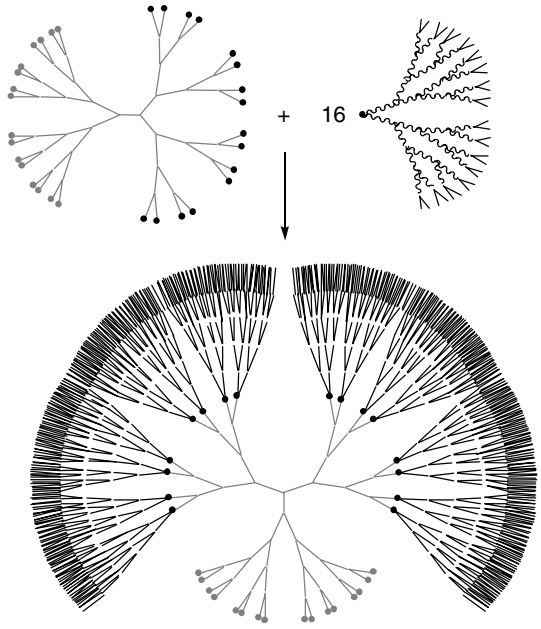
trifunctional and built from $P(S)Cl_3$. However, the same type of reactions can be carried out from hexafunctional cores built from $N_3P_3Cl_6$ derivatives, in particular from the hexaaldehyde **D_6** (Chart 1) [11]. Even more branched cores can be used such as $N_4P_4Cl_8$ [12], or the octafunctional phthalocyanine **D_8** [13]. However, this way of increasing the number of end groups cannot be considered as a "new method" for the improved synthesis of dendrimers, even if it is particularly interesting for low generations.

2.3. Use of dendrons

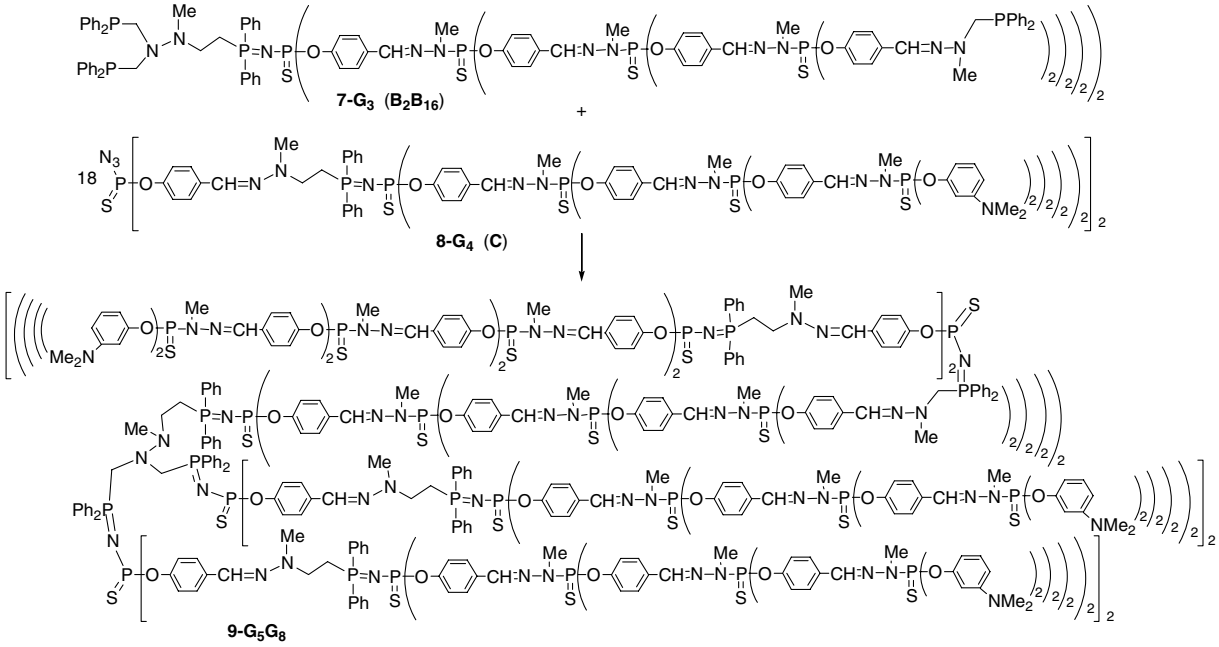
Dendrons are a particular type of dendritic molecules, which possess different functional groups at the level of the core and at the periphery. Despite the fact that dendrons are synthesized step by step, they allow a spectacular increase of the number of end groups and of the number of the generation when they are linked in the last step of the synthesis to other dendritic molecules. This can be illustrated when dendrons are grafted by their core to the surface of small dendrimers (Scheme 4). Concretely, we have obtained a generation 8 dendrimer (**6-G_8**) in one step from the generation 3 dendrimer (**5-G_3**, 24 phosphine end groups, **B_{24}**) by Staudinger reactions with a dendron (**4-G_4**) having an azide (**C**) at the core (Scheme 5) [14]. The generation 4



Scheme 6.



Scheme 8.



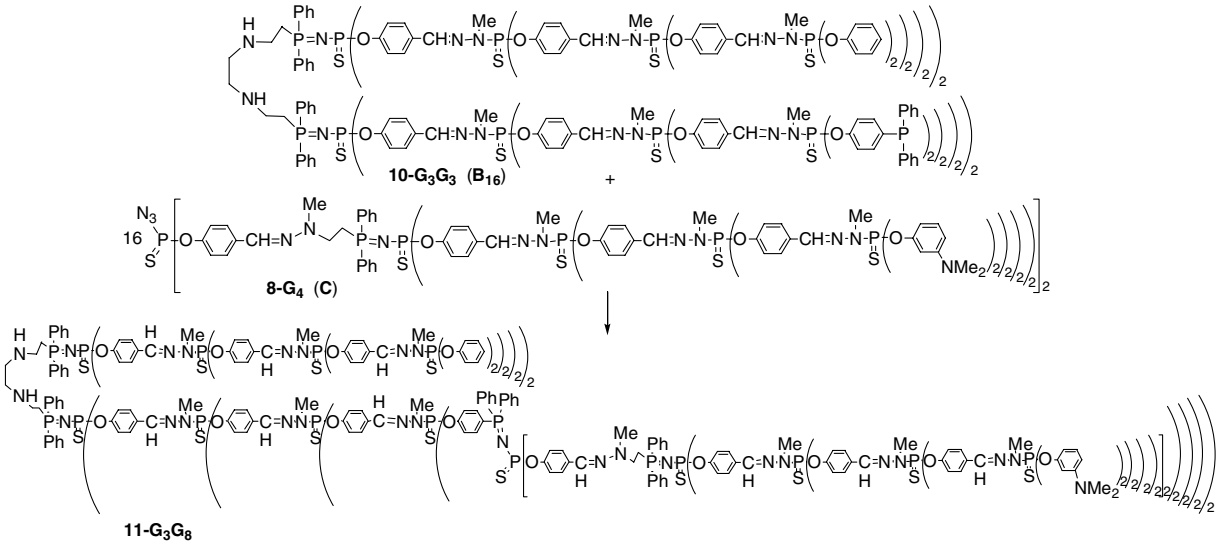
Scheme 7.

dendrons are generally the largest dendrons usable for practical purpose. Indeed, first it is important to be able to detect the completion of reactions by NMR despite the low number of groups that must react (24 here) compared to the high number of end groups (768 here); second, in some cases, steric hindrance may preclude the completion of the reactions.

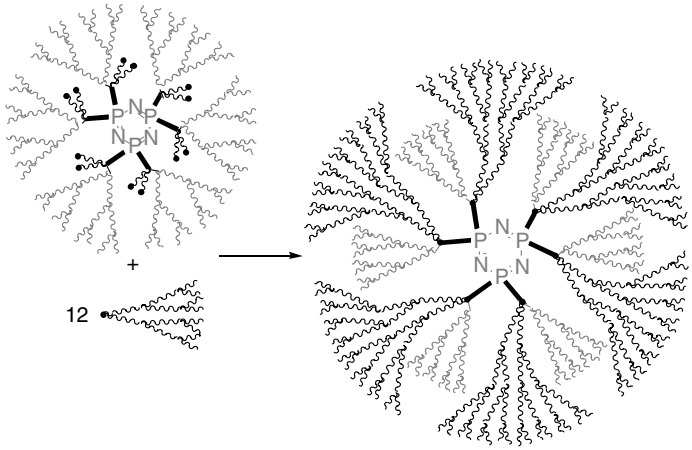
The same type of reaction can be applied using a dendron as core. If this dendron possesses the same type of functions at the core and at the periphery, the reaction will lead to an unsymmetrical dendrimer, having identical functions on the whole surface, but whose internal structure is different from that of classical dendrimers (Scheme 6). This concept has been developed using the dendron **7-G$_3$**, which possesses two phosphino groups at the core and 16 on the surface (**B$_2$B$_{16}$**). The reaction with the dendron **8-G$_4$** having an azide (**C**) at the core affords the unsymmetrical dendritic molecule **9-G$_5$G$_8$** (Scheme 7) [14]. This notation highlights the unsymmetrical nature of this compound, in which the focal point is decentered.

If the initial dendrimer possesses two types of end groups, each of them being located in particular areas of the surface, it is possible to react only one type of end groups with a dendron, leading to a doubly unsymmetrical dendrimer. The asymmetry comes from the number of end groups on each side of the macromolecule, as seen in the previous example, but also from the nature of these end groups (Scheme 8). Starting from the unsymmetrical dendrimer **10-G$_3$G$_3$**, which possesses 16 phosphino end groups on one side, the reaction with the monoazido dendron **8-G$_4$** affords the doubly unsymmetrical dendritic macromolecule **11-G$_3$G$_8$** (Scheme 9) [15]. This dendrimer possesses 16 O–Ph end groups on one side, and 512 O–C$_6$H$_4$NMe$_2$ end groups on the other side.

Finally, the same type of procedure can be applied to functions located in the interior of dendrimers (Scheme 10). This reaction has been carried out with the particu-

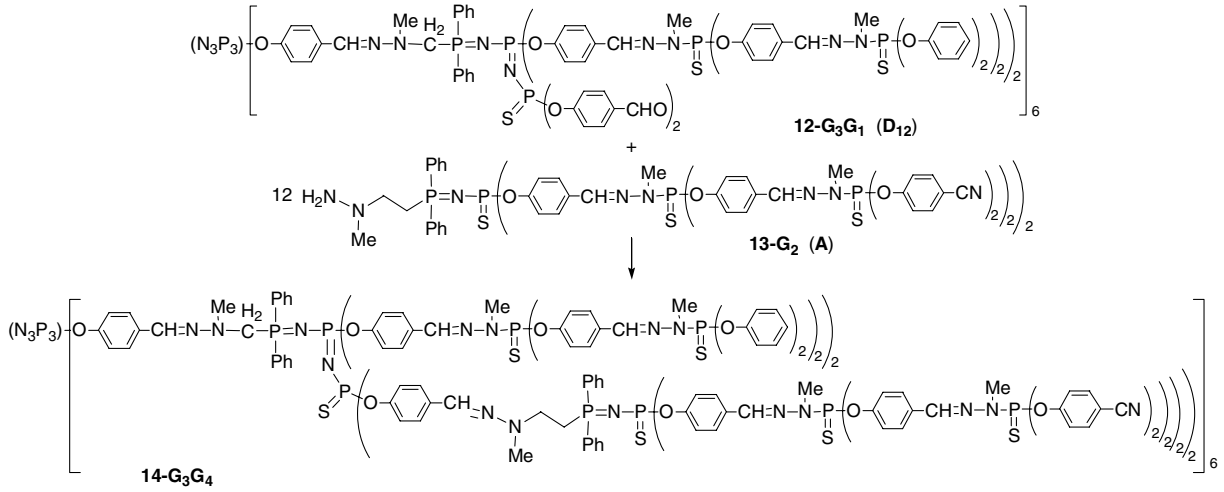


Scheme 9.

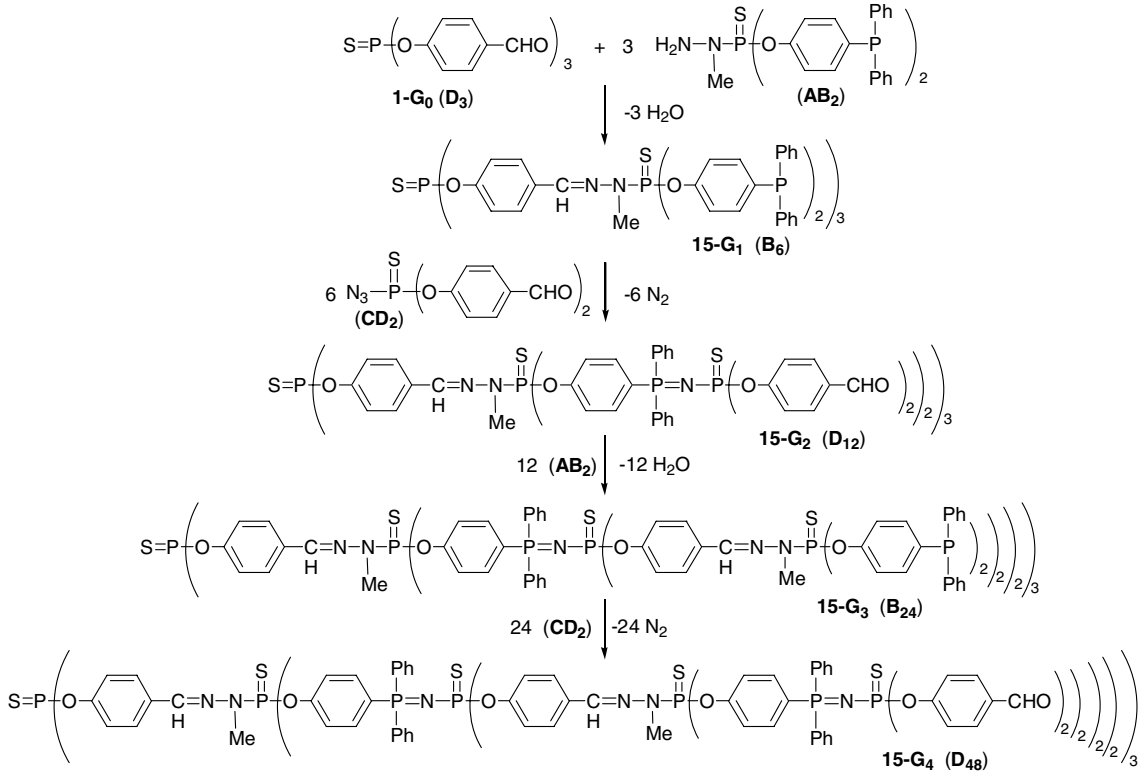


Scheme 10.

larly original dendrimer **12-G_3G_1**, which possesses 12 aldehyde groups in the interior of its structure [16], for condensation reactions with the dendron **13-G_2**, having a NH_2 function at the core (Scheme 11). The reaction is relatively slow due to the steric hindrance when the dendron penetrates inside the dendrimer, but it is finished after 10 days at room temperature to afford the multi dendritic compound **14-G_3G_4** [15]. This compound possesses two types of end groups, in several localized areas distributed on the whole surface. The role of steric hindrance must be emphasized in this case: the reaction with the 3rd generation dendron **13-G_3** never went to completion even after several weeks, whereas the expected type of multidendritic compound (G_3G_5) has been obtained by the step by step growing of new dendritic branches inside the dendrimer **12-G_3G_1**, starting from the internal aldehydes [16] and applying the types of reactions already shown in Scheme 1.



Scheme 11.



Scheme 12.

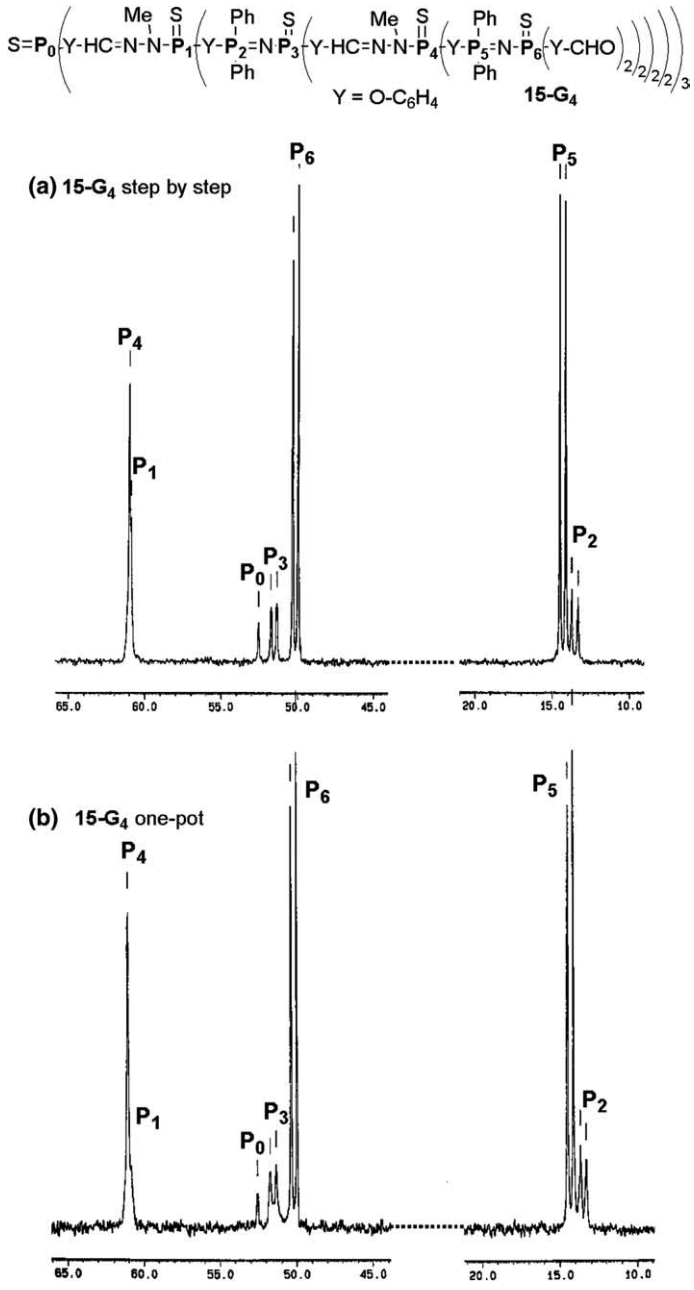
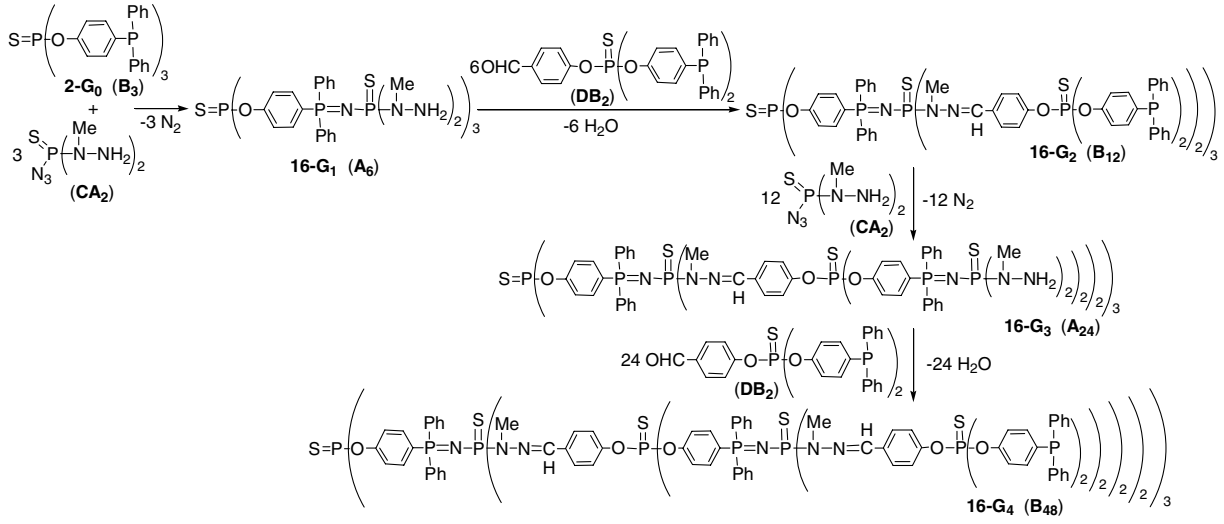


Fig. 2. ^{31}P NMR spectra of **15-G$_4$**: (a) synthesized step by step; (b) synthesized one pot.

2.4. Use of orthogonal systems: sets of complementary and independent functionalities

Before our work, the orthogonal coupling strategy using two types of branched units for the synthesis of dendrimers was only applied to protected monomers, which of course necessitated independent and selective deprotections, and generated by-products. The major improvement of our contribution to this strategy consisted in using two pairs of unprotected complementary functions, able to react quantitatively and spontaneously without any activating agents. As shown in parts 2 and 3 of this paper, we have in hand the desired functions that are on one side the **A** (NH_2) and **D** (CHO) functions, and on the other side the **B** (PPh_2) and **C** (N_3) functions, which react in condensation and Staudinger reactions, respectively. Indeed, both reactions are quantitative, there is no need for any activating agent, and the only by-products (H_2O and N_2) are totally benign. In fact, the goal was to design the suitable branched monomer. Among the combinations that could be imagined, specifically we designed first **AB$_2$** and **CD$_2$** monomers, then in another attempt, we designed **CA$_2$** and **DB$_2$** monomers.

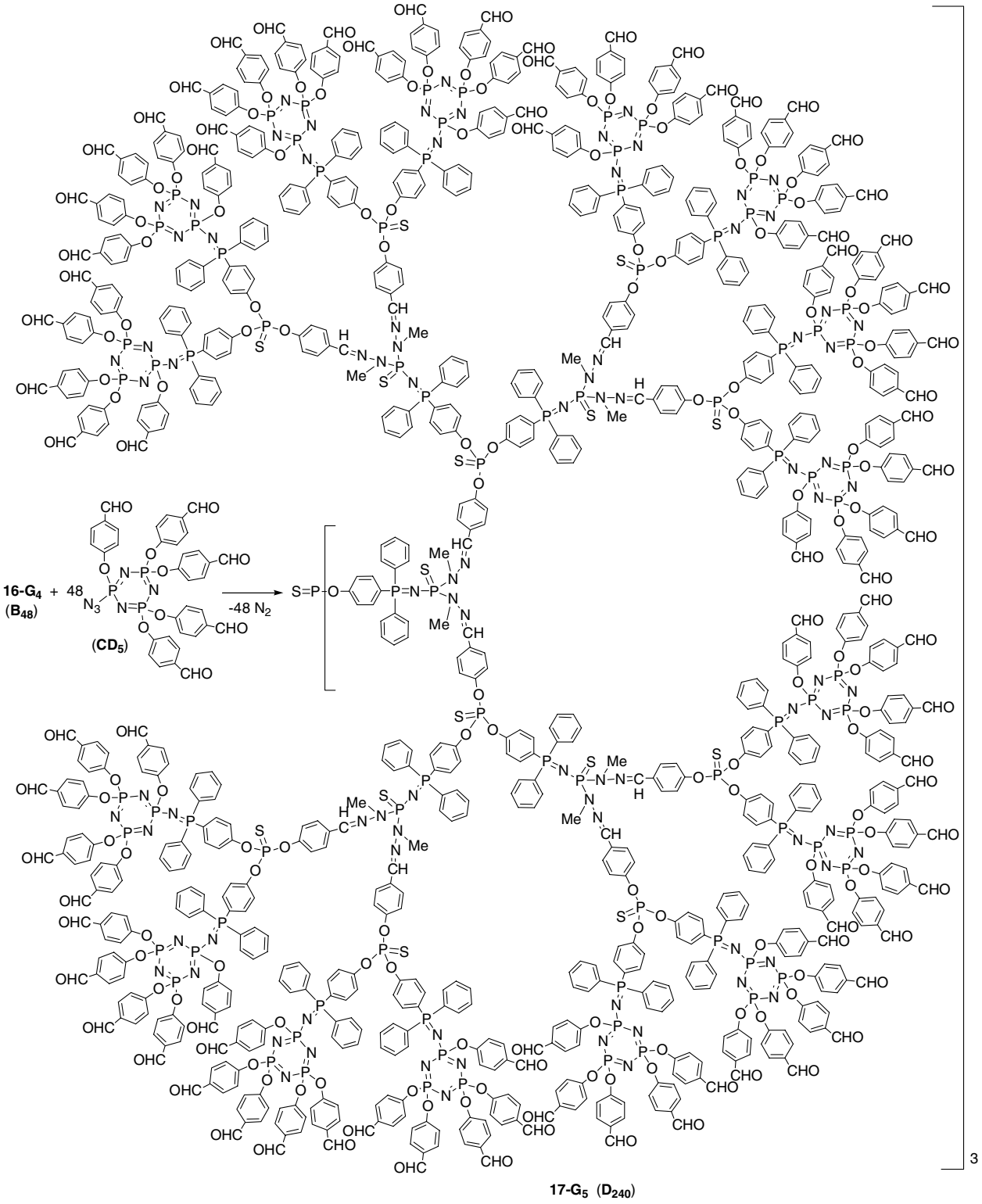


Scheme 13.

The use of the $\mathbf{AB_2/CD_2}$ set is depicted in Scheme 12 [17]. Starting from a $\mathbf{D_3}$ core, the reaction with the $\mathbf{AB_2}$ monomer affords directly the 1st generation ($\mathbf{B_6}$); in a second step, the reaction with the $\mathbf{CD_2}$ monomer affords directly the 2nd generation ($\mathbf{D_{12}}$). Using again the $\mathbf{AB_2}$ then the $\mathbf{CD_2}$ monomers, the 4th generation **15-G$_4$** ($\mathbf{D_{48}}$) is finally obtained in only four steps starting from the core. These compounds are layered dendrimers made of O–C_6H_4–Z–P(S) linkages, in which Z is alternately CH=NNMe or Ph_2P=N, and the end groups are alternately either phosphines or aldehydes, depending on the generation considered. This method is so powerful that we tried to obtain directly in a one-pot (but multi-step) experiment the 4th generation. Starting from the core, a strictly stoichiometric amount of reagent is added, waiting between each addition the time necessary for the completion of the reactions at each step. The spectroscopic characteristics of the 4th generation obtained by the one-pot process are very close to those obtained for **15-G$_4$** in the step by step process (with purification at each generation) as shown by the ^{31}P NMR spectra (Fig. 2).

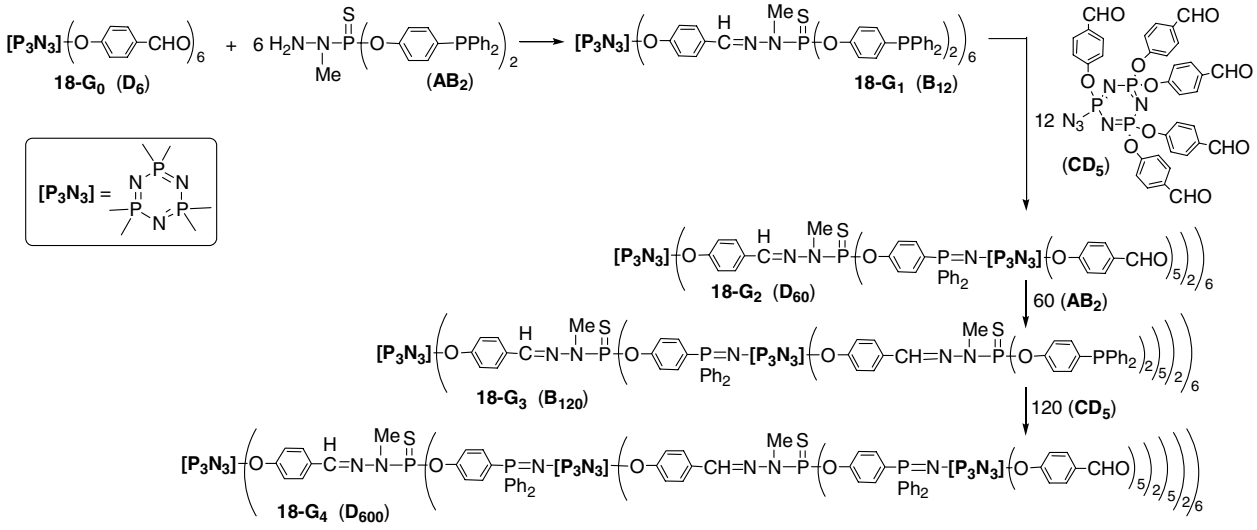
In fact, a real ''Lego'' chemistry can be developed using the same concepts. For this purpose, we have designed $\mathbf{CA_2}$ and $\mathbf{DB_2}$ monomers. The Staudinger reaction of the $\mathbf{CA_2}$ monomer with a $\mathbf{B_3}$ core affords the 1st generation **16-G$_1$** ($\mathbf{A_6}$), then the condensation reaction with the $\mathbf{DB_2}$ monomer affords the 2nd generation (Scheme 13) [18]. The repetition of both steps affords the 4th generation **16-G$_4$** in only four quantitative steps from the core. This $\mathbf{CA_2/DB_2}$ method gives alternately either NH_2 or PPh_2 end groups, depending on the generation, instead of the PPh_2 and CHO end groups obtained in the $\mathbf{AB_2/CD_2}$ method. Of course, all these end groups can be easily reacted with a variety of reagents to functionalize the surface in a different way. In particular, we have shown that it is possible to graft a highly branched monomer to multiply rapidly the number of end groups in the last step. The Staudinger reaction of the 48 phosphine end groups of **16-G$_4$** with 48 equivalents of a $\mathbf{CD_5}$ monomer gives in one step the dendrimer **17-G$_5$**, possessing 240 aldehydes as end groups (Scheme 14). This highly branched $\mathbf{CD_5}$ monomer can be used not only on the surface, but also during the building of the dendrimer, to replace the $\mathbf{CD_2}$ monomer in the $\mathbf{AB_2/CD_2}$ method of synthesis, as shown in Scheme 15 [19]. This $\mathbf{AB_2/CD_5}$ method allows multiplying the number of end groups either by 2 or by 5, depending on the step considered. Starting from the $\mathbf{D_6}$ core, the 4th generation **18-G$_4$** is also obtained in four steps, but this compound possesses 600 end groups, instead of 48 for the $\mathbf{AB_2/CD_2}$ method. The presence of unsymmetrical cyclotriphosphazenes in all these compounds complicates the ^{31}P NMR spectra, but a perfect fit between the theoretical spectrum and the real spectrum confirms the structures, as shown in Fig. 3 for **18-G$_2$**.

The $\mathbf{CD_5}$ monomer was synthesized because it is possible to carry out specific functionalizations on cyclotriphosphazene scaffolds [20]. In particular, it is possible to graft specifically either 5 or 1 function on $N_3P_3Cl_6$, leaving 1 or 5 Cl available for further functionalizations, respectively. Of course, this type of reactions is not limited to $\mathbf{CD_5}$ compounds, and we have also synthesized the $\mathbf{AB_5}$ monomer, with the idea of replacing the $\mathbf{AB_2}$ monomer in the $\mathbf{AB_2/CD_2}$ method. In this case, a problem of steric hindrance may occur, since the highly branched monomer has to be linked to a $\mathbf{D_6}$ core, which is itself congested. The reaction is slow but goes to completion in 4 days



Scheme 14.

at 100 °C, and affords as expected the 1st generation **19-G$_1$**. The next step with the **CD$_2$** monomer occurs without any problem at room temperature. The **AB$_5$** monomer is used again in the next step, then again the **CD$_2$** monomer, to afford finally the 4th generation **19-G$_4$** (Scheme 16) [19]. Dendrimers **18-G$_2$** and **19-G$_2$**, as well as dendrimers **18-G$_4$** and **19-G$_4$** have the same number of aldehyde end groups (60 and 600, respectively), but



Scheme 15.

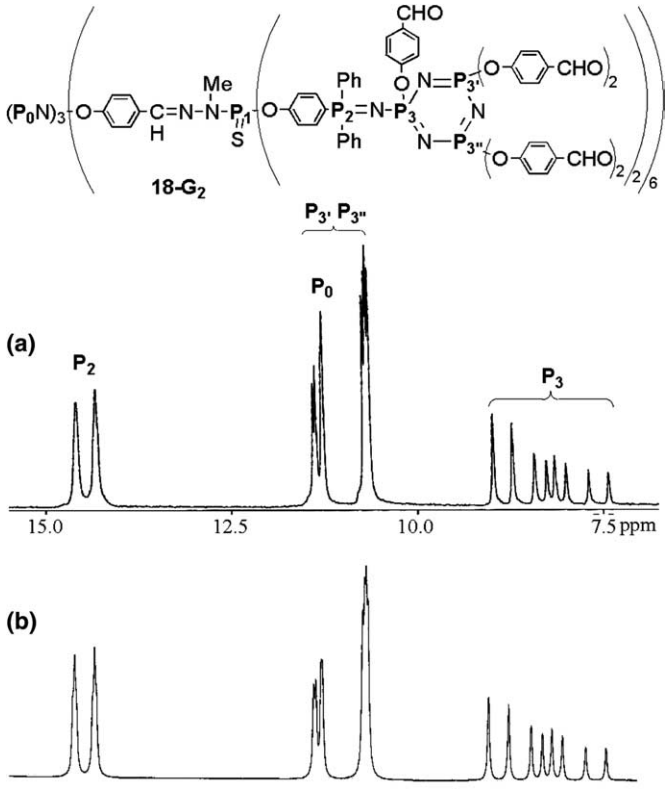
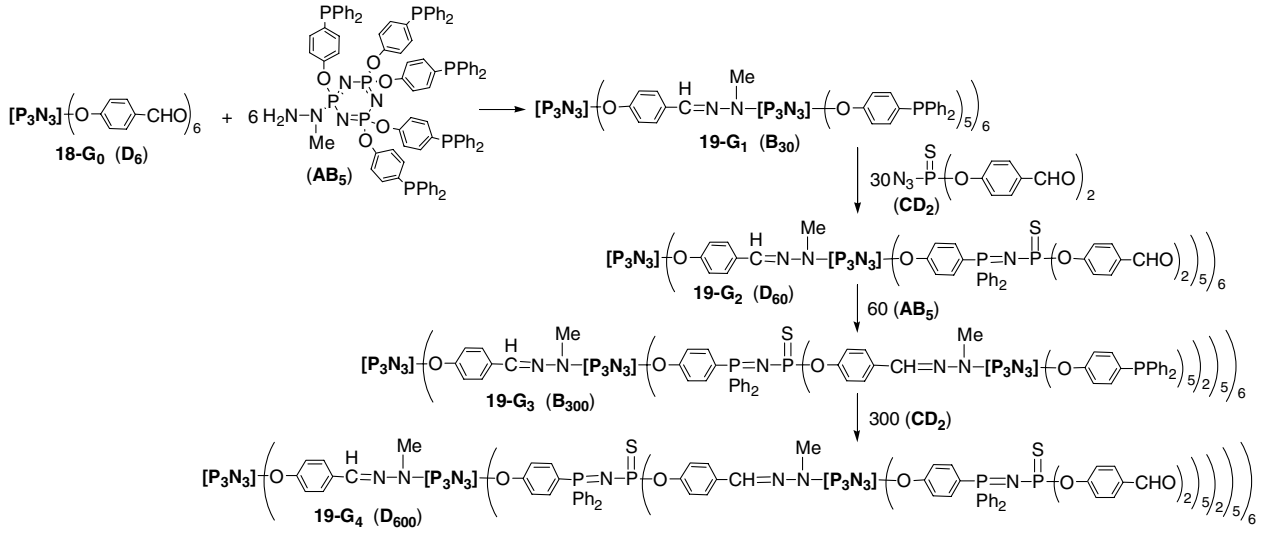


Fig. 3. (a) ^{31}P NMR spectrum of **18-G$_2$** (singlet corresponding to P_1 at 64.4 ppm not shown); (b) theoretical spectrum of **18-G$_2$** (signal for P_1 not shown).

their internal structure is different. A simple drawing allows a visual comparison of the crowding of the 2nd generation in both cases, showing that the interior of **19-G$_2$** is the most crowded (Fig. 4). Despite this fact, we finally tried to use both **AB$_5$** and **CD$_5$** monomers in the same method of synthesis. Starting from **19-G$_1$**, the Staudinger reaction with the **CD$_5$** monomer affords the 2nd generation **20-G$_2$**, then the condensation with the **AB$_5$** monomer affords the 3rd generation **20-G$_3$** (Scheme 17) [19]. This compound obtained in only three steps possesses 750 aldehyde end groups, and is made of cyclotriphosphazene nucleus at all generations, including at the core. The reaction of **20-G$_3$** with the **CD$_5$** monomer was not attempted, because



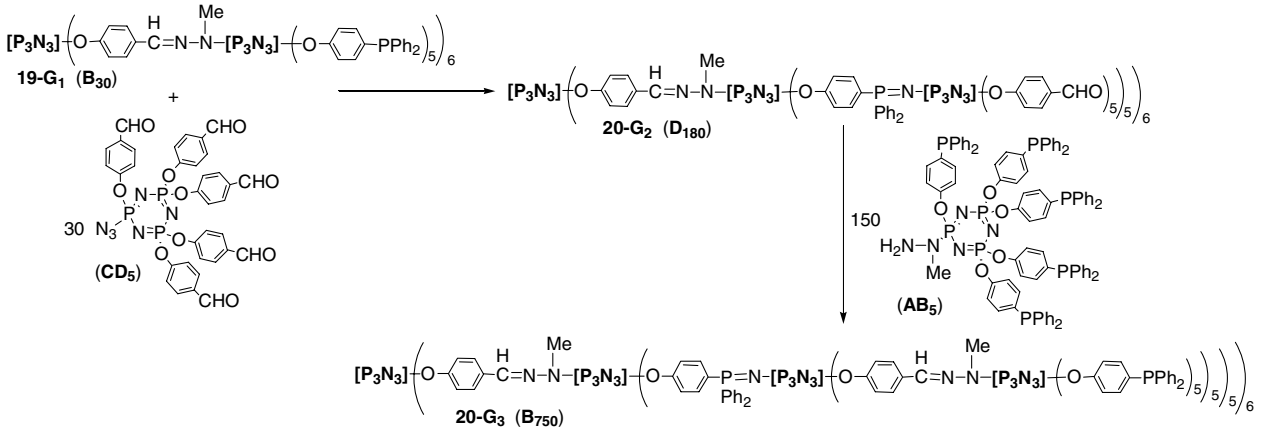
Scheme 16.

Fig. 4. Expanded chemical structure of **18-G$_2$** and **19-G$_2$**.

of the expected steric hindrance of the 3rd generation outer shell. However, this method is the most powerful to date to maximize the number of end groups in a minimum of steps. Fig. 5 displays a comparison of the number of end groups obtained at each step (not at each generation), starting in all cases from a hexafunctional core, and using the methods described in this paper. Obviously, the use of the **AB$_5$/CD$_5$** monomers induces a dramatic increase compared to all the other methods, and all methods using two branched monomers are more powerful than our first **AX$_2$/YD** method.

3. Conclusion

We have shown in this paper that the long time and multi steps processes generally needed for the synthesis of dendrimers are not fatally a prerequisite to enter in the chemistry of dendrimers. The diverse new methods of synthesis that we have proposed in the field of phosphorus-containing dendrimers allowed for instance growth, in a single step, of a dendrimer from 3rd to 8th generation, or to synthesize a 3rd generation dendrimer having 750 end groups in only three steps. Furthermore, all these methods use very clean and



Scheme 17.

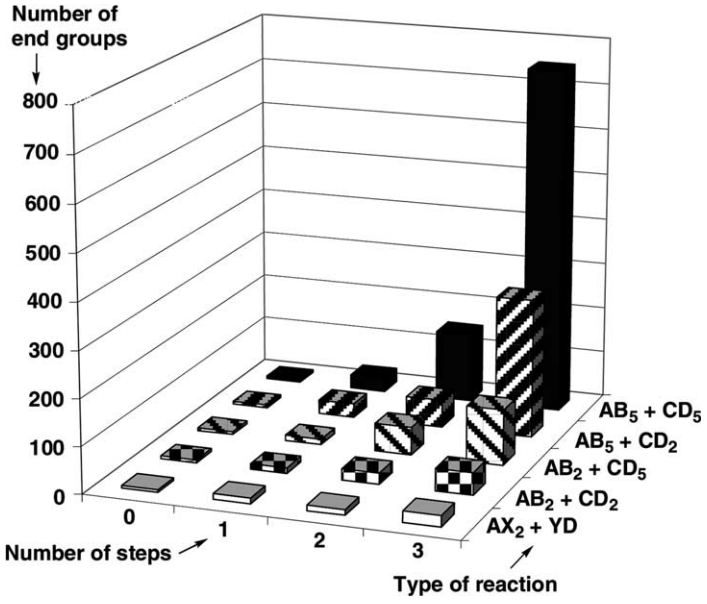


Fig. 5. Comparison of the variation of the number of end groups at each step, depending on the method of synthesis used. The $AX_2 + YD$ method is shown in Scheme 1; $AB_2 + CD_2$ in Scheme 12; $AB_2 + CD_5$ in Scheme 15; $AB_5 + CD_2$ in Scheme 16; and $AB_5 + CD_5$ in Scheme 17.

quantitative reactions whose by-products are only water and dinitrogen. However, we consider that there is still a large room to find improved methods of synthesis of dendrimers, and that this field is still largely opened to the imagination of chemists.

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