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Phosphorus-Containing Dendrimers: From Material Science to Biology

Jean-Pierre Majoral, Anne-Marie Caminade, Régis Laurent, and Pierre Sutra

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

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ABSTRACT: *Various methods of synthesis of phosphorus-containing dendrimers are described. The reactivity of several of these macromolecules is then studied at several levels, mainly on the surface, and also at the level of the branches and of the core. Functionalizations confer to these macromolecules interesting properties, and allow the development of new applications, which are emphasized in this review.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:474–485, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10075

INTRODUCTION

A very special type of nanosized molecules called dendrimers [1] have attracted considerable attention of chemists since several years. Indeed, dendrimers are highly branched polymers having a defined structure in the sense that their dispersity, their size, their weight, their topology, their branches composition, and their surface functionalities are precisely controlled (Fig. 1). The terminal end groups are generally easily accessible and reactive and can be modified at will, in order to finely tune the properties of dendrimers. Furthermore, other types of dendritic structures are available, in particular dendrons (also called dendritic wedges), which in addition to the surface end groups also possess one reactive group located at the core (Fig. 1). All these dendritic compounds are synthesized in a stepwise manner, by the repetition of a sequence of two or three reactions, which allows to lengthen the branches and to multiply the number of end groups. Each sequence of reactions produces what is called a new "generation." Another type of dendritic compounds is hyperbranched polymers, which are synthesized in only one step, but whose structure is poorly defined and reproducible (Fig. 1).

First dendrimers were purely organic compounds [2], but heteroatom-containing dendrimers have rapidly played an important role, with emphasis on silicon-based and phosphorus-based dendrimers [3]. Our first attempts to synthesize phosphorus-containing dendrimers dates back to 1994 [4] and since that time we have developed several other methods of synthesis. Indeed, the search for other methods remains an active area, since the synthesis of dendrimers is time-consuming. However, the main problem has always been to find quantitative reactions so as to ensure the reaction of all the end groups at each step. In parallel to the synthesis, we have also studied the reactivity of the functions located at several levels (surface, core, or branches). Our main concern now is to develop the applications of these original compounds. This paper reports our progression in this field, from the first syntheses to the current applications.

This paper is dedicated to the victims of the explosion that occurred in Toulouse on September 21, 2001.

Correspondence to: Jean-Pierre Majoral and Anne-Marie Caminade; e-mails: majoral@lcc-toulouse.fr, caminade@lcc-toulouse.fr.

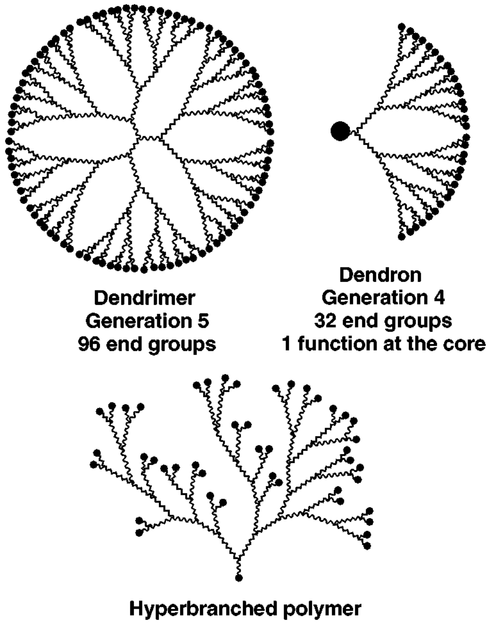
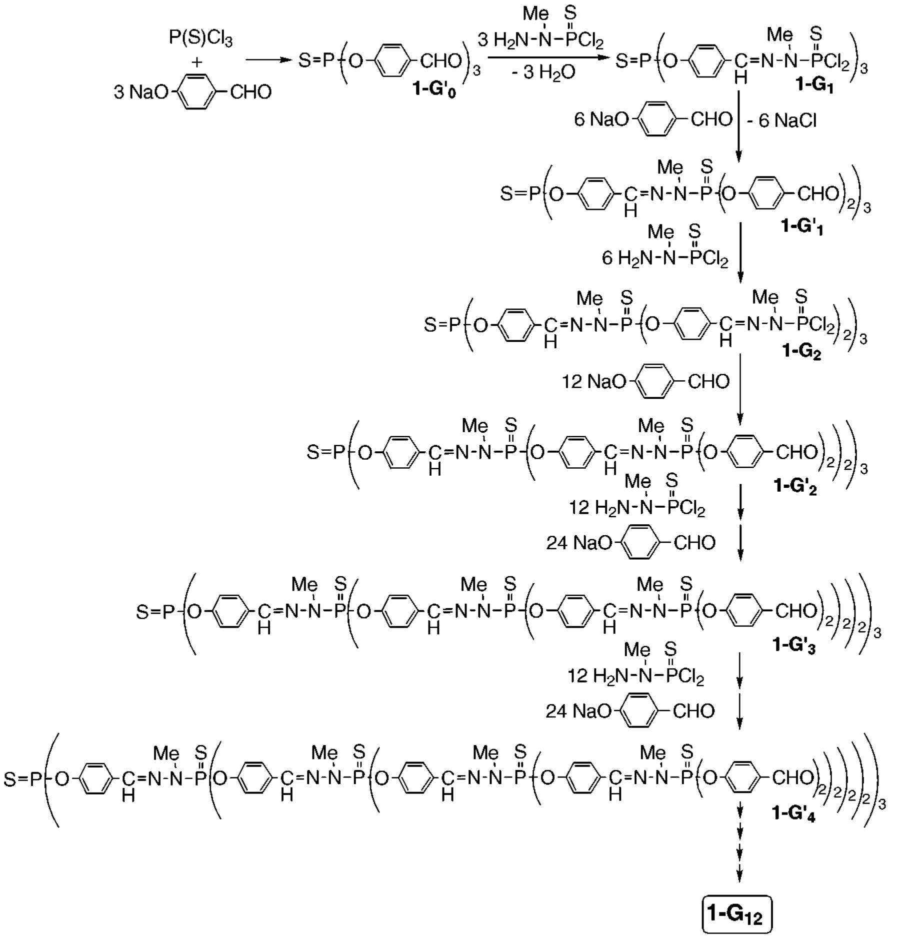


FIGURE 1 Various types of dendritic molecules: dendrimer, dendron and hyperbranched polymer.

RESULTS AND DISCUSSION

Syntheses

The first method of synthesis of phosphorus-containing dendrimers that we described consisted in the repetition of two steps, starting from a core having phosphorus–chlorine bonds, such as $P(S)Cl_3$ (Scheme 1). The first step is the nucleophilic substitution of chlorine by hydroxybenzaldehyde under basic conditions, leading to the trialdehyde **1-G′₀**. The second step is the condensation of the aldehydes with $H_2NNMeP(S)Cl_2$. This reaction induces the multiplication of the number of end groups, with phosphorus acting as the divergence point, and affords the first generation of the dendrimer **1-G₁** [4]. Both reactions are quantitative and the only by-products are sodium chloride and water. The repetition of these two steps allows to build the dendrimer [5], the growth of which is easily monitored by ^{31}P NMR spectroscopy. The largest compound we have isolated is the twelfth generation **1-G₁₂**, which is also the largest compound theoretically accessible



SCHEME 1 Synthesis of the phosphorus-containing dendrimers **1-G$_n$** ($1 \leq n \leq 12$).

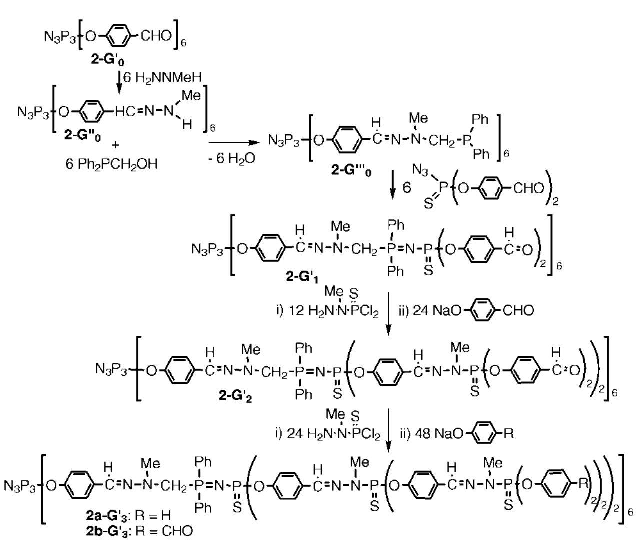
because of the crowding of the surface [6]. This compound is also the highest generation obtained up to now for any type of dendrimer. Its theoretical molecular weight is more than 3,000,000, but it remains soluble in several organic solvents. All of these dendrimers are remarkably thermally stable up to temperatures 200 or 400°C, depending on the type of end groups; however, they are sensitive toward laser UV irradiation, as shown by MALDI-Tof mass spectrometry [7].

This method of synthesis allows several modifications. For instance, $N_3P_3Cl_6$ (hexachlorocyclotriphosphazene) can be used as the core instead of $P(S)Cl_3$ so as to have a higher number of branches at the same generation [8]. The thiophosphorhydrazide can be replaced by $H_2NNMeP(O)Cl_2$, either at each generation [9], or precisely where desired within the structure [10], or only as end groups [11], since the $P(O)Cl_2$ groups are more reactive than the $P(S)Cl_2$ groups in certain circumstances.

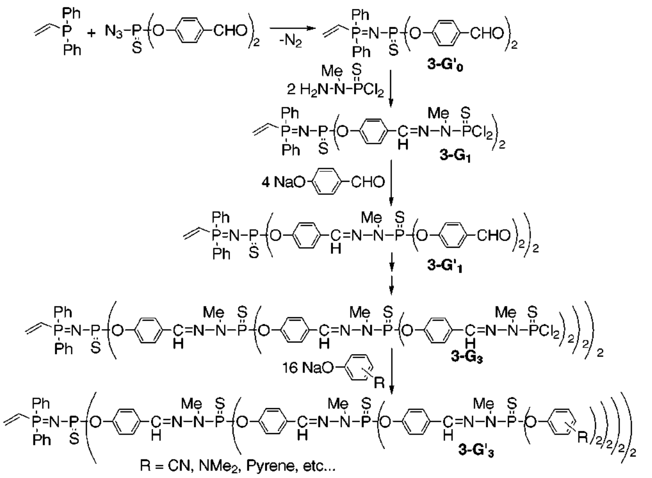
Another modification consists in the introduction of P=N—P=S linkages within the skeleton. In the first attempts, we introduced these linkages at each generation [12], but later we found it more interesting to place these linkages only at some generations [13], precisely where desired to perform special reactions, which will be emphasized later. The introduction of the P=N—P=S linkages necessitates three steps starting from the aldehyde groups. These three steps are illustrated in Scheme 2, starting from the hexaaldehyde **2-G'₀**. The first step is condensation with methylhydrazine. The second step consists in grafting the diphenylphosphine by a condensation reaction. The third step is a Staudinger reaction of the phosphine with the azide $N_3P(S)[OC_6H_4CHO]_2$, leading to the next generation having aldehyde end groups, compound **2-G'₁** in this case [14]. Starting from these aldehyde groups, the two-steps process shown in Scheme 1 can be applied again. In the case of dendrimer **2-G'₁**, this process was applied up to the third generation. Various types of phenols can be used in the last step for the functionalization of the surface [14] (Scheme 2).

The two-steps method combined with the creation of P=N—P=S linkages can also be used for the synthesis of dendrons [15]. For instance, the Staudinger reaction of diphenylvinylphosphine with $N_3P(S)[OC_6H_4CHO]_2$ affords compound **3-G'₀** possessing one vinyl group and two aldehyde groups, from which the synthesis was carried on up to the third generation **3-G'₃** [16], using the two-steps process (Scheme 3).

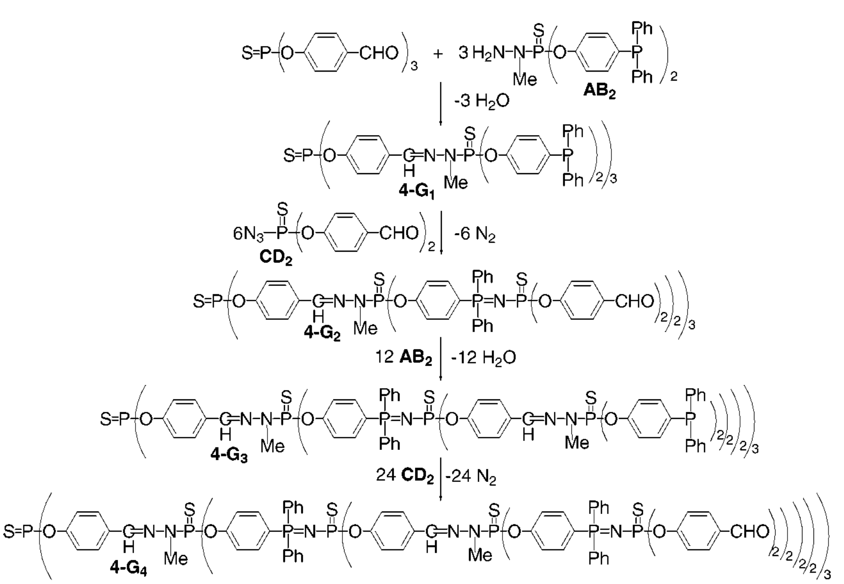
We have tried to find other methods of synthesis of phosphorus-containing dendrimers but most of these attempts were limited to the first or second generations because of the nonquantitative reactions [17]. However, we have recently found an improved method of synthesis of dendrimers, using for the first time AB_2- and CD_2-type monomers. This method allows to multiply the number of branches at each step, and not every two steps as in all the previous methods. Thus, dendrimer **4-G₄** having 48 end groups is obtained in only four steps (Scheme 4). Furthermore, this compound can also be obtained with a rather good purity in a one-pot (but multistep) process, thanks to the quantitative reactions used (condensation and Staudinger reactions) and to the nature of the by-products (water and nitrogen) [18]. Another improvement to shorten the time dedicated to synthesis consists in obtaining



SCHEME 2 Synthesis of dendrimers having six P=N—P=S linkages within their structure.



SCHEME 3 Synthesis of phosphorus-containing dendrons.

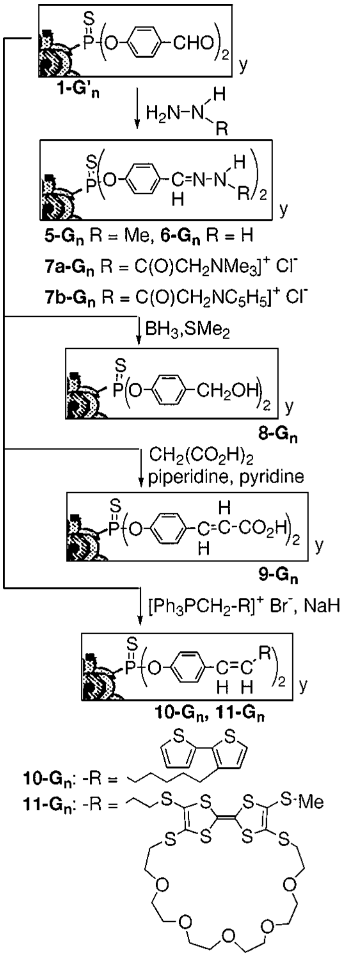


SCHEME 4 Rapid synthesis of dendrimers: one step = one generation.

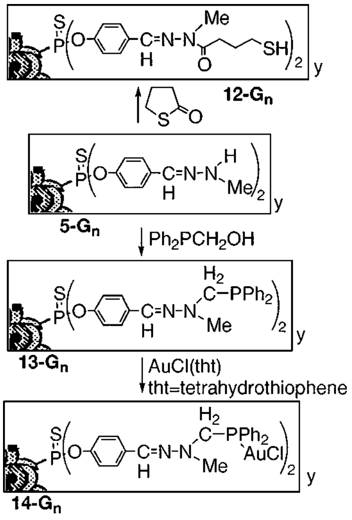
hyperbranched polymers in a one-step process. We have shown that the deprotection of the phosphino groups of $N_3P(S)[OC_6H_4PPh_2 \rightarrow BH_3]_2$ by using DABCO induces the formation of hyperbranched polymers via Staudinger reactions. However, these hyperbranched polymers compared with perfect dendrimers constituted of the same repetitive units do not really have the same properties [19].

Reactivity

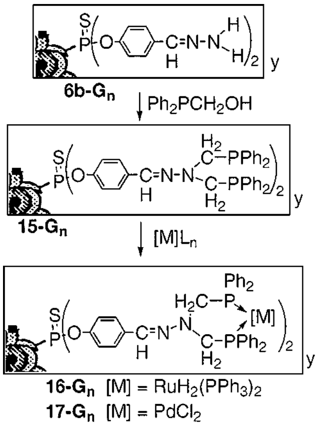
The type of dendrimers we have used to study the reactivity of the surface are all built up using the method described in Scheme 1, either from a trifunctional core ($P(S)Cl_3$) or a hexafunctional core ($N_3P_3Cl_6$). All these dendrimers possess on the surface at each step either aldehyde or $P(X)Cl_2$ ($X = O, S$) groups, both being particularly reactive functions [20]. Thus, starting from these functions, we have grafted many other functional groups on the surface of dendrimers. Only some representative examples of this surface reactivity will be given in the following schemes. In these schemes (Schemes 5–8) only one end group, representative of all the end groups, is drawn. The reaction we mainly used starting from the aldehyde end groups is the condensation reaction with various primary amines and hydrazines. For instance, chiral derivatives of methylbenzylamine were grafted in this way [21]. The reaction of methylhydrazine or hydrazine (used in very large excess to avoid cross-linking reactions) allows to have NH or NH_2 functions as end groups



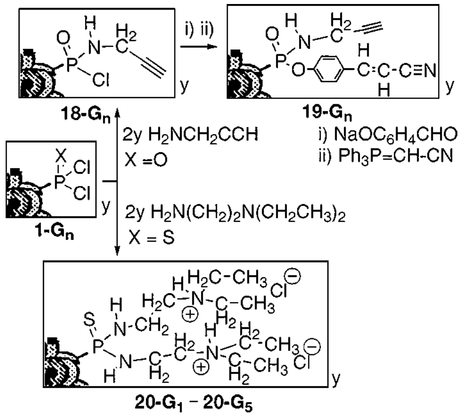
SCHEME 5 Various types of end groups of dendrimers obtained from aldehydes.



SCHEME 6 Various types of end groups of dendrimers obtained from methylhydrazones.



SCHEME 7 Complexes of diphosphino end groups of dendrimers obtained from hydrazones.

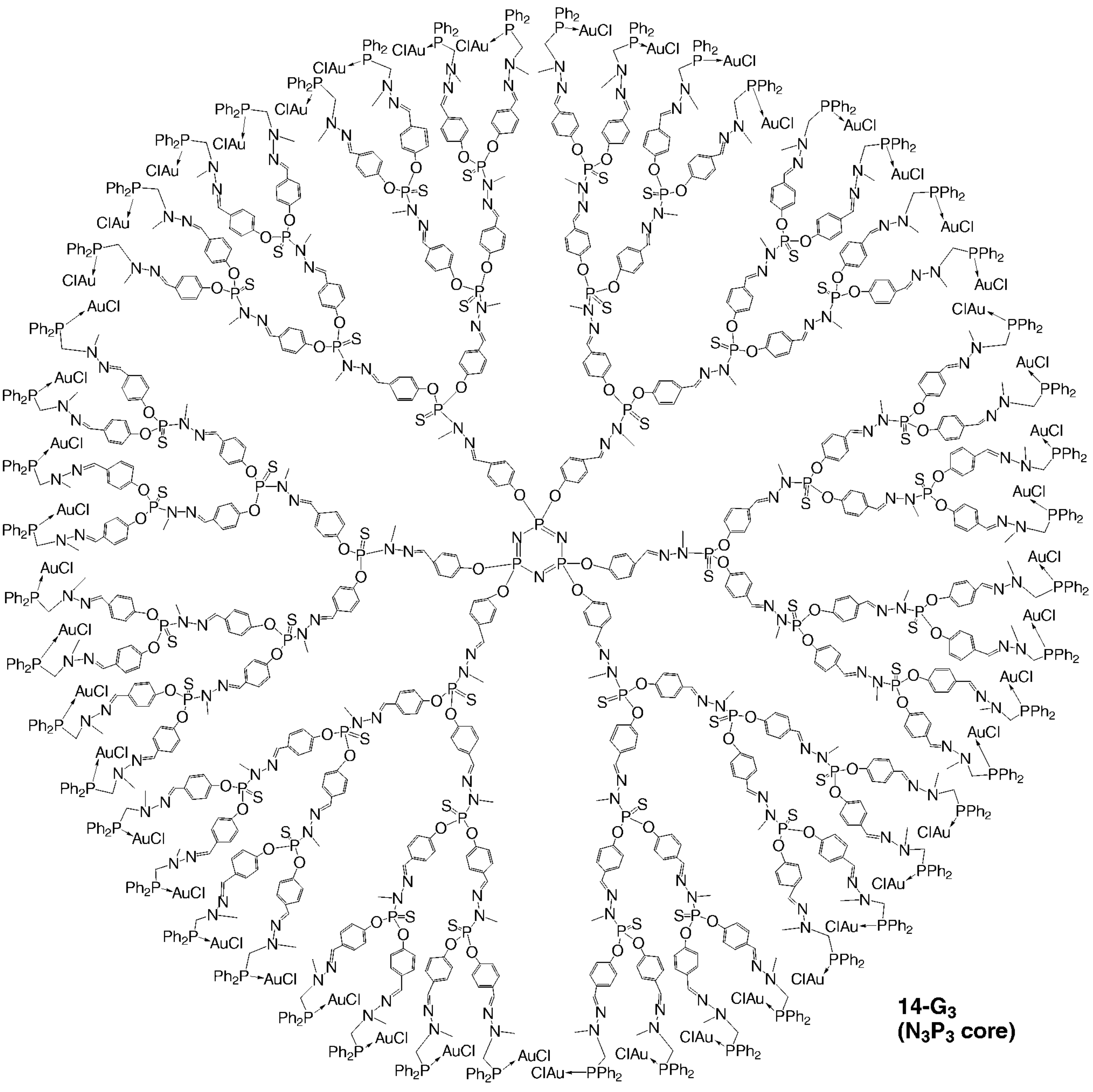


SCHEME 8 Examples of reactivity of the $P(S)Cl_2$ end groups of dendrimers.

of dendrimers **5-G*n*** and **6-G*n*** [22], whose reactivity is described in the next paragraph. Condensation reactions with Girard-T or Girard-P reagents lead to the water-soluble dendrimers **7a-G*n*** or **7b-G*n***, respectively [23]. The aldehyde groups can also be reduced specifically by using BH_3, no reduction of the hydrazones constituting the skeleton of the dendrimer being observed under these conditions [24]. Dendrimers **9-G*n*** having cinnamic acid end groups are obtained via a particular type of Knoevenagel condensation using maleic acid [24], but the method we mainly used to obtain functionalized alkenes on the surface of dendrimers consists in applying Wittig reactions with phosphorus ylides. Dendrimers **10-G*n*** having bithiophene derivatives [25] and **11-G*n*** having TTF-crown ether derivatives [26] are obtained in this way. Other types of functionalized alkenes, particularly amino acid derivatives were grafted using Horner–Wadsworth–Emmons reactions [27].

The presence of NH or NH_2 end groups also opens the way to a versatile reactivity. A ring opening reaction of γ-thiobutyrolactone by dendrimers **5-G*n*** leads to the S–H functionalized dendrimers **12-G*n*** [28], but the most important reaction is the condensation with Ph_2PCH_2OH (Scheme 6). Indeed, this reaction leads to the grafting of phosphines on the surface, which are then used for the complexation of various metals [29]. Monophosphine end groups are able to complex iron, tungsten, or rhodium derivatives [30]. Gold is also complexed, leading to dendrimers **14-G*n*** (Fig. 2) (up to $n = 10$), which were imaged by electron microscopy [31]. The presence of Au-Cl on **14-G*n*** allows also the grafting of Fe/Au clusters on the surface of the dendrimers [32]. With the diphosphino end groups, various organometallic derivatives of transition metals are grafted, such as ruthenium (compound **16-G*n***) [33], palladium (compound **17-G*n***) (Scheme 6), platinum, or rhodium [34]. NH_2-terminated dendrimers of type **6b-G*n*** or others [35] are used also in condensation reactions with various aldehydes [36].

We studied the reactivity of $P(S)Cl_2$ end groups toward functionalized phenols, such as ferrocene derivatives (chiral [37] or not [38]), and pesticide derivatives [39] but our main use of these end groups consisted in the reaction with various functionalized amines. These reactions led for instance to multitri- or multitetra-functionalized dendrimers, meaning dendrimers having simultaneously three [40] or four [11] types of functional groups on the surface, such as compounds **18-G*n*** and **19-G*n*** (Scheme 8). Tetraazamacrocycles were also grafted to dendrimers in this way [41]. A particular illustration of the reactivity of $P(S)Cl_2$ end groups with amines is given by the reaction of dendrimers **1-G*n***



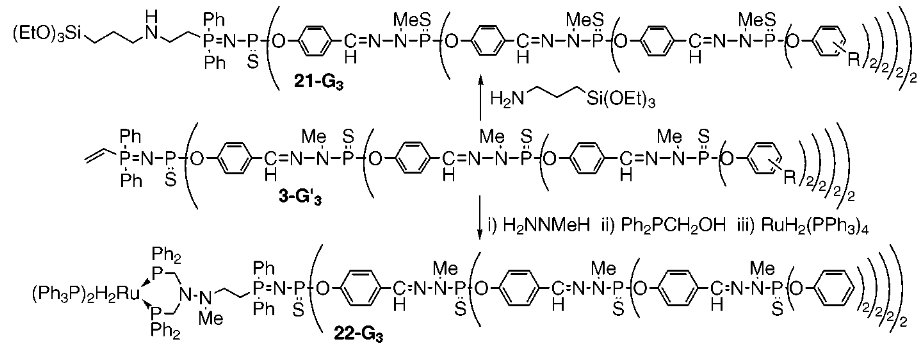
14-G3 (N3P3 core)

FIGURE 2 Structure of the third generation dendrimer complex **14-G3**.

with diethylethylenediamine in the stoichiometry 2 amines per $P(S)Cl_2$ group, leading to the polycationic dendrimers **18-G$_n$**, which are water-soluble (Scheme 8) [42].

Various functionalized amines were also used in Michael-type additions at the vinyl core of dendrons **3-G'$_n$** [43]. For instance, the reaction of $H_2N(CH_2)_3Si(OEt)_3$ leads to dendron **21-G$_n$** having one triethoxysilyl group at the core [44]. On the other hand, the successive reactions of methylhydrazine, Ph_2PCH_2OH, and a ruthenium hydride derivative lead to dendron **22-G$_3$**, having one diphenylphosphino–rutheniun complex located at the core [45] (Scheme 9). The presence of various functional groups at the core allowed us to develop the reactivity of these dendrons for the synthesis of dendritic macromolecules having special architectures and different end groups [16,46]. The structures of some of these are illustrated in Fig. 3.

The reactivity of P=N—P=S linkages precisely placed within the branches also allowed us to obtain dendrimers having very original structures



SCHEME 9 Examples of reactivity of the vinyl group located at the core of dendrons.

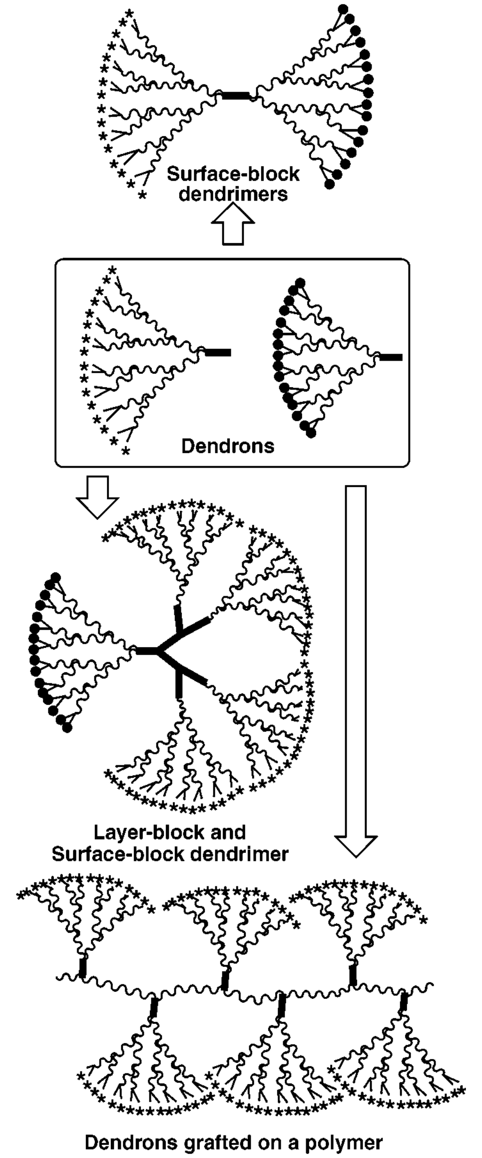
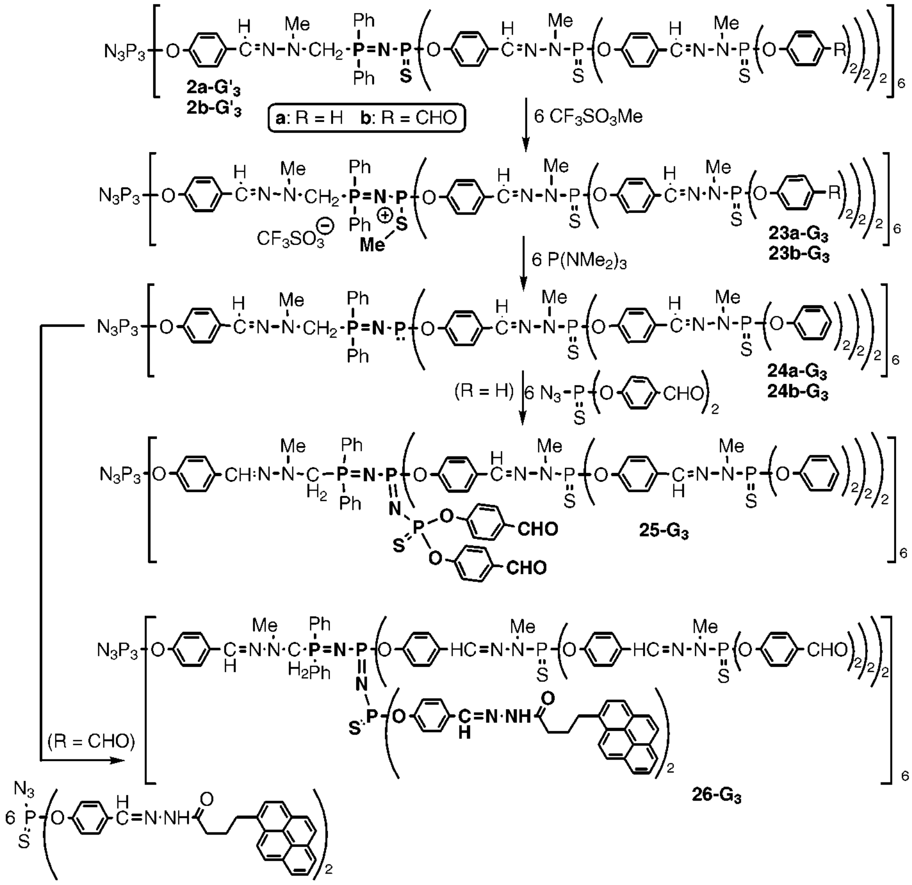


FIGURE 3 Various types of dendritic molecules synthesized from dendrons.

[47]. Indeed, these linkages have a mesomeric form (P^+—N=P—S^-), which favors the reaction of electrophiles on sulfur. We first used methyl triflate [13], then functionalized triflates [48] to obtain polycationic dendrimers having charges within the skeleton. An example is given in Scheme 10, starting from compound **2-G'$_3$**. Alkylation of sulfur generally induces the weakening of the P—S bond, which is easily cleaved by using a nucleophilic phosphine such as $P(NMe_2)_3$ [49]. This reaction leads to tricoordinated phosphorus atoms located inside the dendrimer, such as compound **24-G$_3$**. These tricoordinated phosphorus atoms were mainly used in Staudinger reactions with various functionalized azides [50], and particularly with azides having aldehyde [14] or pyrene [51] functions, affording compounds **25-G$_3$** and **26-G$_3$** (Fig. 4), respectively (Scheme 10). The presence of aldehyde internal groups is particularly important since it could allow to develop many reactions inside the dendrimer, provided enough space is available. The fluorescent derivative **26-G$_3$** was designed in order to characterize the presence of cavities inside the dendrimer. Indeed, pyrene derivatives are known to undergo the formation of excimers upon irradiation, provided the pyrene groups can move enough to reach the required position. The fluorescence of excimers is observed in the case of dendrimer **26-G$_3$**, indicating that enough free space is available within the dendrimer. Thus, starting from the aldehyde internal groups of **25-G$_3$**, we developed a very original reactivity. For instance, we were able to grow new branches within the dendrimer, using the two-step or three-step processes previously shown on the surface of dendrimers in Schemes 1 and 2. These reactions were carried out up to the third generation for the new branches. This step-by-step process leading finally to **G_3G_3**-type compounds is illustrated in



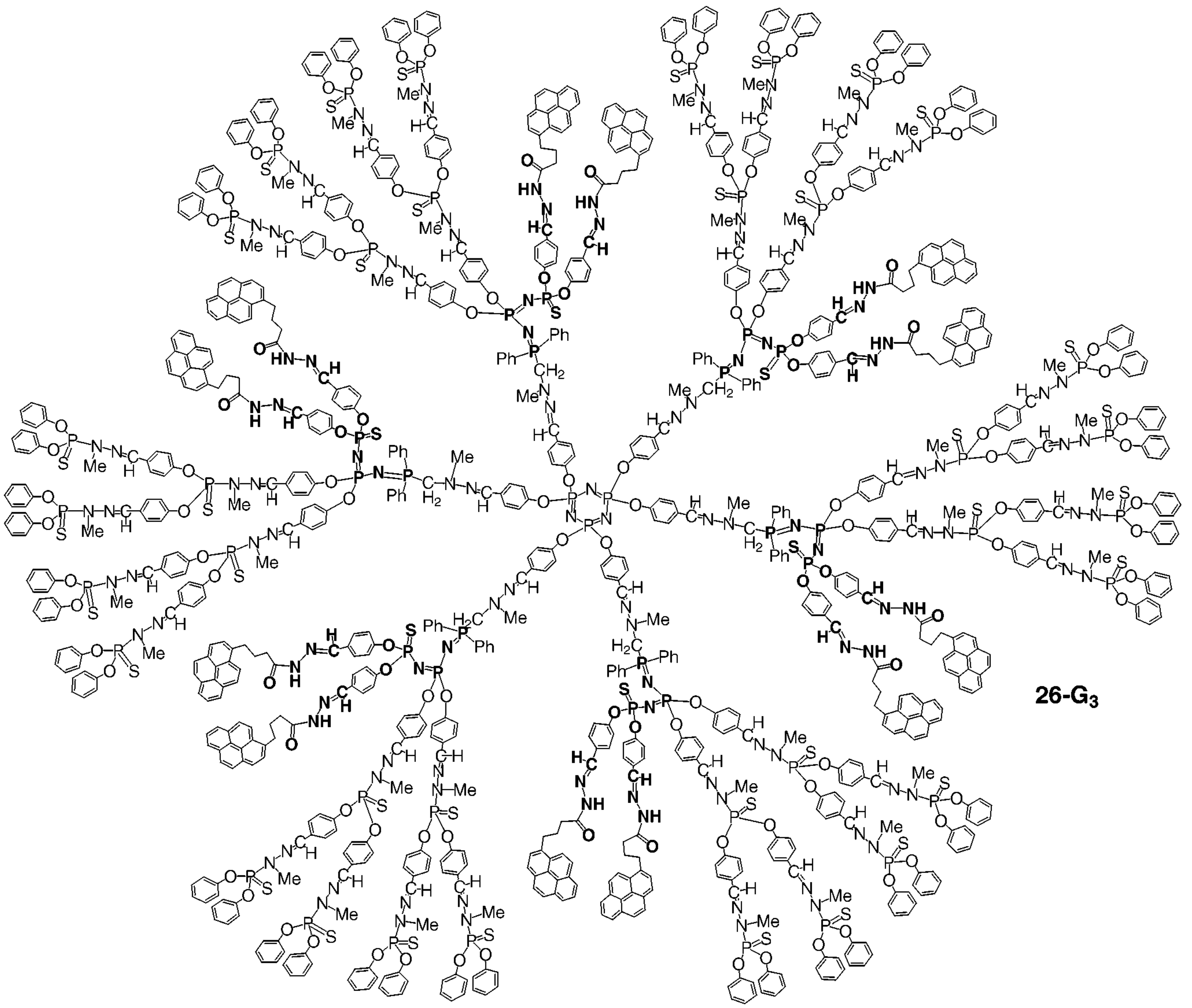
SCHEME 10 Examples of reactivity of the P=N—P=S linkages located in the interior of dendrimers.

Scheme 11 way A [14]. At each step of this synthesis various functional groups are present inside the dendrimer; therefore, we have also studied the reactivity of these internal groups, particularly for the complexation of gold [52] and the formation of zwitterionic zirconocene complexes [53]. It is also interesting to note that other **G_3G_3**-type compounds can be obtained in only one step starting from compound **25-G_3**, using dendrons possessing one NH_2 group at the core (Scheme 11, way B) [43].

Properties and Applications

The majority of properties and applications which we studied were done with dendrimers obtained by the method described in Scheme 1 and variously functionalized on the surface. Some physical properties of dendrimers having aldehyde end groups were studied, particularly by X-ray photoelectron spectroscopy [54], dielectric spectroscopy [55], and dipole moment measurements [6]. However, most of the properties and uses of our phosphorus-containing dendrimers concern material sciences (modification of material surfaces, elaboration of materials including dendrimers), catalysis, and biology (formation of hydrogels, transfecting agents).

We have modified the surface of several types of materials using dendrimers variously functionalized. For instance, covalent modifications of quartz plates surfaces previously functionalized by amines are obtained using dendrimers **1-G'$_n$**, which possess aldehyde end groups (Fig. 5). Characterization of these modified surfaces by atomic force microscopy indicates the formation of a monolayer of dendrimers, usable for the immobilization of human serum albumin [56]. The surface of electrodes can also be modified, using electroactive dendrimers. For instance, dendrimers **10-G$_n$** (bithiophene end groups) are irreversibly electropolymerized onto the anode, leading to the deposition of a blue conducting film, which renders the electrode active in water [25]. Dendrimers **11-G$_n$** (TTF-crown ether end groups) also form a film onto the electrode during electrolysis, but this electrodeposition is totally reversible by reduction; this film acts as sensor for the

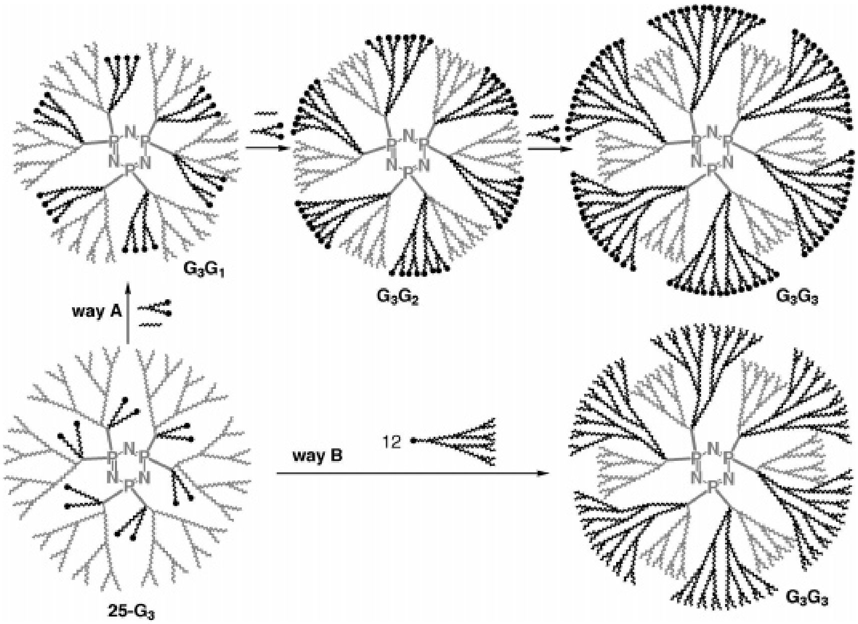


26-G$_3$

FIGURE 4 Structure of the third generation dendrimer **26-G$_3$** possessing fluorescent labels in the interior.

detection of barium salts. Another type of surface coating is observed when the dendrimers having thiol end groups **12-G$_n$** are reacted with the gold cluster Au$_{55}$(PPh$_3$)$_{12}$Cl$_6$. These dendrimers induce the elimination of all ligands, and the formation of crystals of gold, which were demonstrated for the first time to be constituted of bare Au$_{55}$ clusters, only protected by a thin coating of dendrimers on the surface of the crystals [28].

The reaction of alcohol- or acid-ended dendrimers (**8-G$_1$** and **9-G$_1$**) with another cluster Ti$_{16}$O$_{16}$(OEt)$_{32}$ leads to the hybrid nanostructured materials incorporating both the dendrimer and the cluster. It was demonstrated that the interaction between both components occurs via transalcoholysis when **8-G$_1$** is used and via bridging carboxylate groups when **9-G$_1$** is used. X-ray diffraction studies of the materials indicate that locally ordered arrays of crystals are formed, the dendrimer acting as a spacer and organizer for the clusters [24]. Another type of hybrid material is obtained using dendrons such as **21-G$_3$**, having a triethoxysilyl group at the core. Indeed, these dendrons are used in sol-gel processes in the presence of Si(OEt)$_4$ and water, with a catalytic amount of tetrabutylammonium fluoride, to afford silica functionalized in the bulk by the dendrons (Fig. 6). In several cases these materials are mesoporous or nanoporous with a narrow pore size distribution, depending on the length of the linker between Si(OEt)$_3$ moieties and the dendron [44]. Depending on the type of end groups located on the surface of the dendron and on the accessibility, various applications can be envisaged, for instance in the field of heterogeneous catalysis.



SCHEME 11 Two ways to graft new branches within a dendrimer.

Indeed, catalysis using dendrimers constitute one of our goals, and we have already demonstrated that the palladium derivatives **17-G$_n$** and the ruthenium derivatives **16-G$_n$** and **22-G$_3$** can act as homogeneous catalysts. Compounds **17-G$_n$** catalyze Stille couplings, whereas compounds **16-G$_n$** and **22-G$_3$** catalyze Knoevenagel condensations and diastereoselective Michael additions. In all cases, the percentage of conversion is very high, and a slight increase of the catalytic properties is observed with increasing generations of the dendrimer, for an identical concentration in metallic centers. However, the most important advantage of using dendrimers as catalysts is that they can be easily separated from the products by simple precipitation, resolubilized, and reused several times with only a slight decrease of the catalytic properties [45].

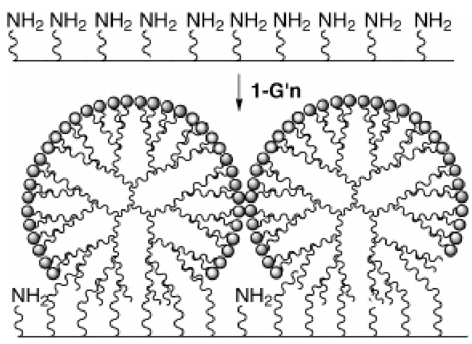


FIGURE 5 Modification of the surface of materials by dendrimers.

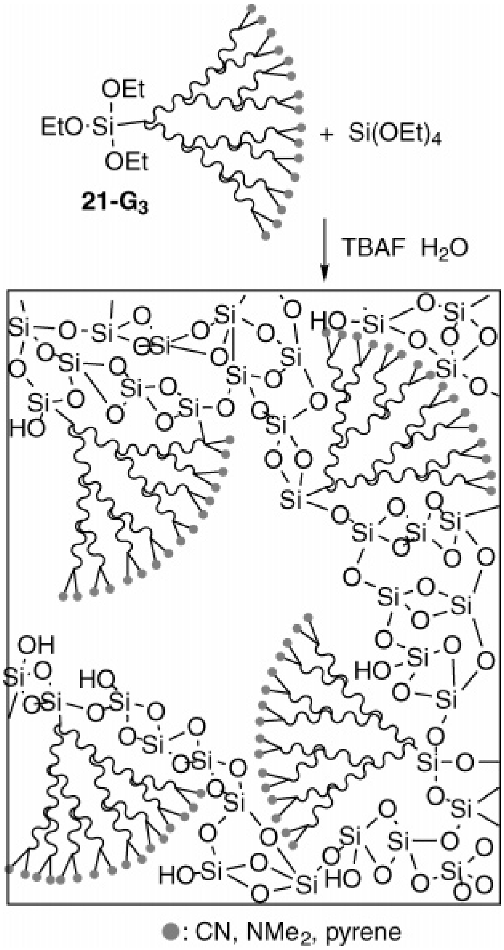


FIGURE 6 Silica functionalised in the bulk by dendrons.

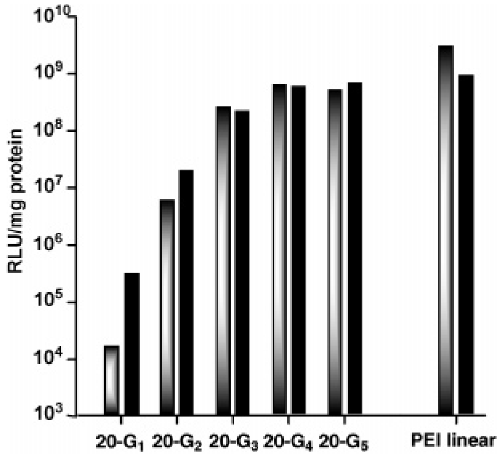


FIGURE 7 Efficiency of dendrimers **20-G$_1$-20-G$_5$** for the transfection of the Luciferase gene, compared to linear polyethyleneimine.

All the properties and applications mentioned above concern dendrimers soluble in organic solvents, but we have also prepared dendrimers which are water-soluble, by only changing the type of functions located on the surface. For instance, the ammonium derivatives **7a-G$_n$**, **7b-G$_n$**, and **20-G$_n$** are all soluble in water. The Girard's derivatives **7a-G$_n$** and **7b-G$_n$** possess the very interesting and unexpected property to form gels when they are left in solution in water at low concentration (ca. 1% in weight) for several days at room temperature or heated for several hours. These gels are rigid, they do not flow when left on a surface, and they can even be crushed into pieces. Hydrogen bonds and π-stacking effects may account for the formation of these gels, which are able to encapsulate many water-soluble substances during their formation [23].

Another original property of some water-soluble dendrimers concerns their transfection efficiency. Indeed, we have shown that dendrimers **20-G$_n$** can act as transfecting agents for the luciferase gene into eucaryotic cells in vitro, in the presence of serum [42]. An increase of efficiency is observed with increasing generations up to 4–5, which have an efficiency similar to that of polyethyleneimine, one of the chemical "standards" used in transfection experiments (Fig. 7).

CONCLUSION

More than 20 years after the first syntheses, dendrimers still constitute a very aristocratic family of polymers. The main problem for their development is their long and tedious syntheses, and even though the synthetic ingenuity of chemists has afforded recently new ways of synthesis, studies are still needed in this field. The challenge now is to propose original applications for these so aesthetic macromolecules. In this perspective, phosphorus-containing dendrimers offer a high potential of development. Indeed, the variety of modifications at the level of the core, of the branches, and of the surface that we have already experienced should help in the development of forthcoming applications.

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