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## Nanomaterials Based on Phosphorus Dendrimers

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### ABSTRACT

Dendrimers constitute an increasingly important field of research in chemistry for more than 15 years. After pioneering works concerning synthesis, the interest in dendrimers is now mainly driven by their properties and applications. This Account will emphasize the properties of a special class of dendrimers, that is, phosphorus-containing dendritic macromolecules, as tools for the elaboration of nanomaterials. Indeed, these dendrimers can be considered themselves as materials, or they can be used as an intrinsic constituent of a material or as a modifier of the surface of a material. In this latter case, a fundamental work about surfaces covalently modified by dendrimers recently opened the way to the elaboration of DNA chips.

### 1. Introduction

The development of nanomaterials, that is, materials based on nanometer-size particles, is one of the major challenges for this new century. For a while, the search for miniaturization was done primarily by an approach of the type top-down, that is, by dividing macroscopic devices. However, it is now recognized that the bottom-up approach from the molecular level should be the next development for future technologies. In this perspective,

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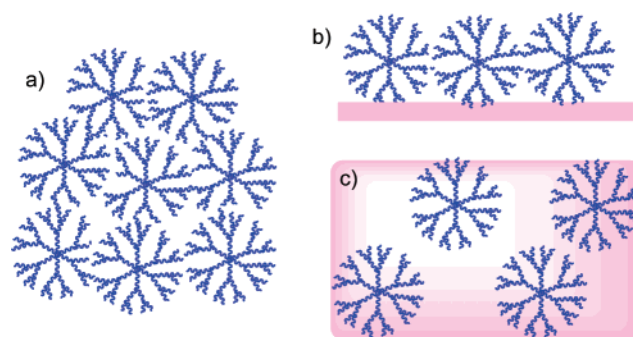


FIGURE 1. Type of uses of dendrimers in materials sciences: (a) in the bulk; (b) on the surface of a material; (c) inside a material.

nanosized molecules are attracting a considerable attention, and a particular emphasis is put on a special class of polymers named dendrimers. Indeed, dendritic macromolecules made of well-defined branching units emanating from a central core undoubtedly constitute a major field of research with more than 6000 reports published within the last 15 years. After pioneering works concerning syntheses, interest in dendrimers is now mainly driven by applications in various fields of chemistry, biology, and physics but also materials science and nanotechnologies.<sup>1,2</sup> Indeed, dendrimers can be considered themselves as materials when they are in the solid state, or they can be used for creating new materials or for modifying the surface of existing materials (Figure 1). Beside purely

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Jean-Pierre Majoral received his Ph.D. from the Université Paul Sabatier of Toulouse in 1972. In 1972–1973, he worked as a Postdoctoral fellow with Prof. A. Katritzky (University of East Anglia, Norwich, U.K.). He became Directeur de Recherche at the Centre National de la Recherche Scientifique in Toulouse in 1978, where he is presently Directeur de Recherche Classe Exceptionnelle. His research interest is mainly focused on the use of main group elements, especially phosphorus, in different areas of chemistry. Presently, he and his research team are involved in the preparation, properties, and applications of macromolecules such as dendrimers and hyperbranched polymers. Emphasis is also laid on the studies of interactions between heavier main group elements and group 4 elements (titanium, zirconium, hafnium) with applications in organic and organometallic chemistry. He is a member of the Polish Academy of Sciences and of the Academia Europaea and has published more than 360 publications and patents.



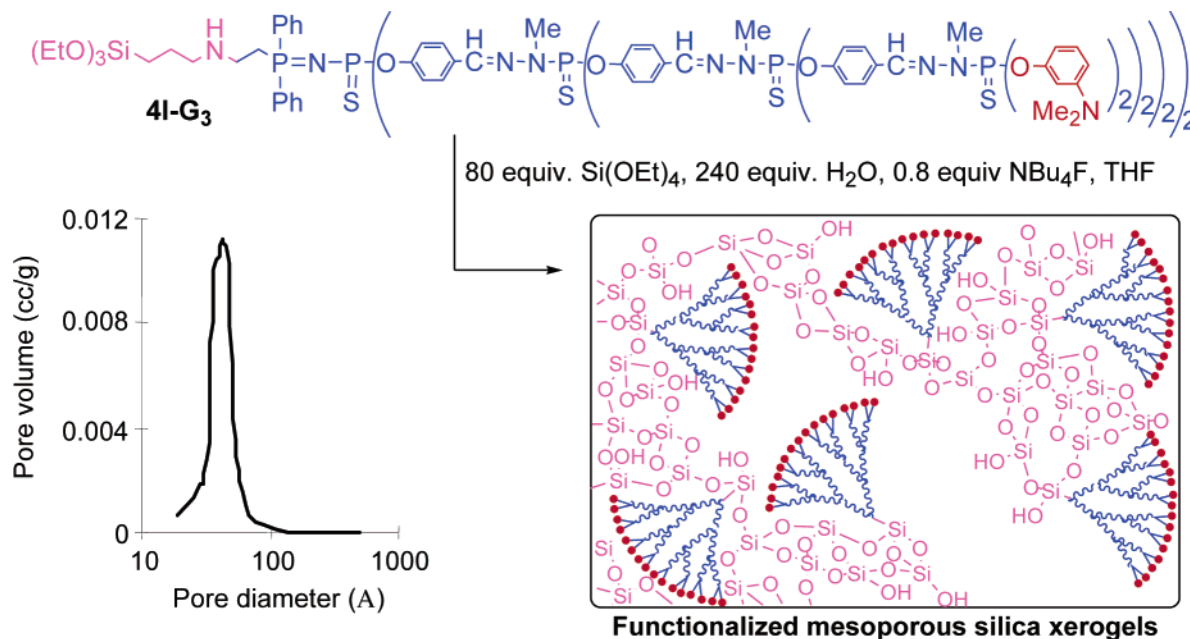


FIGURE 3. One of the dendrons used for obtaining functionalized silica xerogels and the corresponding BJH pore size distribution.

### III. Phosphorus Dendrimers as Building Blocks of Materials

Dendrimers can play a key role in the chemical construction of organized matter. Our first attempts in this field concern the cohydrolysis and polycondensation of dendrons bearing a hydrolyzable Si(OEt)<sub>3</sub> group at the core with an adequate number of equivalents of Si(OEt)<sub>4</sub> and water. Various sizes of dendrons (generations 1, 2, and 3) possessing various types of end groups (**b**, **j**, **k**, and **l**, Chart 1) were reacted with various amounts of Si(OEt)<sub>4</sub>. A large variety of dendron-silica xerogels were obtained, and some of them were found to be mesoporous with a narrow pore size distribution. Figure 3 shows the Barrett, Joyner, and Halenda (BJH) pore size distribution (mean value 45 Å) for the xerogel obtained from dendron **4I-G<sub>3</sub>**.<sup>32</sup>

An analogous sol-gel process can be applied to dendrimers possessing triethoxysilyl end groups and Si(OEt)<sub>4</sub> to afford hybrid organic-inorganic solids. Such a process was already applied, in particular, to dendrimers having silicon at each branching point, but the highly flexible skeleton of these dendrimers induces a poor homogeneity of the size of pores.<sup>33,34</sup> The use of phosphorus-containing dendrimers also affords hybrid solids, which give, after heating at 550 °C for several hours, a highly porous material with a good reproducibility, which could be related to the expected semirigidity of these dendrimers; these materials might be used as absorbents or insulating materials.<sup>35</sup>

In contrast to silicate materials, the elaboration of organic-inorganic hybrid materials built from nonsilicate precursors is often difficult to control, but strategies based on the assembly of nano building blocks (ANBB) with well-defined structures are useful. This concept was applied to the reaction of the small dendrimers **1i-G<sub>1</sub>** and **1m-G<sub>1</sub>** with the cluster [Ti<sub>16</sub>O<sub>16</sub>(OEt)<sub>32</sub>], which gives a hybrid gel made of dendrimers and clusters of which the indi-

vidual internal structure is conserved. The organic-inorganic interfaces are obtained by transalcoholysis between some ethoxy groups of the cluster and some alcoholic groups of dendrimer **1m-G<sub>1</sub>** or by nucleophilic substitutions coupled with a proton transfer from the acid end groups of **1i-G<sub>1</sub>** giving bridging carboxylates (Figure 4). These solid gels are mesostructured hybrid materials in which clusters are regularly spaced by the dendrimers.<sup>36</sup>

If larger dendrimers are used, such as the fifth generation **1i-G<sub>5</sub>** or the seventh generation **1i-G<sub>7</sub>** with titanium or cerium alkoxides, the complexation of the metal centers by the acidic functions of the dendrimers occurs first through bridging carboxylates; then these sites act as anchoring points for the development of the inorganic network all around the dendrimer, which acts as a template, affording a hybrid material. After thermal decomposition, the pore packing observed by TEM is spongelike with mesopores of 9–30 Å; macroporosities are also detected.<sup>37</sup> Control of porosity in all these hybrid organic-inorganic materials should lead to several applications in various fields such as catalysis, separation techniques, or coatings.

The formation of another type of network is responsible for an astonishing and up to now unique property of dendrimers having Girard-P or Girard-T reagents as end groups such as **1g-G<sub>n</sub>**, **2g-G<sub>n</sub>**, **1j-G<sub>n</sub>**, and **2j-G<sub>n</sub>**; they form hydrogels when dissolved in water at relatively low concentrations (0.25%–1.8% in weight) and left several days at room temperature or heated several hours at 60–65 °C.<sup>38</sup> A single molecule of the fourth generation of the dendrimer is able to gel about 500 000 molecules of water! These hydrogels are rigid, they do not flow, and they can even be crushed into pieces. Freeze-fracture electron microscopy of the gels shows fragments of chains made of dendrimers, imprisoning large pockets of water. The dendrimer network is likely due to supramolecular inter-



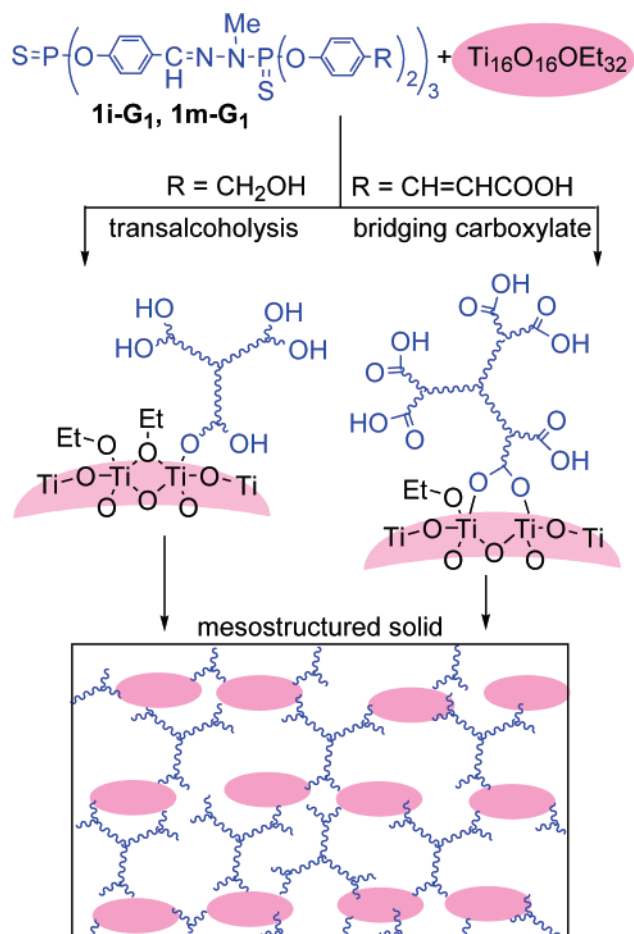


FIGURE 4. Mesostructured solids obtained by assembly of dendrimer **1i-G<sub>1</sub>** or **1m-G<sub>1</sub>** with the cluster  $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$ .

actions between the end groups of the dendrimers: hydrogen bonds,  $\pi$ -stacking, and hydrophilic/hydrophobic interactions can occur, since these phosphorus dendrimers have a hydrophobic interior and a hydrophilic surface (Figure 5). These gels are able to encapsulate a large amount of various substances (up to 30% in weight for nickel acetate) during their formation; these gels could be used for the controlled delivery of active substances.<sup>39</sup>

#### IV. Phosphorus Dendrimers on the Surface of Materials

Depending on the type of end groups, we have shown that phosphorus-containing dendrimers may create various types of networks by supramolecular assemblies. The thiol-terminated dendrimers **1f-G<sub>n</sub>** and **2f-G<sub>n</sub>** may serve as matrix for generating crystals of naked  $\text{Au}_{55}$  clusters starting from  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ . A thin layer of dendrimers induces the formation and the growing of the crystals of clusters and protects them against decomposition (Figure 6).<sup>40</sup> It must be emphasized that numerous previous attempts to generate such crystals failed. These crystals of gold clusters might be promising candidates for future nanoelectronic devices working with quantum dots.

The surface of electrodes can be also modified by dendrimers possessing electroactive end groups. We have

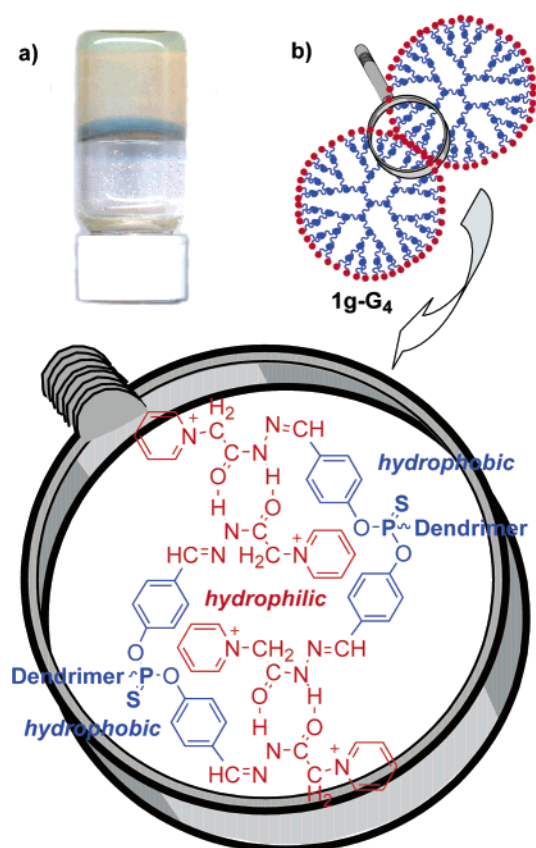
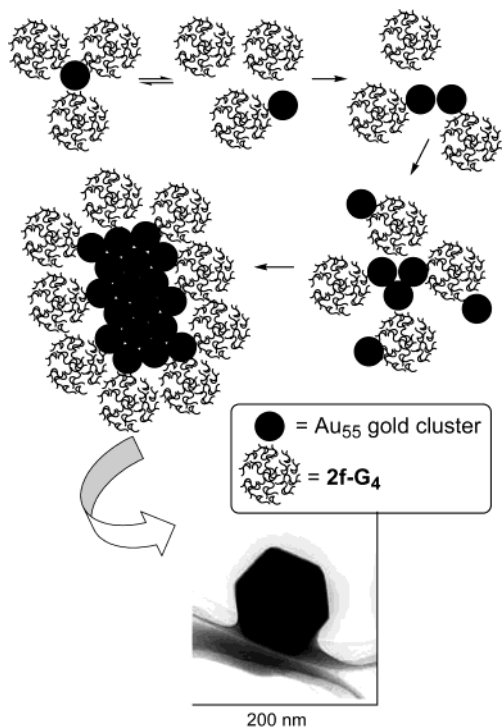


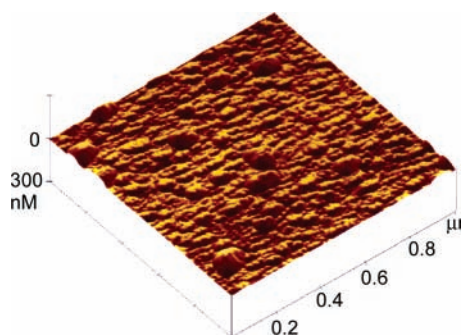
FIGURE 5. Hydrogel (a) in a reversed flask obtained with 1% in weight of **1g-G<sub>4</sub>** in water and (b) possible supramolecular associations of dendrimers **1g-G<sub>4</sub>** creating the network, which imprisons water.

used various ferrocenes<sup>41–43</sup> such as **1e-G<sub>n</sub>**, bithiophene (**1n-G<sub>0</sub>-G<sub>4</sub>**),<sup>44</sup> or TTF (**1o-G<sub>3</sub>**)<sup>45</sup> derivatives and studied their electrochemical behavior by cyclic voltammetry. A deposition of a conducting film of dendrimers onto the electrode is often observed during the oxidation step, whatever the type of dendrimer used.<sup>46–49</sup> This deposit is generally reversible during the reduction step, and the dendrimers are recovered intact in solution. Nevertheless, repeated cycling allows growth of the film on the electrode, thus modifying it. The electrode reversibly modified by electrodeposition of the TTF-crown-ether dendrimer **1o-G<sub>3</sub>** can be used as electrochemical sensor for barium; the crown-ether part of the film made of dendrimers is able to control the reversible complexation/expulsion sequence of  $\text{Ba}^{2+}$ .<sup>45</sup> On the other hand, the oxidation is irreversible with the bithiophene derivatives (**1n-G<sub>n</sub>**) due to an electropolymerization process of these groups with an increasing efficiency when the dendrimer is larger.<sup>44</sup> These electrodes modified by the polymerized dendrimers are highly electroactive in aqueous media, whereas electrodes modified by poly(bithiophene) are almost inactive in these conditions. Such behavior should open interesting perspectives in the field of electrochemically controlled release or electroanalysis.

Dendrimers may also be used to modify the surface of existing materials. These modifications can be irreversible (covalent anchorage) or reversible (ionic anchorage). The surface of quartz plates previously modified by amino-

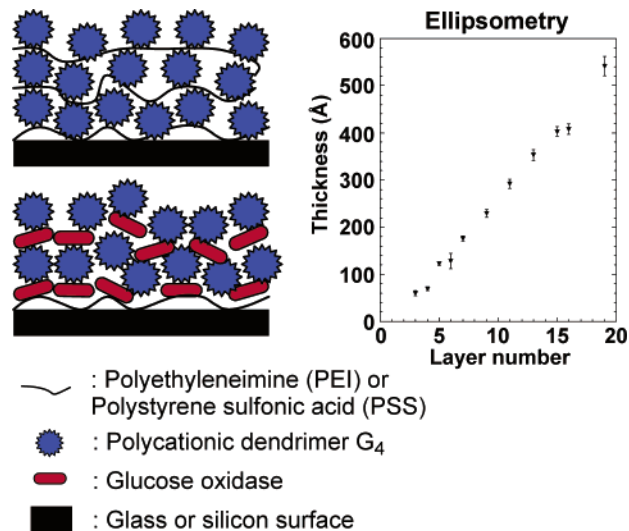


**FIGURE 6.** Method of synthesis of crystals of naked  $\text{Au}_{55}$  gold clusters using dendrimers  $2f\text{-G}_4$  and shape of the crystals obtained.



**FIGURE 7.** Atomic force microscopy (AFM) view of a quartz surface covered by dendrimers  $1b\text{-G}_5$ , and used for the immobilization of human serum albumin (see clusters).

silane reacts with aldehyde-terminated dendrimers such as  $1b\text{-G}_5$ . Several aldehyde groups of each dendrimer are involved in the covalent grafting to the quartz surface; thus dendrimers are strongly bound.<sup>50</sup> A significant lowering of the wettability of the modified plates is observed compared to the untreated plates, showing the hydrophobic character of these dendrimers.<sup>51</sup> Furthermore, many aldehyde functions remain available for further reactions, as shown by the covalent grafting of a second layer of dendrimers having  $\text{NH}_2$  end groups. Interestingly, the plate modified by aldehydic dendrimers can be used for the immobilization of proteins, as shown by the attachment of human serum albumin (Figure 7).<sup>50</sup> A four-generation dendrimer with 96 thiol functions at its periphery was used to generate densely packed monolayers on various substrates such as silicon, by using a special experiment set up.<sup>52</sup> Several monolayers of dendrimers, eventually with other components, can be su-



**FIGURE 8.** Multilayers composed of monolayers of polycationic dendrimers and polystyrene sulfonic acid or glucose oxidase and thickness measured by ellipsometry.

perimposed step by step on a surface, either covalently as shown above or even by ionic interactions when dendrimers having charges on the surface are used.<sup>53</sup> Indeed, hybrid layered assemblies with a control of the internal supramolecular structure at the nanometer level can be built. Surface plasmon field-enhanced fluorescence spectroscopy is used to monitor the luminescent properties of dendrimers with a phthalocyanine core integrated into such a multilayer assembly.<sup>54</sup> Moreover, the build-up of multilayers composed of polycationic phosphorus dendrimers and polystyrenesulfonic acid (PSS) in an alternate way was realized, as well as that of multilayers formed alternately of polycationic dendrimers and glucose oxidase (Figure 8).<sup>53</sup>

We recently applied these results to the elaboration of biochips for the immobilization of biomolecules such as oligonucleotides (Figure 9). Dendrimers are first covalently grafted to the surface of the material in the way described above; then modified oligonucleotides ( $\text{NH}_2$  attached to the 5'-terminus) are grafted to the dendrimer, using the remaining functional groups, to afford the Dendri-chip. If another oligonucleotide having complementary bases and a fluorophore at one end is added, the hybridization is detected by fluorescence. Applying a classical deshybridization process affords again the Dendri-chip. These biochips have two main advantages: first, these chips are particularly stable with time and temperature, in contrast to what was previously reported for DNA chips manufactured with PAMAM dendrimers;<sup>55,56</sup> thus, they can be reused several times (more than 10 times) without any modification of the signal/noise ratio.<sup>57</sup> In addition, the signal/noise ratio is very high and allows a very good detection for amounts of complementary oligonucleotides lower than 1 pmol. This sensitivity is 10- to 100-fold higher than with all the other functionalized glass slides we tested (11 examples).<sup>58</sup> Figure 10 illustrates the comparison between the slides obtained with phosphorus dendrimers having aldehyde end groups, and a commercially available

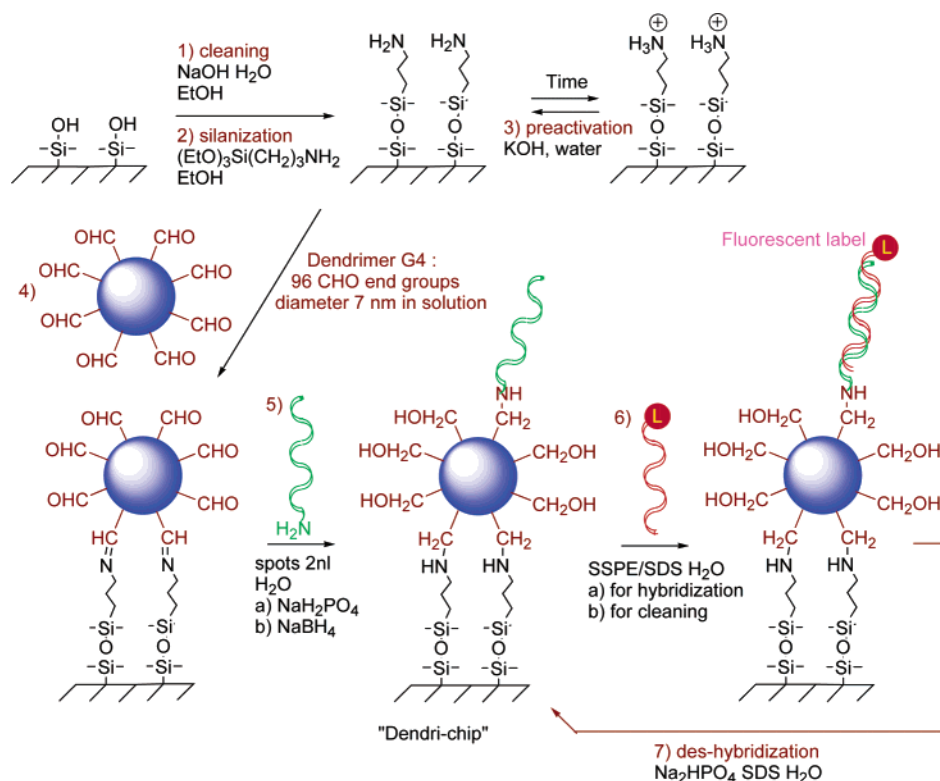


FIGURE 9. Principle of synthesis of biochips using dendrimers and oligonucleotides and the hybridization/deshybridization process.

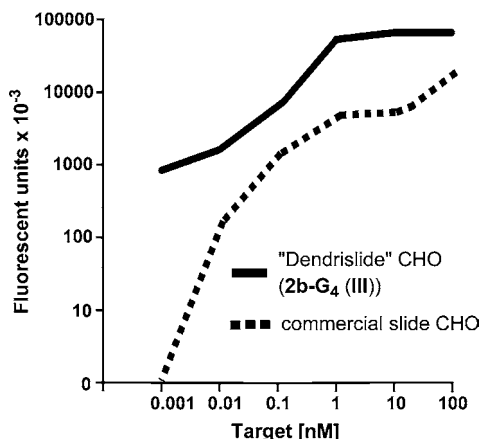


FIGURE 10. Detection sensitivity of a slide having dendrimer **2b-G<sub>4</sub>** as linker (dendrislide) compared with a commercially available slide having small aldehyde-functionalized linkers. A single-stranded 35-mer oligonucleotide (10  $\mu$ M) was spotted on the functionalized slides, then the target Cy-5-labeled 15-mer oligonucleotide was hybridized at concentrations from 0.001 to 100 nM.

aldehyde slide, of which the results are representative of all 11 glass slides tested.

## Conclusion

The extraordinarily versatile behavior of phosphorus gave rise to several hundreds of dendritic macromolecules, and many of them possess interesting properties and applications. Most of them are thermally stable over 300 °C, and some of them exhibit original supramolecular properties, giving thin layers on materials or hydrogels. Applications are already demonstrated in the field of modified surfaces giving sensitive and reliable biochips. Other applications

can be anticipated for the delivery of active substances, as insulating materials, or in the fields of nanoelectronics and (electro)chemical (bio)sensors. In all these cases, the nanometric size of the dendrimers plays a key role, which should be important for future nanotechnologies. Furthermore, the phosphorus dendrimers that we described here bring specific properties in terms of thermal stability, semirigidity of the structure, and ease of functionalization, not only of the end groups but also in all parts of the structure. In addition to the uses related to materials sciences, which were emphasized in this Account, phosphorus-containing dendrimers possess also properties potentially important in catalysis,<sup>59–61</sup> biology, and life science, in particular as transfecting agents<sup>62,63</sup> and anti-proliferation species.<sup>64</sup>

In conclusion, this Account demonstrates that phosphorus-containing dendrimers are not simple curiosities in the field of dendrimers but that they are useful tools for many applications from materials science to biology.

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