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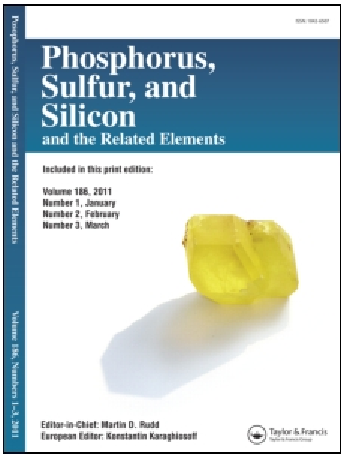

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Phosphorus-Containing Dendrimers: Synthesis and Properties

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# PHOSPHORUS-CONTAINING DENDRIMERS: SYNTHESIS AND PROPERTIES

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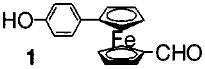
*Several series of phosphorus-containing dendrimers have been designed to study the variation of their properties, depending on the type, the location (surface, branches, core, and cavities), and the number of functions implied.*

*Keywords:* Azobenzene; dendrimer; ferrocene; hydrazone

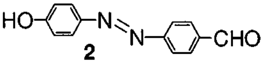
Dendrimers are giant treelike molecules synthesized by the repetition of a sequence of reactions, which allow fine controlling over their size and their architecture.[1] Besides practical applications, they offer the unique opportunity to study how a property or a functionality can be influenced by the location (on the surface, within the branches, at the core, in the cavities) and the number of chemical groups implied (Figure 1).

We described a few years ago a new family of dendrimers based on phosphorus at each branching point, each generation being synthesized in two steps (Scheme 1).[2]

The presence of $P(X)Cl_2$ and CHO end groups allowed us to largely develop the reactivity of the surface, leading to the grafting of a variety of functional groups,[3] including asymmetric derivatives,[4] and catalytic entities.[5] This synthetic process can be modified at several levels. First, several types of compounds, having both a phenol and an aldehyde, can replace hydroxybenzaldehyde. In particular, we have used the ferrocene derivative **1**[6] and the azobenzene derivative **2**.



**1**



**2**

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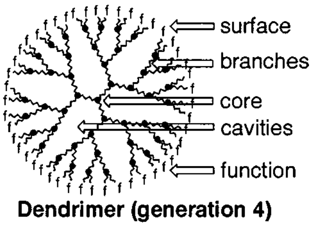
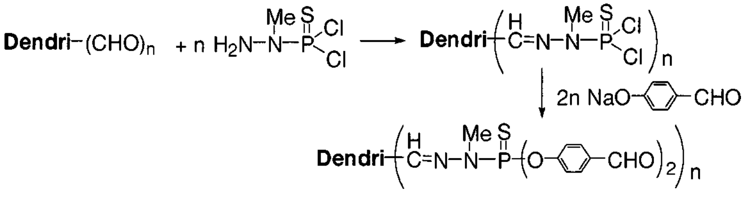


FIGURE 1

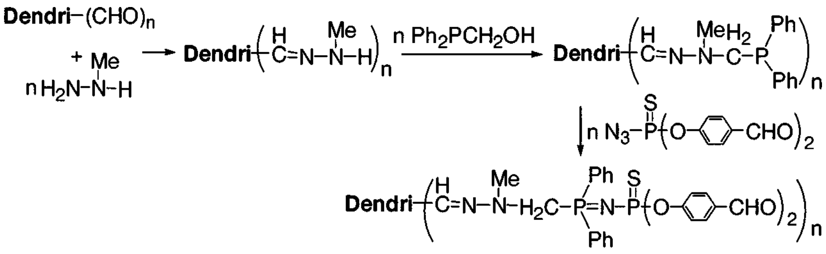
Second, —$CH_2PPh_2$=N— linkages can be "inserted" within the P—N linkages, according to Scheme 2.[7]



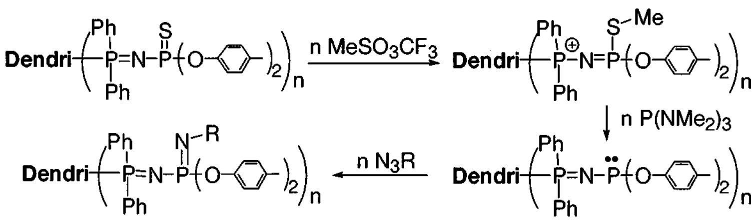
SCHEME 1

This process lengthens the number of steps but induces the formation of P=N—P=S linkages, which open the way to a versatile reactivity beginning in all cases by the alkylation of sulfur by electrophiles. This alkylation induces a weakening of the P—S bond, which is easily cleaved, leading to tricoordinated phosphorus atoms located within the branches. Staudinger reactions with azides allow the grafting of various functional groups inside the dendrimer.[8]

All of these series of dendrimers constitute the ideal "material" to study the variations of the global properties of a dendrimer, depending on the location of each function. Our first report in this field concerned the variation of the dipole moment, which increases exponentially with



SCHEME 2



SCHEME 3

the generation, whereas this value divided by the number of dipolar entities (P=S groups) decreases with the generation.[9]

## INFLUENCE OF FUNCTIONS LOCATED ON THE SURFACE OF DENDRIMERS

We studied the chiroptical properties of dendrimers having chiral entities covalently linked to the surface. The molar optical rotation values for dendrimers increase exponentially with the generation, corresponding to a simple addition of the value found for each chiral group.[4] A similar trend is observed concerning the electrochemical properties of various generations of dendrimers having the ferrocene **1** as end groups.[6] All the ferrocene end groups behave independently, giving rise to a single electrochemical wave whose intensity depends additively on the number of ferrocene groups. Catalytic entities can also be linked to the surface of dendrimers. A very slight increase of efficiency for the catalysis of Knoevenagel reactions and Michael additions is observed on going from the first to the third generation for dendritic ruthenium derivatives.[5]

## INFLUENCE OF FUNCTIONS LOCATED WITHIN THE BRANCHES OR AT THE CORE

When the ferrocene derivative **1** is used as building block of the skeleton, two waves are observed in electrochemistry: one for the oxidation of the ferrocenes on the surface and one for all the internal ferrocenes, due to a different electronic influence of aldehyde and hydrazone on the ferrocene. However, the progressive burying of the ferrocene within the structure induces its progressive reluctance to be oxidized for a dendrimer having one ferrocene located at the core.[6]

Analogous trends are observed for the photochemical behavior of dendrimers having the azo derivative **2** at various levels. We have shown both a progressive reluctance of the azo groups to undergo the photoisomerization (E→Z) and the thermal back isomerization (Z→E), when the azo groups are progressively buried within the dendrimer.

## INFLUENCE OF FUNCTIONS LOCATED WITHIN THE CAVITIES

In order to be sure that the functions to be studied will stay within the cavities, these functions are covalently linked to the skeleton of the dendrimer, using a sufficiently large and flexible linker to avoid close interactions with the dendritic structure. For this purpose, we used the series of reactions described in Scheme 3, the R substituent being $P(S)[OC_6H_4CH{=}NNHC(O)(CH_2)_3pyrene]_2$. The property studied in this case is the modification of fluorescence induced by interactions between pyrene groups. No difference was observed between the values obtained for this dendrimer and a model compound having such linkage. This implies that the pyrene derivative can move as freely in the dendrimer than in the model in solution. Such behavior confirms our previous results, which show that small molecules can go freely inside a dendrimer,[7,8] and that very large molecules such as second generation dendrons can be grafted inside a dendrimer.[10]

Thus, the use of a single family of phosphorus-containing dendrimers easily tunable to precisely the place of desired functions allowed us to demonstrate that the variation of properties is influenced by the location of the functions, their number, the generation, and the electronic properties of the substituents.

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