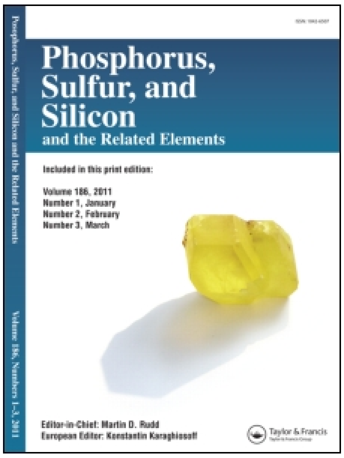

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Phosphorus-Containing Dendrimers: Towards Applications

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PHOSPHORUS-CONTAINING DENDRIMERS: TOWARDS APPLICATIONS

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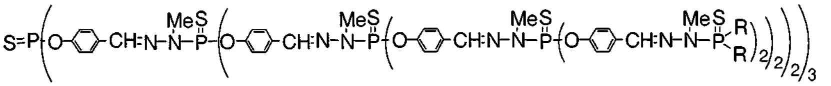
The properties and applications of phosphorus-containing dendritic macromolecules in various fields, including material science and biology, are reported.

Keywords: Dendrimer; dendron; electrode; gel; materials; transfection

The exponential increase of interest observed within the last ten years for the monodisperse hyperbranched polyfunctional polymers, called dendrimers, is directly linked to the unusual properties expected for such compounds.[1] Indeed, their surface can be easily modified by various functional groups, thus modifying the global properties of the macromolecule. Seven years ago, we designed a series of phosphorus-containing dendrimers easily tunable to place precisely particular functions on the surface, within the framework, and at the core.[2] Furthermore, we are able to synthesize various types of dendritic macromolecules, including dendrons and asymmetrical dendrimers.[3]

The type of linkage we most generally use for these phosphorus-containing dendritic macromolecules is depicted on Scheme 1 for a fourth generation dendrimer.



SCHEME 1

Address correspondence to J.-P. Majoral, Laboratoire de Chimie de Coordination, 205 route de Narbonne, 31077 Toulouse cedex 4, France.

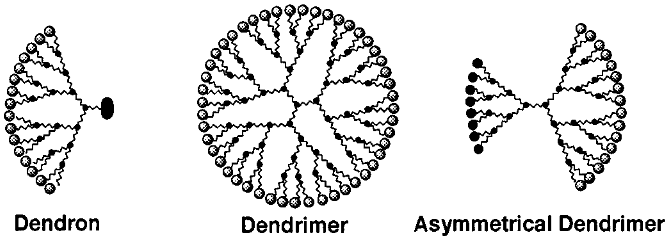


FIGURE 1

We have shown that the solubility and thermal stability as well as the properties of these compounds depend mainly on the type of end groups.

PROPERTIES OF DENDRITIC MACROMOLECULES SOLUBLE IN ORGANIC SOLVENTS

We mainly used dendrimers soluble in organic solvents in the field of material science. The first interactions of dendrimers with materials that we experienced consisted of covalently grafting dendrimers that have aldehyde end groups ($R = OC_6H_4CHO$) on the surface of quartz plates modified by 1,3-silylamines. A monolayer of dendrimers was obtained, as shown by Atomic Force Microscopy. These plates modified by dendrimers on the surface constitute a first step towards biosensors; for instance, human serum albumine interacts with this surface.[4] The surface of electrodes can be also modified using electroactive dendrimers, having TTF derivatives as end groups. They are reversibly deposited on the surface of electrodes during oxidation; these modified electrodes can be used as sensors for Ba^{2+}.[5]

The second type of interaction between dendrimers and material science consists of incorporating the dendrimer in the material—the dendrimer acts as a template for the formation of the material. We choose to induce covalent interactions in order to ensure the incorporation of dendrimers in the bulk. Dendrimers having either alcohol or carboxylic end groups react with the titanium cluster $Ti_{16}O_{16}(OEt)_{32}$ via either transalcoholysis or the formation of bridging carboxylate. In

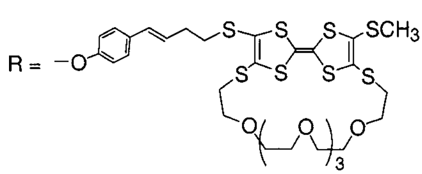


FIGURE 2

both cases, a mesostructured material is obtained, constituted of locally ordered arrays of clusters bridged by dendrimers.[6] In these cases, the interactions of dendrimers and material use the functions located on the surface of the dendrimers. Another approach consists of using only a single function located at the core of a dendron in order to keep free the functions located on the surface. For this purpose, dendrons possessing a triethoxysilyl group at the core and various types of functions on the surface were used. The triethoxysilyl group is able to undergo a sol-gel process in the presence of water and $Si(OEt)_4$. The result is the obtaining of functionalized silica, the dendrons being incorporated in the bulk through the C—Si—O linkage located at the core. The functions located on the surface of the dendrons remain free and should be accessible, since some of these silica have been shown to be mesoporous with a narrow pore size distribution.[7] Depending on the type of these functions, various properties are expected, as in heterogeneous catalysis.

PROPERTIES OF WATER-SOLUBLE DENDRIMERS

We have shown that water-soluble dendrimers offer the largest palette of properties and uses, ranging from material science to biology. First, water-soluble phosphorus-containing dendrimers having quaternary ammonium salts as end groups (types **A** and **B**) are able to react by ionic interactions with glass surfaces modified by polyanions. The alternate use of polyammonium dendrimers and polyanions allows the successive deposit of a monolayer at each step.

The same type of water-soluble dendrimers can be used as formulating agents. When c.a. 1.5% in weight of these dendrimers (types **A** and **B**) are dissolved in water and then heated, a translucent gel is obtained within a few days. Despite the presence of 98.5% of water (1 molecule of the fourth generation dendrimer “freezes” around 70,000 molecules of water!), this gel is solid and can be crushed into pieces. The formation of this gel is reversible neither thermally nor by adding a large excess of water. However, addition of acetonitrile dissolves the gel, leading to a solution that can be gelled again by the slow removal of acetonitrile. Several water-soluble components can be added to the solution prior to gelation and are incorporated during the gelation process.

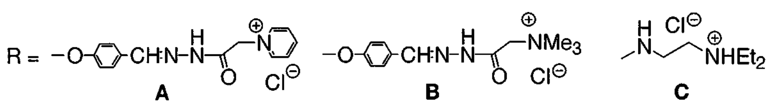


FIGURE 3 Types of end groups used for water-soluble dendrimers.

Lyophilization of these hydrogels gives fragile aerogels, which have almost retained the size and shape of the initial hydrogels.[8]

Other types of water-soluble dendrimers possess interesting transfection properties. The experiments were done on NIH 3T3 cells in the presence of serum for the transfection of the luciferase gene. It was shown that the transfection efficiency depends both on the type of ammonium salt linked to the surface of the dendrimer and on the generation used. The best results are obtained for pH sensitive ammonium groups (Type **C**) linked to the fourth generation dendrimer.[9]

In conclusion, we have shown that phosphorus-containing dendritic macromolecules possess a lot of interesting and unusual properties seldom found in other types of molecules. Work is in progress to continue to develop these applications of dendrimers in various other fields, such as catalysis[10] or drug delivery.[11]

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