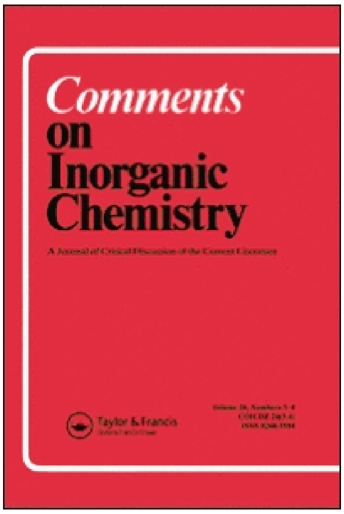

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Organically Functionalized Metallic Oxo-Clusters: Structurally Well-Defined Nanobuilding Blocks for the Design of Hybrid Organic-Inorganic Materials

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Hybrid organic-inorganic materials, in which organic and inorganic components are combined over a length scale ranging from a few Angstroms to a few tens of nanometers, are nanocomposites which offer huge potentialities for high added value applications. Numerous hybrid organic-inorganic materials have been developed in the past few years, mainly by taking advantage of the mild chemical conditions of the sol-gel process. Yet, the sol-gel process generally yields amorphous materials which exhibit some polydispersity in the size and composition of the inorganic components of the hybrids. Moreover, controlling the interactions between the inorganic and organic components is not an easy task. One possible solution to overcome the polydispersity problem and achieve better control of the interactions is to use perfectly defined inorganic nanobuilding blocks such as metal oxo-clusters which exhibit sizes around 10 Å. When properly functionalized, they can be assembled, without being damaged, into various types of structures. Examples taken from polyhedral oligomeric silsesquioxanes, monoorganotin oxo-clusters, transition metal oxo-clusters and organically modified polyoxometalates will be presented and discussed relative to their synthesis, functionalization and assembling strategies.

Keywords: *hybrid materials, nanobuilding blocks, sol-gel, polyhedral oligomeric silsesquioxanes, monoorganotin oxo-clusters, transition metal oxo-clusters, organically modified polyoxometalates*

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I. INTRODUCTION

Organic-inorganic hybrids are materials in which organic components and inorganic components, generally oxo-polymers, are intimately mixed.[1] Because these materials are designed at the molecular or at a low molecularity level, at least one of the components exhibits a size ranging from a few Angströms to a few tens of nanometers. These materials are nanocomposites which offer tremendous pontentialities for applications with high added values. The dispersion of organic molecules, such as dyes, into mineral matrices or, conversely, the dispersion of sub-micronic mineral fillers into organic polymers are two simple examples. Indeed, the proposed definition is very general and covers a huge variety of combinations that seems only limited by the imagination and the skill of the chemists of different communities.

A simple classification, based on the nature of the links and interactions that the organic and inorganic components exchange, has been proposed for hybrid materials.[1h] Two main classes have been defined. Class I corresponds to all the systems where there are no covalent or iono-covalent bonds between the organic and inorganic components. In such materials, the various components only exchange interactions such as van der Waals forces, hydrogen bondings or electrostatic forces. On the contrary, in class II materials, at least parts of the organic and inorganic components are linked through strong chemical bonds (covalent or iono-covalent).

The properties that can be expected for such materials depend evidently on the chemical nature of their components, but they also depend on the synergy of these components. Thus, the interface in these nano-composites is of paramount significance, and one key point of their synthesis is the control of this interface.

Even though several hybrid materials, such as polysilsesquioxanes (T-resins),[2] have been used for a long time, an increase in the variety and complexity of the combinations of organic and inorganic components has appeared in the past ten years. This rise is mainly associated with the strong interest devoted to this field by the sol-gel community.[3] Indeed, the mild chemical conditions of the sol-gel process (low temperature, organic solvents, molecular precursors) make compatible "fragile" organic compounds, syntheses of organic polymers and building of mineral frameworks, such as oxo-polymers. Moreover, films, fibers and monolithic pieces can be easily prepared by taking advantages of the sol-gel process.[3a]

In the first part of this review article, a brief background of the chemistry involved in the sol-gel process will be presented. Some examples of class I and II materials, in which the inorganic component is prepared from molecular precursors, such as alkoxides or organically modified alkoxides, will also be given. In the second part, the building of hybrid materials from preformed inorganic nano bricks will be discussed on examples taken from the chemistry of polyhedral oligosilsesquioxanes, modified polyoxometalates, monoorganotin oxo-clusters and transition metal oxo-clusters.

II. SOL-GEL CHEMISTRY AND HYBRID ORGANIC-INORGANIC MATERIALS

II.A. Sol-Gel Chemistry Background

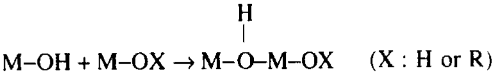
Sol-gel process in organic media mostly used metal alkoxides, $M(OR)_n$, as molecular precursors.[4] M represents a metal, n is its valence or oxydation state, and OR is an alkoxy group which corresponds to a deprotonated alcohol. From these precursors, the sol-gel process allows the synthesis, in solution, of oxo or hydroxo macromolecular species through inorganic polymerization reactions.[3] The first step of this polymerization corresponds to the introduction of a hydroxy group on the metal by hydrolysis of an alkoxy group :

$$\mathrm{M-OR+H_2O \longrightarrow M-OH+ROH}$$

The formation of the inorganic framework can then proceed by oxolation (formation of an oxo bridge) which is a condensation reaction in which water or alcohol is eliminated :

$$\mathrm{M-OH+XO-M \longrightarrow M-O-M+XOH} \qquad \mathrm{(X : H\ or\ R)}$$

For the metals which can exhibit coordination numbers higher than their valence, actually almost any but silicon, the inorganic framework can also result from olation (formation of an hydroxo bridge) which corresponds to an addition reaction :



$$\mathrm{M{-}OH + M{-}OX \rightarrow M{-}\overset{\overset{\displaystyle H}{|}}{O}{-}M{-}OX} \qquad \mathrm{(X : H\ or\ R)}$$

The structure and morphology of the final inorganic framework strongly depend on the relative contribution of these three reactions (hydrolysis, oxolation, olation).[3] The formed oxo-polymers can exhibit highly branched structures. If some of them reach macroscopic sizes, the reaction bath turns into a gel in which the solvent, side products and smaller oxo-polymers are trapped.[3,5] The growth of the oxo-polymers can also be limited, by poisoning for instance, and sols made of small entities remaining in suspension are obtained. Precipitates can also be obtained when the growing oxo-polymers become incompatible with the solvent.[6] The control of the growth of the oxo-polymers, and consequently the tailoring of their structures and mophologies, is mainly achieved through chemistry.[1,3] The principal parameters are the nature of the metal, with a quite clear cut between silicon and other metals, the nature of the alkoxy groups, the degree of oligomerization of the precursors (monomer, dimer, trimer, etc.), the solvent, the temperature, the hydrolysis ratio (H_2O/M), the use of catalysts (acid, basic, nucleophile) or of complexing ligands.

The drying, which leads to xerogels, is also a crucial step towards the final materials.[7] First of all, the reactions involved in sol-gel process are generally partially equilibrated. Therefore, removing the volatile components (water, alcohol, solvent) induces a chemical evolution. Moreover, this evolution generally depends on the elaboration conditions: a thin film or a monolithic piece, prepared from the same chemical system, will likely exhibit different inner structures. On the other hand, the capillary pressures, which result from the evaporation of the volatile components, strongly stress the inorganic framework, and cracking or shattering of the materials upon drying are frequently observed.

II.B. Class I Hybrid Materials: Some Examples

Metal alkoxides, $M(OR)_n$, are pertinent precursors for the inorganic component of class I hybrid materials.[1] Indeed, organic molecules can be mixed, in a common solvent, with metal alkoxides prior to their hydrolysis.[8] With such a procedure, organic dyes such as rhodamins, pyranins, coumarins or molecules exhibiting non-linear optical properties have been incorporated into silica, aluminosilicate and more seldomly transition metal oxides matrices.[9]

Silicon, titanium or zirconium alkoxides can also be mixed with various polymers disolved in alcohol or tetrahydrofuran (THF).[10] Hydrolysis of such systems can lead to the in-situ formation of a mineral filler.

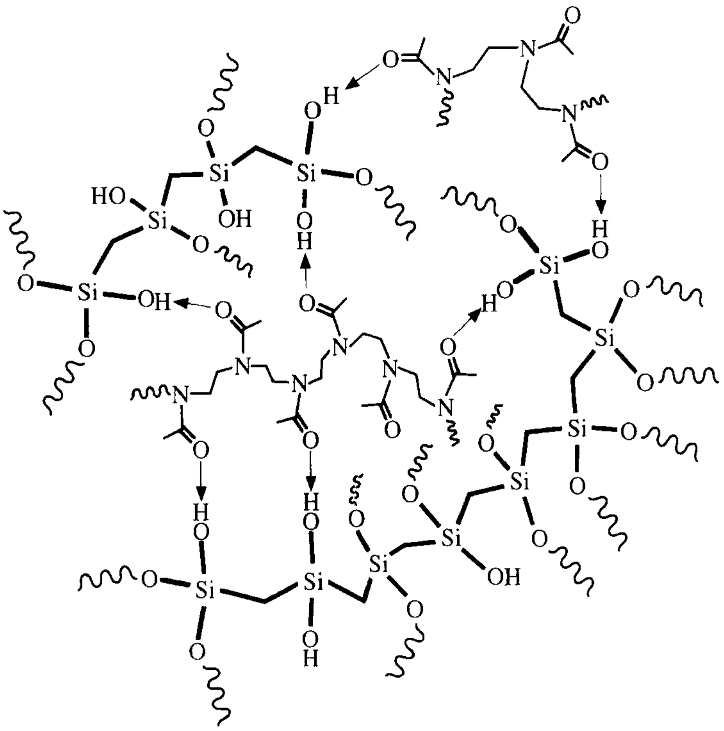
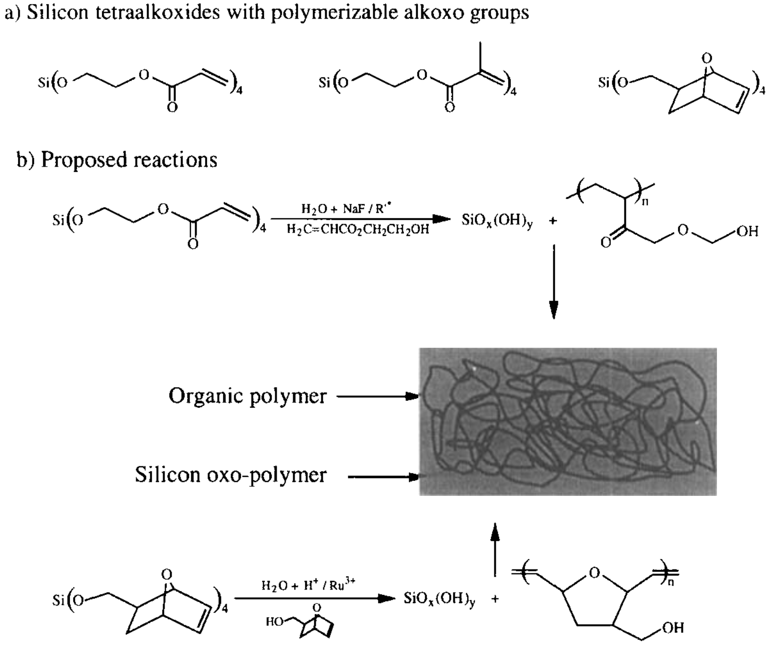


FIGURE 1 Schematic structure of a class I hybrid organic-inorganic material made of silica oxo-polymers and poly(2-methyl-2-oxazoline) (Ref. 10h). Hydrogen bonds are drawn as arrows

This route, as generally evidenced by the transparency of the materials, results in smaller and more homogeneously dispersed inorganic particles, compared to the conventional blending, under high viscosity conditions, of polymers and preformed inorganic filler.[11] The chemical control of the organic/inorganic interface allows to avoid, or adjust, the phase separation. Thus, with polymers such as poly(2-methyl-2-oxazoline)[10h] or poly(N-vinylpyrrolidone)[10j], the formation of hydrogen bonds between the carbonyl groups of the polymer and the hydroxy groups, generated upon hydrolysis of the metal alkoxides, allows a good compatibility between both components, even for high amounts of the inorganic component (Fig. 1). These materials once dried are colorless and transparent, ascribed to the interpenetration of both frameworks at a molecular level.

As a last example of class hybrid materials, those prepared by B. Novak *et al.*, where two frameworks are simultaneously grown and interpenetrate each other, are worth mentioning.[1a,12] To minimize the shrinkage commonly observed in sol-gel process when going from the gels to the dried materials, silicon alkoxides in which the alkoxy groups could be polymerized were used. Moreover, the solvent was the parent alcohol, thus also able to polymerize. Therefore, the precursors, the solvent and the side products of the hydrolysis-condensation reactions were all involved in the formation of the final hybrid materials (Fig. 2). With such systems and a control of the kinetics of both polymerizations (organic and inorganic), quite large monolithic pieces were prepared in a wide polymer/silica composition domain.


a) Silicon tetraalkoxides with polymerizable alkoxo groups

b) Proposed reactions

FIGURE 2 Silicon alkoxides (a) and reactions (b) proposed for the simultaneous formation of interpenatrating organic and inorganic networks (class I) (Ref. 12)

II.C. Class II Hybrid Materials: Precursors and Examples

II.C.1. Precursor for class II hybrid materials

If the few M-OR bonds which usually remain after hydrolysis are neglected, the alkoxides $M(OR)_n$ do not allow us to establish strong chemical bonds between the inorganic and the organic components. Thus, for class II hybrid materials, heterofunctional precursors, such as those described by the formula RMX_{n-1}, are needed.[1] In these precursors, X represents groups (OR, Cl,...) that will be hydrolyzed to yield the inorganic framework. On the contrary, R represents organic groups which are bound to the metal in such a way that they are not removed upon hydrolysis. The link can be a M-C bond if the metal electronegantitivity allows it, such as for silicon and tin. For transition metals, this type of bond being unstable toward hydrolysis, other types of links have to be used.

II.C.1.a Silicon compounds

For silicon, a large number of precursors corresponding to the formula $RSi(OR')_3$ are commercially available and have been used for a long time in industry.[13] They can be prepared by hydrosilylation with $HSi(OR')_3$ or $HSiCl_3$, followed in the latter case by the replacement of the chlorines by alkoxides groups:

$$HSiX_3 + H_2C = CH - R'' \longrightarrow R'' - CH_2CH_2 - SiX_3 \quad (X : OR' \text{ or } Cl)$$

$$R'' - CH_2CH_2 - SiX_3 + 3R'OH \longrightarrow R'' - CH_2CH_2\text{–}Si\,(OR')_3 + 3HCl$$

For some complex organic moieties, the alkene $H_2C{=}CHR''$ is not always available or can not be used. Substitution or addition reactions on precursors such as $(R'O)_3Si(CH_2)_3Cl$, $(R'O)_3Si(CH_2)_3N{=}C{=}O$ or $(R'O)_3Si(CH_2)_3O_2CC(CH_3){=}CH_2$, prepared by hydrosylilation, are the usual alternative.[14] As an example, the addition of an alcohol on an isocyanate functionalized trialkoxysilane is presented below :

$$(R'O)_3\,Si\,(CH_2)_3\,N = C = O + HOR \longrightarrow (R'O)_3\,Si\,(CH_2)_3\,NH - CO_2R$$

The reactions between $(R'O)_3SiCl$ and a grignard reagent or an organolithium were also used in some specific cases.[15] Actually, almost any organic moieties or organometallic fragments[16] can be linked to silicon through a bond stable toward hydrolysis, resulting in a huge variety of precursors for silicon based class II hybrid materials.

II.C.1.b Tin compounds

As silicon, tin can form with carbon chemical bonds which are stable toward hydrolysis.[17] However, precursors such as $RSnX_3$ (X=Cl or OR′) have been less studied than their silicon analogs. Indeed, only the trichlorotins where R is CH_3, n-C_4H_9 or C_6H_5 are commercially available. Recently, B. Jousseaume *et al.* have developped syntheses for new functionalized trichloro-organostannanes.[18a] These precursors are prepared in a two steps route. First, the target organic group is bound onto a tricyclohexylstannyl moiety, Cy_3Sn, by coupling the corresponding chloride with a Grignard reagent or by hydrostannation :

$$\mathrm{Cy_3SnCl + RMgX \longrightarrow Cy_3SnR + MgClX}$$

$$\mathrm{R:(CH_2)_{2-3}\,CH{=}CH_2,\ (CH_2)_3\,CCl{=}CH_2,\ p{-}C_6H_4CH{=}CH_2}$$

or

$$\mathrm{Cy_3SnH + H_2C = CHR \longrightarrow Cy_3SnCH_2CH_2R}$$

$$\mathrm{R:(CH_2)_{1-4}\,OH,\ (CH_2)_{1-3}\,OAc}$$

The second step is a redistribution with tin tetrachloride, where the Sn-R bond is cleaved and reformed :

$$\mathrm{Cy_3SnR + SnCl_4 \longrightarrow RSnCl_3{+}Cy_3SnCl}$$

The targeted trichloroorganotins are finally isolated and purified by liquid-liquid extraction and distillation.

For some of the organic groups (3-butenyl, 4-pentenyl and 4-vinylphenyl), the trichloroorganostannanes were successfully transformed into trialkoxides by reaction with a tertiary alcohol in the presence of diethylamine:

$$\mathrm{RSnCl_3{+}3HOR'{+}3HNEt_2 \longrightarrow RSn\left(OR'\right)_3 {+}3HClHNEt_2}$$

$$\mathrm{R{:}(CH_2)_{2-3}CH{=}CH_2,\ p{-}C_6H_4CH{=}CH_2\ and\ R'{:}C\,(CH_3)_2C_2H_5}$$

The functional trichloroorganotins can also be transformed into trialkynylorganotins by reaction with alkynyllithium:[18b]

$$\mathrm{RSnCl_3{+}3R' - C \equiv C - Li \longrightarrow RSn\left(-C \equiv C' - R'\right)_3 {+}3LiCl}$$

$$\mathrm{R:(CH_2)_2\,CO_2CH_3,(CH_2)_{3-5}\,OAc,(CH_2)_5\,O_2CHC = CHCH_3}$$

$$\mathrm{and\ R'{:}\ Me\ or\ Bu}$$

These latter compounds appear to be interesting precursors for tin-based class II hybrid materials. Indeed, the Sn-C(sp) bonds can be hydrolyzed at room temperature and without any catalyst. Moreover, the oxo species which are formed are similar to those obtained from alkoxides.[18b] Finally, the hydrolysis by-product is a gas (low molecular weight alkyne) and, therefore, can be easily removed from the reaction medium.

II.C.1.c Transition metal compounds

For more electropositive metals, such as transtion metals, the M-C bond has too ionic character and is not stable toward hydrolysis, making it useless for class II hybrid materials prepared by the sol-gel process. For metals such as Ti, Zr, Al, V, Nb, Ce, Sn, the alternative links generally used are those formed by the reactions with strong complexing ligands (SCL), such as the ones obtained by deprotonation of β-diketones β-ketoesters, α-hydroxyacids, α-aminoacids or carboxylic acids.[19] The synthesis of such modified precursors is classically achieved from the alkoxides and the protonated ligands :

$$M(OR)_n + xHSCL \longrightarrow M(OR)_{n-x}(SCL)_x + xROH$$

These ligands being bidentate, the complexation will cause an increase of the metal coordination. Moreover, the formation for many of these ligands of a metallo-cycle containing 5 or 6 bonds considerably increases the strength of the M-SCL link (Fig. 3) toward hydrolysis. The hydrolysis of these new modified precursors will mostly, if not exclusively, involve the alkoxy groups. It is worth mentioning that prior to offering acces to class II hybrid materials with transition metals, the strong complexing ligands have been widely used to control the reactivity of transition metal alkoxides.[3,20] Indeed, those ligands allow us to reduce the inorganic functionality and act as a poison toward the growth of the oxo-polymers.

II.C.2 Some examples of class II hybrid materials

A huge quantity of class II organic-inorganic hybrid materials have been described in the literature and review articles.[1] Most of these materials have been prepared by the sol-gel process from the heterofunctional precursors previously discussed. Often, in order to increase the amount of inorganic component, simple akoxides, $M(OR')_n$, from the same or

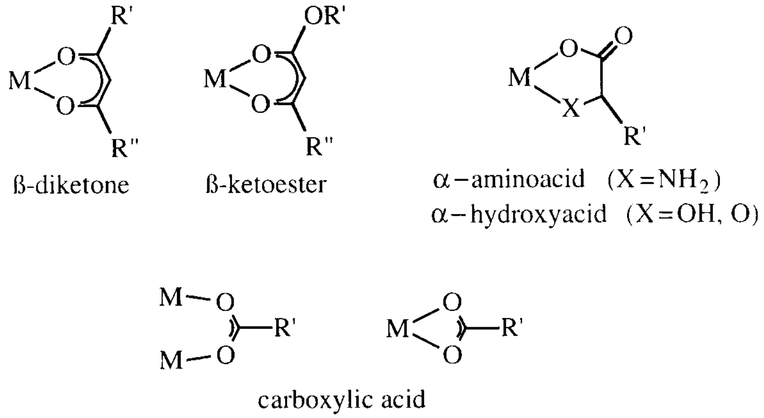


FIGURE 3 Some examples of complexing ligands used to prepared transition-metal-based class II hybrid materials

other metals, are co-processed. Some of these hybrid materials have even been given special names such as ORMOSIL (ORganically MOdified SILicates) and ORMOCER (ORganically MOdified CERamics).[21]

In these class II hybrids, the organic groups, R, which are not hydrolyzed can play different roles.

(i) These groups can bear no peculiar function, as alkyl or aryl groups bond to silicon or tin, or complexing ligands such as acetylacetone on transition metals. These groups will mainly act as (inorganic) network modifiers. These groups can have major importance for the kinetics or the control of the hydrolysis-condensation reations.[3,22] Moreover, and even though no peculiar function is present, the organic group can bring some special properties, such as hydrophobicity or plasticity, to the final material.[23] This type of class II hybrid material is generally a good matrix to host small organic molecules, optically active, for example.[24]

(ii) The R groups can also bear an active molety, but is not polymerizable. R acts again as a network modifier, but it will give to the final materials some specific property. A large number of this type of class II hybrid materials have been elaborated, mostly with silicon. Among the active parts used, one can mention: various chromophores for very different optical applications (non-linear optics, information storage, laser),[24] crown-ethers for transportation of ions through membranes[25] or organometallic fragments for catalysis.[16]

(iii) Finally, the R groups can bear a polymerizable function (i.e., methacrylate, epoxy) and therefore allow us to build an organic polymer along with the oxo-polymer. R will be considered a network former, yet, not being hydrolyzed, it will also act as a network modifier. The very large majority of works on this type of materials has been carried out on silicon and the principal applications are in protective coatings.[26]

To clarify the double role (former/modifier) played by such R groups, the hybrid systems derived from zirconium n-propoxide complexed by acetoacetoxyethylmethacrylate (AAEM) are good examples.[19e,f] In those systems, the heterofunctional precursor can be globally written as $Zr(OPr^n)_{4-x}(AAEM)_x$, where x represents the complexation ratio. Actually, when x goes from 0 to 1 two major species are in equilibrium: $Zr(OPr^n)_4$ and $Zr(OPr^n)_3(AAEM)$, if oligomerization is neglected. Changes of x correspond to modifications of the relative proportion of both precursors. The complexing ligand which allows the formation of the organic polymer also limits the growth of the oxo-polymers by reducing the inorganic functionality of the precursor toward hydrolysis. Conversely, the growth of the oxo-polymers hinders, mainly by steric effects, the growth of the poly(AAEM). Both polymerizations appear interdependent. Indeed, when the hydrolysis and the polyaddition (free radical) of $Zr(OPr^n)_{4-x}(AAEM)_x$ solutions are simultaneously initiated, the semi-local structure of the so-obtained hybrid systems depends on the complexation ratio (Fig. 4). For a low complexation ratio, quite dense and large oxo-polymers are associated by short poly(AAEM) chains. On the contrary, for a large complexation ratio, smaller and more tenuous oxo-polymers cross-link comparatively longer poly(AAEM) chains.

An other interesting example of class II hybrid materials is those related to the special heterofunctional precursors (Fig. 5a) in which two or more trialkoxysilyl groups cap, through Si-C bonds, a molecular organic spacer such as a phenyl, a biphenyl, an alkene or an alkyne.[1d,15,27] Hydrolyzing such precursors results in bridge

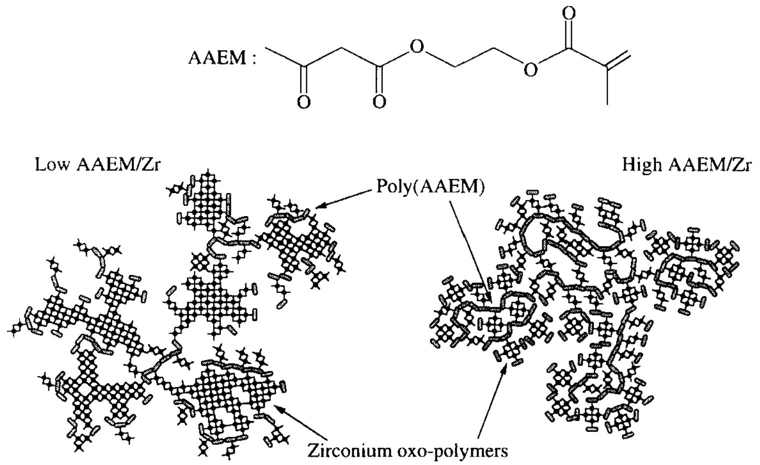


FIGURE 4 Schematic structures of class II hybrid materials made from zirconium n-propoxide complexed by the acetoacetoxyethylmethacrylate (AAEM) (Refs. 19e and 19f)

polysilsesquioxanes (Fig. 5b). Precursors with various functionality and rigidity have been mainly developed to prepare materials of tailored porosity. Yet, controling the porous volume and the specific area of the resulting materials is not an easy task, as they have been shown to depend not only on the precursor geometry, but also on the chemical conditions of the hydrolysis (solvent, catalysis,...)[15] Interestingly, when precursors based on $(RO)_3Si\text{-}C{\equiv}C\text{-}$ moieties are used, the organic spacers can be removed once the inorganic network has been formed by hydrolysis-condensation. Indeed, the Si-C(sp) bonds can be softly cleaved by methanol with mild heating (60°C) and F^- ions as catalyst.[27a,b]

Several hybrid materials have also been developed from preformed polymers end-capped by trialkoxysilyl groups. Polymers such as poly(dimethylsiloxane), poly(tetramethylene oxide) and poly(aryleneetherketone) have been used. Hydrolysis-condensation of such end-capped polymers allows cross-linking and strong grafting to silica or transition metal oxo-polymers used as mineral fillers or matrices, depending on the relative proportions.[11,28]

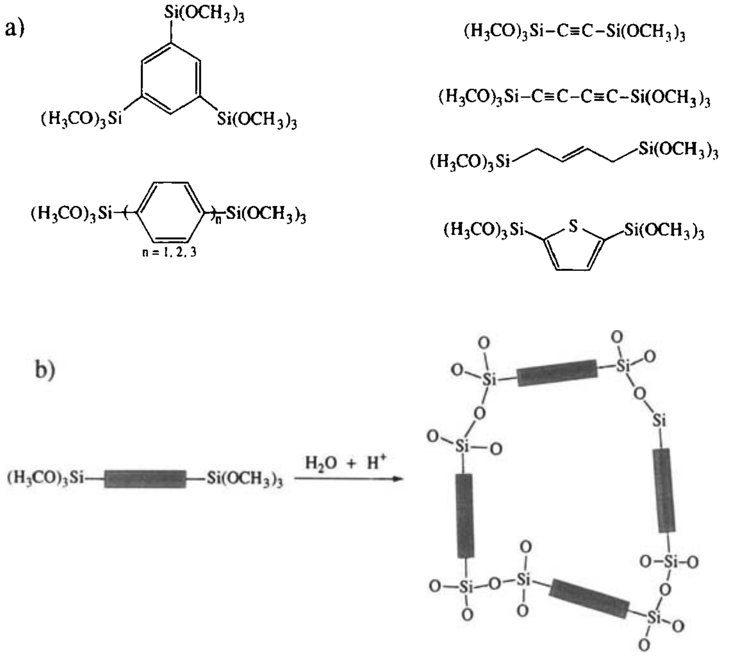


FIGURE 5 Some precursors for bridged polysilsesquioxanes (a), and schematic structure of these bridges polysilsesquioxanes (Refs. 1d, 15 and 27)

III. CLASS II HYBRID MATERIALS BY ASSEMBLING WELL-DEFINED INORGANIC NANOBUILDING BLOCKS

As briefly shown in the previous part, a wide spectrum of hybrid materials can be prepared by hydrolysis-condensation of various heterofunctional precursors. Yet, even though the understanding of the rules that control the growth and the morphology of the oxo-polymers synthesized by the sol-gel process is continuously improved,[3,20] those materials commonly exhibit some polydispersity in the size and composition of their components. Indeed, upon the hydrolysis of alkoxide solutions, large oxo-polymers, responsible for the gelification, are formed, but smaller condensed species are also present.[3,5,6] Such size distributions, even though they did not hamper the synthesis of new materials, might raise problems in preparing materials with perfectly defined properties. Moreover, they could make difficult a fine understanding and modeling of the structure/physical properties relationships in organic-inorganic materials.

One way to achieve some control over the growth and morphology of inorganic materials, obtained from molecular precursors, is the use of organic templates which self-organized into complex structures.[29] The use of perfectly calibrated preformed objects that keep their integrity in the final material is also a method to reach a better definition of the inorganic component. In the hundreds nanometers range, colloidal metal oxides can play this role of calibrated preformed entities.[29d–f] Metal-oxo clusters, which exhibit much smaller sizes (5–25 Å), are another possibility which has already been used for hybrid materials. Those works have mainly dealt with class II hybrid materials, therefore exhibiting strong chemical links between the inorganic and organic components.

The different steps of such a route are first to prepare, with the higher possible yields, to isolate and to functionalize, if necessary, the nanobuilding blocks. Then they have to be assembled in a controlled way to elaborate a material. Such an approcah is close to the one classically followed in polymer science where more or less complex monomers are first prepared and then assembled or co-assembled through polymerization reactions. In the following, only nanometer size bricks based on M-O-M frameworks will be presented.

III. A. Synthesis of Various Nanobuilding Blocks

Silicon, tin or transition metal chemistry offer a large number of metal oxo-clusters with sizes ranging from 5 to 25 Å, which are potential nanobuilding blocks for hybrid materials.

III.A.1. Nanobuilding blocks based on silicon

The silicon-based nanobuilding blocks used so far in the preparation of hybrid materials are those related to the cage structures following the general formula $(XSiO_{1.5})_n$, in which n is an even number ranging from 6 to 18.[30] The X groups point toward the outside of the cage (Fig. 6). In these compounds, as very often, silicon is four-coordinate The most studied nanobrick for hybrid materials is the one containing eight silicon atoms. It exhibits an almost cubic shape with one silicon atom at each corner. The oxygen atoms are at the center of the edges, slightly shifted toward the outside.[31]

Within the general formula $(XSiO_{1.5})_n$, a classification can be made on the nature of the X groups. They can be hydrogen atoms, leading to the so-called polyhedral oligohydridosilsesquioxanes (POHSS), which are commonly abbreviated T_n^H (T is the usual designation for a silicon bearing three oxygen atoms). X can also be organic moities bound to silicon through a Si-C bond, leading to polyhedral oligosilsesquioxanes (POSS). Finally, X can be siloxy groups (RR'R''SiO-). In this last case, the organic moieties are bound to the cage framework through Si-O-Si links and those nanobricks are named spherosilicates. The most studied siloxy groups correspond to $OSiMe_2R$ with R: H, CH_3, $CH=CH_2$ (vinyl), $CH_2CH=CH_2$ (allyl). Some interesting polyhedral oligosilsesquioxanes, $(RSiO_{1.5})_n$, or spherosilicates, $(RMe_2SiOSiO_{1,5})_n$, are those bearing different R groups on the same nanobrick, i.e., $(H_2C=CHCH_2)(c\text{-}C_6H_{11})_7Si_8O_{12}$,[32] or $(HMe_2SiO)_4(H_2C=CHMe_2\,SiO)_4Si_8O_{12}$.[33]

Some slightly different nanobricks have also been used directly in hybrid materials or as precursors for functionalized nanobuilding blocks. These compounds exhibit frameworks which are not fully condensed and correspond to $(c\text{-}C_6H_{11}Si)_8O_{11}(OH)_2$[34] and $(RSi)_7O_9(OH)_3$ [34,35] with R : $c\text{-}C_5H_9$, $c\text{-}C_6H_{11}$, $c\text{-}C_7H_{13}$ (Fig. 7). They are commonly named incomplete polyhedral oligosilsesquioxanes.

Of course, all these compounds exhibit a siloxane framework which is stable under the hybrid materials synthesis conditions (vide infra). Therefore, the nanobrick framework is recovered in the final material. This point is a requirement for their use as nanobuilding blocks. Yet, these nanobuilding blocks should also exhibit at least one functional group which will allow to assemble these discrete species and convert them into a material. The following paragraphs will deal with different syntheses proposed for functionalized nanobuilding blocks. These compounds, based on silicon, have been generally characterized by ^{29}Si NMR but also by ^{1}H and ^{13}C NMR, IR, mass spectroscopy, chromatography and more seldomly by single crystal X-ray diffraction. Readers should refer to the cited litterature for the characteristics of the nanobricks taken as examples.

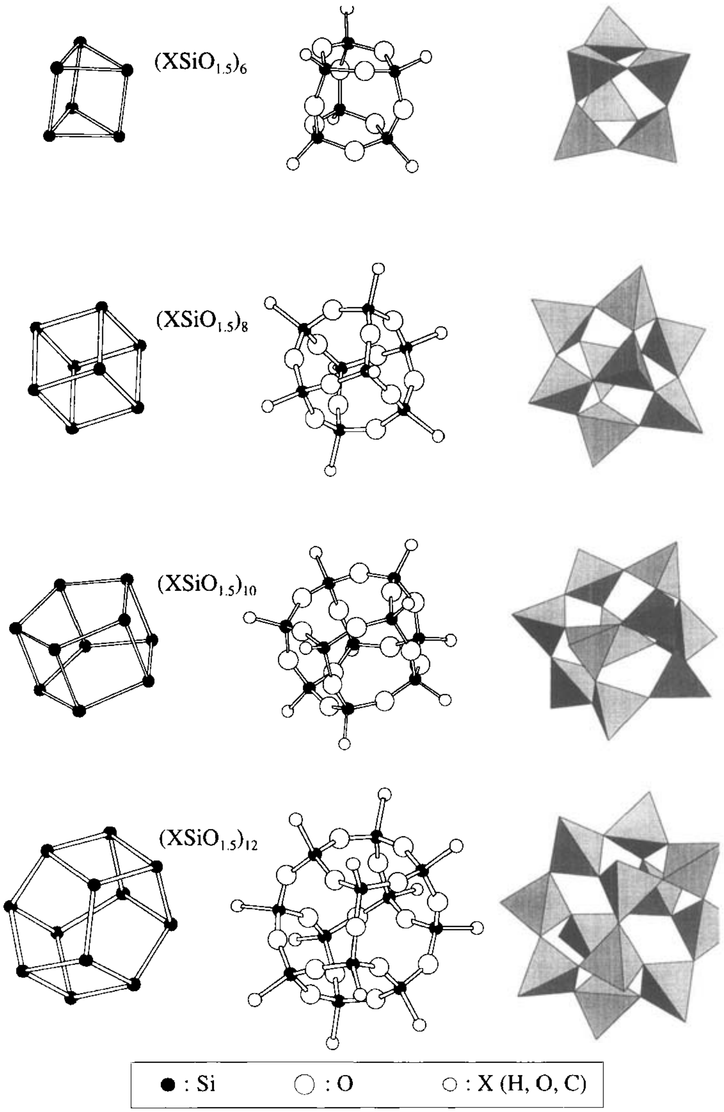
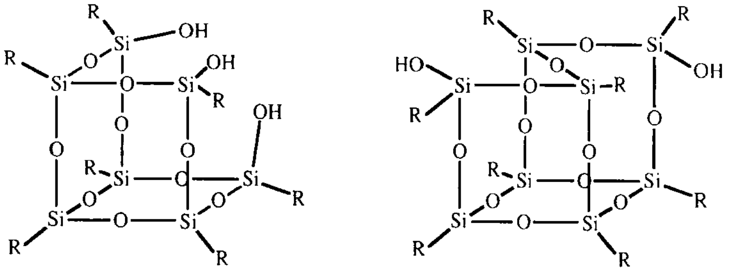


FIGURE 6 Molecular structures of some $(XSiO_{1,5})_n$ cages (on the right: structure with the tetrahedra centered on silicon, on the left: shape given by the silicon atoms only)



$(RSi)_7O_9(OH)_3$

$R = c\text{-}C_5H_9, c\text{-}C_6H_{11}, c\text{-}C_7H_{13}$

$(RSi)_8O_{11}(OH)_2$

$R = c\text{-}C_6H_{11}$

FIGURE 7 Schematic molecular structures of incomplete polyhedral oligosilsesquioxanes (Ref. 34 and 35)

III.A. 1.a Polyhedral Oligohydridosilsesquioxane

The first report on the preparation of a polyhedral oligohydridosilsesquioxane ($H_8Si_8O_{12}$) was made in 1959 with the exceedingly small yield of 0.2%.[36] In 1991, Agaskar proposed a method based on a biphasic reaction medium (HCl_{aq}, methanol, hexane, toluene) containing $FeCl_3$.[37] In such a medium, $HSiCl_3$ is slowly hydrolyzed by the water released from the partially hydrated iron salt. This synthesis leads to a mixture of T_8^H and T_{10}^H, yields being 17.5% and ~8%, respectively, after separation and purification. The other T_n^H compounds (n = 12, 14, 16, 18) can only be prepared with very low yields ~1%) and need to be separated through numerous and complex steps.[38] Those low yields likely explain the preferential use of T_8^H in hybrid materials.

III.A.1.b. Polyhedral oligosilsesquioxane

A classical route to synthesize polyhedral oligosilsesquioxanes, $(RSiO_{1.5})_n$, is the hydrolysis-condensation of silicon trifunctional derivatives, $RSiX_3$ with X : Cl, OCH_3, OC_2H_5.[30,34,35,39] Yet, this method also yields large tridimensional oxo-polymers.[2] Experimental conditions (concentration, solvent, nature of R and X, catalyst, hydrolysis ratio, solubility of the condensation products) have to be optimized to favor the formation of the nanobricks versus oxo-polymers.[30] Mixtures of precursors allow to prepare nanobricks exhibiting a reduced functionality, i.e., $(H_3C)_x(H_2C{=}CH)_{8-x}Si_8O_{12}$.[39b]

This method also allows to synthesize incomplete polyhedral oligosilsesquioxanes. The hydrolysis of c-$H_6H_{11}SiCl_3$ in acetone leads to the nanobricks (c-$C_6H_{11}Si)_8O_{11}(OH)_2$ and (c-$C_6H_{11}Si)_7O_9(OH)_3$ with good yields but very slowly (3–36 months).[34,35] The precursors $RSiCl_3$ with R : c-C_5H_9 or c-C_7H_{13}, which are only slightly different, allow to prepare $(RSi)_7O_9(OH)_3$ within only a few days, while keeping yields around 30%. [35c] The nanobrick (c-$C_6H_{11}Si)_8O_{11}(OH)_2$ can be directly used to prepare hybrid materials by taking advantage of its two silanol groups (vide infra). The compounds $(RSi)_7O_9(OH)_3$, which formally derive from $(RSiO_{1.5})_8$ by removing one silicon, have been mainly used to prepare a large number of monofunctional nanobuilding blocks. This perfect monofunctionalization is performed by reacting them with one equivalent of functional trichlorosilanes, in the presence of triethylamine.[32,34,40] This reaction offers high yields (90–100%).

$$(RSi)_7\,O_9\,(OH)_3 + R'SiCl_3 + 3NEt_3 \longrightarrow R'R_7Si_8O_{12} + 3HClNEt_3$$

$$\text{i.e.}R'\text{: H},\ CH = CH_2,\ CH_2CH = CH_2.\ (CH_2)_2\,C_6H_4CH = CH_2.$$

$$(CH_2)_3\,O_2CC\,(CH)_3 = CH_2$$

Polyhedral oligosilsesquioxanes bearing one or several peculiar functions can also be prepared by modifying another functionalized POSS. With such an approach, nanobuilding blocks bearing epoxy groups were prepared by treating POSS bearing alkene groups with m-chloroperbenzoic acid.[40d,41]

Hydrosilylation on polyhedral oligohydridosilsesquioxanes also offers access to POSS. In this addition reaction, generally catalyzed by Pt derivatives, a Si-H group reacts with an organic group bearing an unsaturation (generally a double bond) to form a Si-C bond.

$$\equiv Si - H + H_2C = CHR$$

$$\longrightarrow x \equiv Si - CH_2CH_2R + (1 - x) \equiv Si - CH\,(CH_3)\,R$$

The proportion, x, of terminal addition (anti-Markovnikov) depends on the reagents and experimental conditions. Following this route, from one to eight organic groups were grafted on a $T_8{}^H$ cage, yielding the derivatives $R_xH_{8-x}Si_8O_{12}$.[42] Yet, the hydrolsilylation involving double bonds, the grafting of this peculiar function, which is of interest to assemble nanobuilding blocks into hybrid materials, raises some problems. Sellinger *et al.* have nicely overcome this limitation by using propargylmethacrylate, $H_2C{=}C(CH_3)CO_2CH_2C{\equiv}CH$. With dichlorodicyclopentadienyl platinum, Pt(dcp), catalyst, the hydrolsilyation only involves the tripple bond.[42f] Thus, reacting T_8^H cubes with four equivalents of propargylmethacrylate leads to nanobricks which carry various amounts of methacrylate functions, $R_xH_{8-x}Si_8O_{12}$ with R : $H_2C{=}C(CH_3)CO_2CH_2C{=}CH_2$ and $H_2C{=}C(CH_3)CO_2CH_2CH{=}CH$, and x = 3 4, 5 being the major compounds.

Recently, Bassindale *et al.* proposed another derivation of the T_8^H cages, using the reaction of Si-H and alcohol, with Et_2NOH as catalyst.[42j] They succeeded in preparing $[H_2C{=}CH(CH_2)_3OSiO_{1.5}]_8$. Yet, the function being bound to the Si-O-Si framework through Si-O-C links, they might be cleaved under hydrolytic conditions.

III.A.1.c. Functionalized spherosilicates

The synthesis of compounds following the formula $(RMe_2SiOSiO_{1.5})_n$, with R : H, CH_3, $CH{=}CH_2$, $CH_2CH{=}CH_2$ and CH_2Cl, has been proposed in the literature from the oligohydrido, $(HSiO_{1.5})_n$, or from the polyanions, $(OSiO_{1.5})_n^{n-}$.

Spherosilicates can be prepared by reacting the T_n^H compounds with at least 2n equivalents of $Me_3NOClSiMe_2R$, this reagent being first obtained by treating $ClSiMe_2R$ with anhydrous Me_3NO.[43] This reaction offers good yields of at least 50% The need for 2n equivalents has allowed to propose the following mecanism:

$$(HSiO_{1.5})_n + 2n\,Me_3NOClSiMe_2R$$

$$\longrightarrow (RMe_2SiOSiO_{1.5})_n + nMe_3NClSiMe_2R + nMe_3NOHCl$$

Feher has also proposed a multi-step synthesis starting from the T_8^H.[44] This method was only described for the preparation of $(Me_3SiOSiO_{1.5})_8$, but can probably be used to funtionalize spherosilicates.

$$(HSiO_{1.5})_n + 8Me_3SnOSnMe_3 \longrightarrow (Me_3SnOSiO_{1.5})_8 + Me_3SnH$$

$$(Me_3SnOSiO_{1.5})_8 + Me_4SbOX$$

$$\longrightarrow (Me_4SbOSiO_{1.5})_8 + Me_3SnOX \quad (X : SiMe_3 \text{ or } CMe_3)$$

$$(Me_4SbOSiO_{1.5})_8 + Me_3SiCl \longrightarrow (Me_3SiOSiO_{1.5})_8 + Me_4SbCl$$

These reactions are quantitative, and the intermediate compound, $(Me_4SbOSiO_{1.5})_8$, can be easily isolated. This compound represents an interesting source of $(SiO_{1.5})_8^{8-}$ in totally aprotic medium. Yet, these two methods start from the T_n^H compounds whose syntheses strongly reduce the overall yield of the reactions (vide supra). Moreover, the first proposed route uses Si-H, and therefore will not allow the synthesis of $(HMe_2SiOSiO_{1.5})_n$.

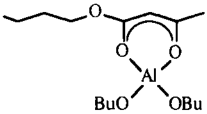
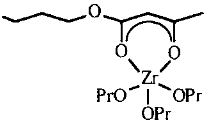
The other synthetic route, which is always chosen in the recent works, uses as precursors the polyanions $(OSiO_{1.5})_n^{n-}$ which exhibit the same cage structure. These compounds can be prepared with very good yields from aqueous silicate solutions or by hydrolysing $Si(OCH_3)_4$ under basic conditions.[45] In both cases, to favor the formation of the cage structures, the key point is the use of quarternary ammonium as charge compensating cations. Several experimental procedures have been described to functionalize the cage by grafting a $SiMe_2R$ moiety on each of the non-bridging oxygen atoms.[46] The silylating reagents are chloro derivatives (RMe_2SiCl) and/or disiloxanes in the presence of hydrochloric acid ($RMe_2SiOSiMe_2R + HCl$). The reactions involved being non-stoichiometric, the silylating reagents are generally used in large excess, ranging from 10 to 100 RMe_2Si moieties for every silicon in a given cage. The addition of dimethoxypropane, which is a dehydrating reagent forming methanol and acetone, as co-reagent or solvent allows to limit the excess of sylilating reagent to about 5 equivalents. The reactions are performed in biphasic medium (aqueous and polar/organic and non-polar). The anions are introduced in the polar phase and the functionalized spherosilicates are recovered in the non-polar one. Following these procedures, spherosilicates $(RMe_2SiOSiO_{1.5})_n$ where R : H, CH_3, $CH{=}CH_2$, $CH_2CH{=}CH_2$, and CH_2Cl can be prepared with yields higher than 50%, relative to the starting anions. Mixtures of silylating reagents allow to reduce, i.e., $(Me_3Si)_x(H_2C{=}CHMe_2Si)_{8-x}(O_8Si_8O_{12})$,[47] or to diversify, i.e., $(HMe_2Si)_x(H_2C{=}CHMe_2Si)_{8-x}(O_8Si_8O_{12})$,[33] the functionality.

Spherosilicates with more complex functions can also be prepared from simple ones (R : H, vinyl,...).[41,42i,47,48] As an example, the hydrosilylation of various unsaturated compounds by $(HMe_2SiOSiO_{1.5})_8$ has allowed to synthesize nanobricks bearing epoxy or β-ketoester functions, trimethoxysilanes groups, or metal (Al, Zr) alkoxides moieties through the complexation by a β-ketoester.[42i,47,48a]

III.A.1.d. Abbreviations for nanobuilding blocks based on silicon

The M, D, T, and Q letters are commonly used to abbreviate a silicon atom bearing 1, 2, 3, or 4 oxygen atoms, respectively. This notation is also used to shorten the formula of the silicon-based nanobricks. Subscripts are used to indicate the number of silicon atoms, and superscripts to designate the function borne. Several silicon-based nanobuilding blocks are reported with their abbreviation in Table I.

TABLE I Abbreviations and formula of several silicon-based nanobuilding blocks

Abbréviations	Formula	
T_n^H	$(HSiO_{1.5})_n$	
R_nT_n	$(RSiO_{1.5})_n$	
$R_7T_7(OH)_3$	$(RSi)_7O_9(OH)_3$	(Fig.7)
$R_8T_8(OH)_2$	$(RSi)_8O_{11}(OH)_2$	(Fig.7)
Q_n	$(OSiO_{1.5})_n^n$	
$Q_nM_n^H$	$(RMe_2SiOSiO_{1.5})_n$	with R : H
$Q_nM_n^V$	$(RMe_2SiOSiO_{1.5})_n$	with R : $CH{=}CH_2$
$Q_nM_n^A$	$(RMe_2SiOSiO_{1.5})_n$	with R : $CH_2CH{=}CH_2$
$Q_8M_8^{MPTS}$	$(RMe_2SiOSiO_{1.5})_n$	with R : $CH_2CH(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$
$Q_8M_8^{VTMS}$	$(RMe_2SiOSiO_{1.5})_n$	with R : $CH_2CH_2Si(OCH_3)_3$
$Q_8M_8^{AAA}$	$(RMe_2SiOSiO_{1.5})_n$	with R : 
$Q_8M_8^{AAAAlOBu}$	$(RMe_2SiOSiO_{1.5})_n$	with R : 
$Q_8M_8^{AAAZrOPr}$	$(RMe_2SiOSiO_{1.5})_n$	with R : 

III.A.2. Nanobuilding blocks based on tin

Like silicon, tin gives with sp^3 carbon stable bonds towards hydrolysis.[17] But its more accessible 5d orbitals make it prone to exhibit a coordination number larger than its valence. This last feature is common with transition metals, and the hydrolysis behavior of tin tetraalkoxides would indeed closely resemble that of transition metals.[49]

Only the case where a single carbon is bound to tin will be discussed. This Sn-C bond allows to graft some peculiar functions, but it also reduces the inorganic functionality of tin and therefore favors the formation of oxo-clusters.[50] The main example will be the nanobrick $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$, which is the only one to have been used in hybrid materials.[51] Other monoorganotin oxo-clusters, in which ligands complex tin, will also be presented. The proper choice of the ligands should allow their use as nanobuilding blocks.

III.A.2.a. Nanobuilding blocks derived from $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$

The molecular structure of $\{(RSn)_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}OH)_6\}^{2+}$ is shown in fig. 8. Its framework is almost spherical and contains twelve tin atoms linked by μ_3-O and μ_2-OH bridges. All the tin atoms bear organic moieties bound by an Sn-C bond. These organic groups point toward the outside of the Sn-O-Sn framework. Six tin atoms are five-coordinate (square pyramid) and the six others are six-coordinate (distorted octahedra). The μ_2-OH bridges are only bound to the latter. This oxo-cluster can be described with three subunits. The first one is a hexameric crown, $(RSnO_2)_6$, which contains only five-coordinate tin atoms. The two others are trimers, $[RSn(OH)]_3O$, based on six-coordinate tin atoms. The complete oxo-cluster framework is obtained by capping each side of the crown by a trimer. The position of the charge compensating anions in the structures, solved by single crystal X-ray diffraction, indicates that the 2+ charge is equally located at both cage poles, formed by the $[RSn(OH)]_3O$ trimers.

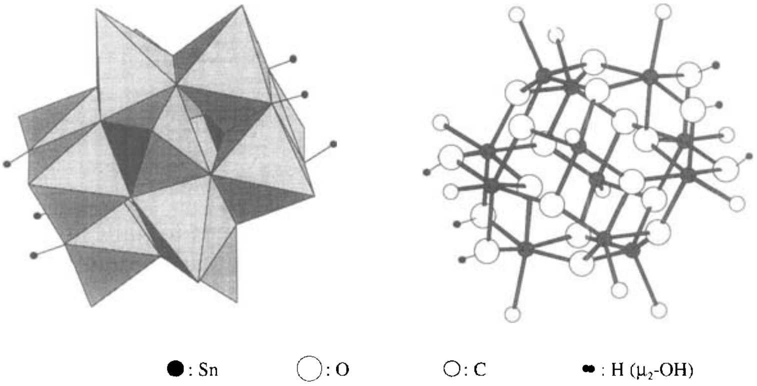


FIGURE 8 Molecular structure of $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$ (only the carbon atoms directly bound to tin have been drawn) (Refs. 52–54)

Several syntheses have been reported for these species. The basic hydrolysis of $RSnCl_3$ (R: isopropyl,[52] n-butyl[53]) leads to the macrocation with chlorides as charge compensating anions, the yields being very low (isopropyl) or fairly high (~80% for n-butyl). The hydrolysis of $RSn(OR')_3$ with R : n-butyl, 3-butenyl and R': isopropyl, tert-amyl, also leads to the macrocation, but with hydroxyls as charge compensating anions.[51a,54] With alkoxides, yields are close to 60%. More recently, the hydrolysis of $RSn(C{\equiv}CR')_3$ was also shown to yield $\{(RSn)_{12}O_{14}((OH)_6\}(OH)_2$.[18b] Finally, refluxing in toluene butyltin hydroxide oxide, BuSnO(OH), with sulfonic acids, $R'SO_3H$ (R': $4\text{-}C_6H_4CH_3$, $4\text{-}C_6H_4NH_2$, $CH_2C(CH_3)_2NHCOCH{=}CH_2$), also leads to the macrocation. In this later case, the positive charges are balanced by sulfonates. Yields range from 30 to 70% depending on the acid.[51d,58]

$\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$ is stable in common organic solvents. It is easily evidenced by solution ^{119}Sn NMR, where it is characterized by two chemical shifts and a set of scalar coupling satellites.[53–56] Actually, in solvents such as $CHCl_3$, CH_2Cl_2, or C_6H_6 the species probed are the ions triplets $\{(RSn)_{12}O_{14}(OH)_6\}X_2$.[54] In solution, the charge compensating anions remain close to the cage poles of the macrocation, where in addition to electrostatic interaction they also exchange hydrogen bonds with the μ_2-OH bridges.[51b,56]

$\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$ can be used as a nanobuilding block for the synthesis of tin based hybrid materials if it carries one or several functions which would allow us to assemble it. This is achieved when R, which is iono-covalently bound to tin, is a 3-butenyl or a statistical mixture of butyl and 3-butenyl.[51a]

The positive charges borne by $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$ can also be directly used to assemble these oxo-clusters (vide infra). Moreover, the absence of ionic dissociation in low dielectric constant solvents allows us to functionalize this nanobrick by its charge compensating anions. The two hydroxyls of $\{((BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ can be easily substituted for other anions by reaction with the associated acids in tetrahydrofuran :

$$\{(BuSn)_{12}\,O_{14}\,(OH)_6\}\,(OH)_2 + 2HX$$
$$\leftrightarrow \{(BuSn)_{12}O_{14}(OH)_6\}\,X_2 + 2H_2O$$

This reaction is equilibrated but can be completely shifted to the right by removing the produced water under reduced pressure, which results in the quantitative synthesis of the nanobrick associated to the X^- anions.

This type of exchange has been successfully performed for various organic anions such as carboxylates (RCO_2^-), phosphinates ($R_2PO_2^-$), sulfonates (RSO_3^-), and phenates ($RC_6H_4O^-$).[51b,56,57] For the carboxylates, ^{119}Sn MAS NMR and FT-IR have shed some light on the nature and geometry (Fig. 9) of the interaction which takes place between the macrocation and the anions in the solid state. In addition to the anion-cation electrostatic interaction, a set of strong hydrogen bonds, in which all the μ_2-OH bridges of the cluster and the oxygen atoms of the carboxylates are involved, were also evidenced. Following this route, $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ could be functionalized with two polymerizable methacrylate anions, one at each pole.[51c,e] The functionalization by a polymerizable group in the charge compensating anions was also recently achieved, but through a single step direct synthesis, by reacting butyltin hydroxide oxide with 2-acrylamido-2-methyl-1-propanesulfonic acid.[51d,58]

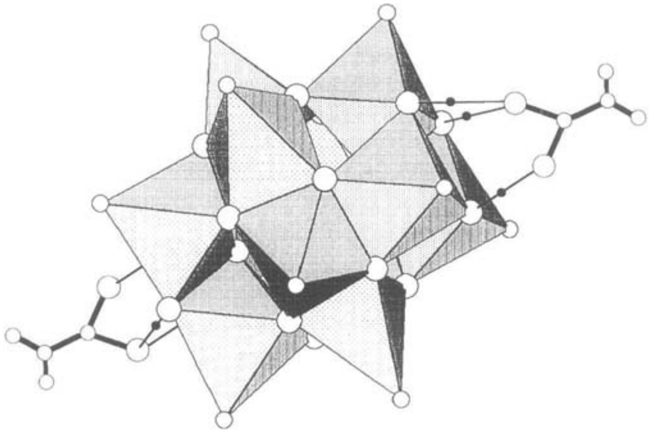


FIGURE 9 Molecular model for $\{(BuSn)_{12}O_{14}(OH)_6\}(O_2CC(CH_3)C{=}CH_2)_2$ (only the carbon atoms directly bound to tin and those of the methacrylate moieties have been drawn)

III.A.2.b. Other nanobuilding blocks based on monoorganotin

Several monoorganotin oxo-clusters containing complexing ligands, mainly carboxylates and phosphinates, directly bound to tin have been described in the literature.[59] The drum shaped hexamers

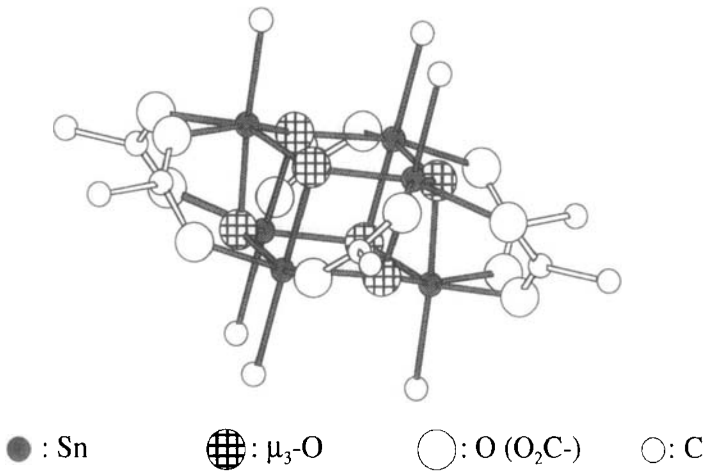


FIGURE 10 Molecular structure of $[BuSnO(O_2CR)]_6$ (only the carbon atoms directly bound to tin and the two first of the carboxylate ligands have been drawn) (Ref. 59)

$[RSnO(O_2CR')]_6$ (Fig. 10) can be given as examples. These clusters have been prepared with simple R and R′ groups (R : CH_3, n-C_4H_9 and R′: CH_3, c-C_6H_{11}, $C(CH_3)_3$, C_6H_5), with good yields, by reacting organostannonic acid, RSnO(OH), and carboxylic acid. The introduction of assembling functionalities could be achieved through the Sn-C bond, resulting in three binding sites on each hexagonal face of the drum. Yet, very few funtionalized monorganotin tin derivatives are available.[18] An easier alternative is to use the complexing ligands to bring the assembling functionality.[60] This leads to six, almost co-planar, binding sites around the drum. The classical syntheses for such clusters involve long (several hour) refluxes at 80° to 110°C, which might be incompatible with ligands bearing highly polymerizable groups, i.e., 4-vinylbenzoate. A milder synthetic route is possible from the previously described dodecamer, $\{(BuSn)_{12}O_{14}(OH)_6\}X_2$, which reacts with carboxylic acids to quantitatively yield the drum, at room temperature.[51b,53,60]

$$\{(BuSn)_{12}\,O_{14}\,(OH)_6\}\,X_2+12HO_2CR \longrightarrow 2\,[BuSnO\,(O_2CR)]_6+12HX$$

III.A.3. Nanobuilding blocks based on transition metals

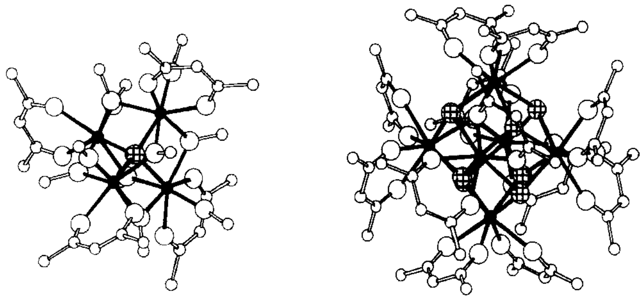
Hybrid materials containing transition metals are an important issue because of some of the characteristics associated to their oxides (i.e. high refractive index, semi-conduction, catalysis).[1] As previously mentionned, the high ionicity of the M-C bond, when M is a transition metal, makes it very sensitive to hydrolysis or nucleophlilic attacks. Therefore, it cannot be used to functionalize transition-metal-based nanobricks. Two routes have been described in the literature to overcome this problem : the functionalization through complexing ligands or M-O-Si-R links.

III.A.3.a. Transition metals and complexing ligands

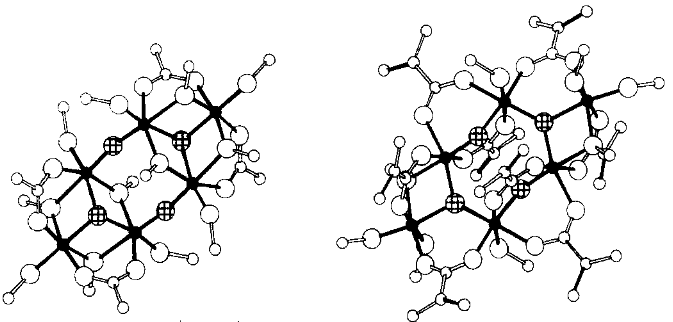
The synthesis and structure of many high valence metals (Ti^{IV}, Zr^{IV}, Ce^{IV}, Nb^{V}) oxo-clusters bearing strongly complexing ligands (β-diketone, β-ketoester, carboxylic acid,...) on their surfaces have been described.[19g,j,61] These species, characterized by single crystal X-ray diffraction, present perfectly defined structures where the metallic centers usually exhibit coordination numbers larger than their valence states (Fig. 11). This is made possible by the bidentate character, chelating or bridging, of the ligands, but also by the existence of μ_3-O, μ_4-O, even μ_5-O, and μ_2-OR bridges.

Such species are usually prepared through the controlled hydrolysis of the corresponding complexed alkoxides, $M(OR)_{n-x}(SCL)_x$, in solution. They are isolated from the ill-defined oxo-polymers concurrently formed by crystallization, frequently resulting in low yields. A large number of oxo-alkoxo-clusters, $M_xO_y(OR)_z$, have also been prepared, especially for titanium(IV), from alkoxides, either by hydrolysis or solvothermal treatment.[62] Post-complexation of their surface metallic atoms, without the destruction of the metal-oxo core, is an interesting synthetic challenge, which has not been achieved so far.

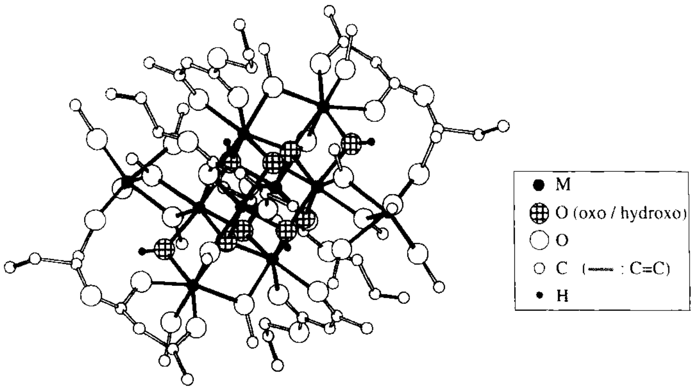
The use of ligands containing an assembling function, such as a polymerizable one, i.e., allylacetoacetate (AAA) or methacrylate (OMc), gives to these clusters at least one of the characteristics required for nanobuilding blocks. With these ligands, $Ti_6O_4(OEt)_8(OMc)_8$, $Zr_{10}O_6(OH)_4(OPr^i)_{18}(AAA)_6$, $Nb_4O_4(OPr^i)_8(OMc)_4$, $Zr_6(OH)_4O_4(OMc)_{12}$, and $Zr_4O_2(OMc)_{12}$ have been prepared and characterized by single crystal X-ray diffraction.[19g,j,61h,i] Yet, because of their small size



$Zr_4(\mu_4\text{-}O)(\mu_2\text{-}OPr^n)_6(OPr^n)_4(acac)_4$ $Ce_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(acac)_{12}$



$Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OPr^i)_6(OPr^i)_6(OAc)_4$ $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OEt)_2(OEt)_6(OMe)_8$



$Zr_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OPr^i)_8(OPr^i)_{10}(AAA)_6$

FIGURE 11 Molecular structures of several metal alkoxo-oxo-clusters with complexing ligands on their surface (for alkoxo ligands, only the carbon linked to the oxygen is drawn) and the presence of several alkoxy groups on their surface, these functionalized nanobuilding blocks likely exhibit poor stability in the presence of water or nucleophiles. In this regard, the stability of titanium(IV) oxo-alkoxo-clusters was shown to depend on their alkoxo/M and oxo/M ratios, as evidenced by ^{13}C and ^{17}O NMR.[63] The larger the oxo/M ratio, the more stable are the clusters. With the same mild hydrolysis conditions, $Ti_{16}O_{16}(OEt)_{32}$ starts to slowly react by its surface ethoxy groups, while $Ti_7O_4(OEt)_{20}$ is quickly destroyed to yield oxo-polymers and other oligomers. Therefore, the formation of hybrid materials in which the functionalized clusters presented above will keep their defined structure should be limited to anhydrous and free from nucleophile synthetic conditions or to very large oxo-clusters.

III.A.3.b. Organically modified polyoxometalates

The polyoxometalates form a peculiar class of compounds which are very interesting for their structure, their electronic properties and their use in different domains.[64] Their size, around 15 Å, make them potential nanobuilding blocks. Yet, at least one organic assembling function has to be introduced. This can be achieved by grafting ≡SiR fragments onto lacunar polyoxometalates.[65] Two examples based on polyoxometalates derived from Keggin's structure (α-$\{XM_{12}O_{40}\}$) are presented below.

The lacunar polyoxotungstate $[SiW_{11}O_{39}]^{8-}$ formally derives from Keggin's structure by the removing of a "WO" fragment. This compound reacts with trichloro or trialkoxysilanes to yield the modified polyoxotungstates, $[SiW_{11}O_{40}(SiR)_2]^{4-}$ (Fig. 12), which can be isolated by crystallization of their potassium, tetramethylammonium, or tetrabutylammonium salts.[65b,c,d] Nanobbuilding blocks bearing two vinyl, allyl, 4-vinylphenyl, or methacryloxypropyl ($H_2C{=}C(CH_3)CO_2(CH_2)_3$) functions have been prepared with yield around 60%. Their tetrabutylammonium salts are soluble in polar aprotic solvents (N,N-dimethylformamide, propylene carbonate, dimethylsulfoxide).

The trivacant polyoxotungstate α-A-$[SiW_9O_{34}]^{10-}$ is formally related to Keggin's structure by the removing of a "W_3O_6" fragment in which the three tungsten atoms come from three adjacent tri-oxo-tungstic groups. Reaction of this compound with $RSiCl_3$ (R : H, $CH{=}CH_2$) yields the tetrafunctionalized polyoxotungstates, $[SiW_9O_{37}(SiR)_4]^{4-}$, which can be isolated as their tetrabutylammonium salts.[65e] Nanobuiding blocks carrying a single assembling function can also be prepared

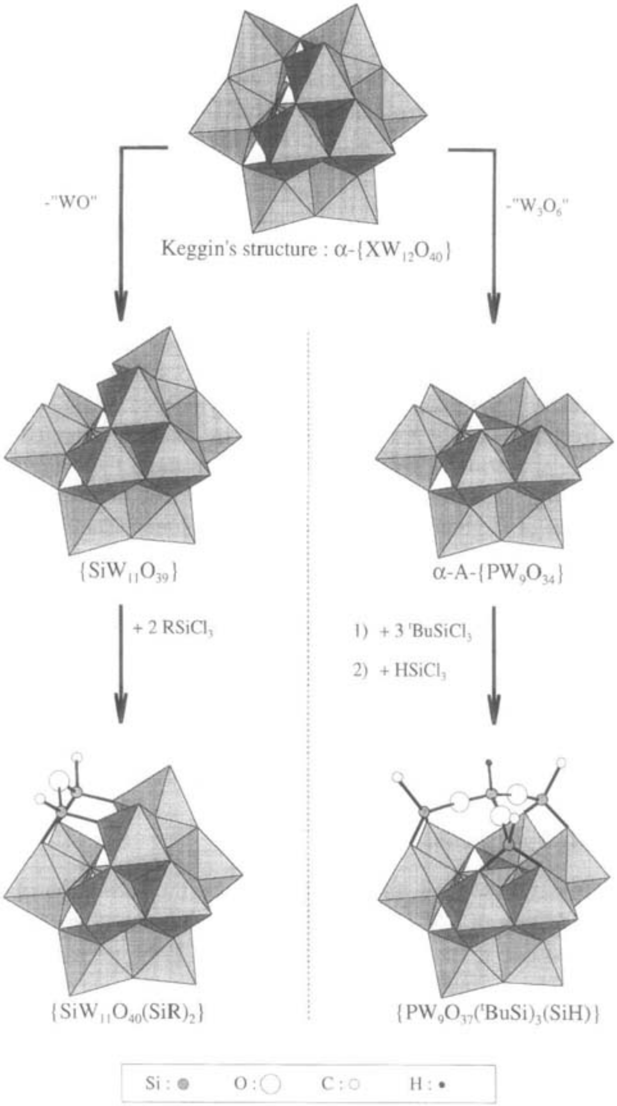


FIGURE 12 Molecular structures, using polyhedra, of organically modified polyoxotungstates (only the carbon atoms directly bound to silicon have been drawn) (Ref. 65)

through a two step process. The reaction of $^tBuSiCl_3$ with α-A-$[PW_9O_{34}]^{9-}$ stops, likely for steric reasons, at the still reactive $[PW_9O_{34}(^tBuSiOH)_3]^{3-}$ species. Then, the condensation of $RSiCl_3$ (R:H, $CH=CH_2$) on this compound yields the monofunctionalized nanobuilding blocks, $[PW_9O_{34}(^tBuSi)_3(SiR)]^{3-}$ (Fig. 13).[65f] The overall yield is about 45% after crystallization of the tetrabutylammonium salt.

III.B. Various Strategies to Assemble the Nanobuilding Blocks

In the previous part, the molecular structures an the syntheses of various functionalized nanobricks have been presented. These nanobuilding blocks are commonly isolated as crystalline solids. Yet, and this is one of the underlying ideas, they form discrete and stable species in solution. Therefore, their topological features evidenced in the solid state, mostly by single crystal X-ray diffraction, are found unchanged in solution. The elaboration of hybrid materials from them therefore required an assembling step. But this step should not destroy or strongly modify the structure of the constituting nanobuilding blocks. The various types of assembling functions allow the use of different chemical reactions. Depending on these reactions and on the number and position of functions borne by a nanobuilding block, different structures can be built. Some nanobuilding blocks, or mixtures of them, can self-assemble, while others need some molecules or polymers as cement. In the following, the nature of the chemical reactions involved in the assembling of the nanobuilding blocks will be used as classification. Some properties of the so-obtained hybrid materials will also be presented.

III.B.1. Hydrosilylation

As previously described, this reaction allows the formation of a Si-C bond by addition of a Si-H onto a double or triple bond. Historically, it was the first one to be used when Agaskar, in 1989, prepared a hybrid material made of $Q_{10}M_{10}{}^V$ functionalized spherosilicates assembled by $(HMe_2SiC_6H_4O_{0.5})_2$ links.[43b] The material obtained was hard, clear, resilient, thermally stable up to 350°C and could absorb more than 50% of its weight of THF.

This reaction has often been used since.[33,66] Many hybrid systems have been prepared from $Q_8M_8{}^H$ or $Q_8M_8{}^V$ nanobuilding blocks and links of different shape such as 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, tetramethylcyclotetrasiloxane, and poly(methylhydrosiloxane).

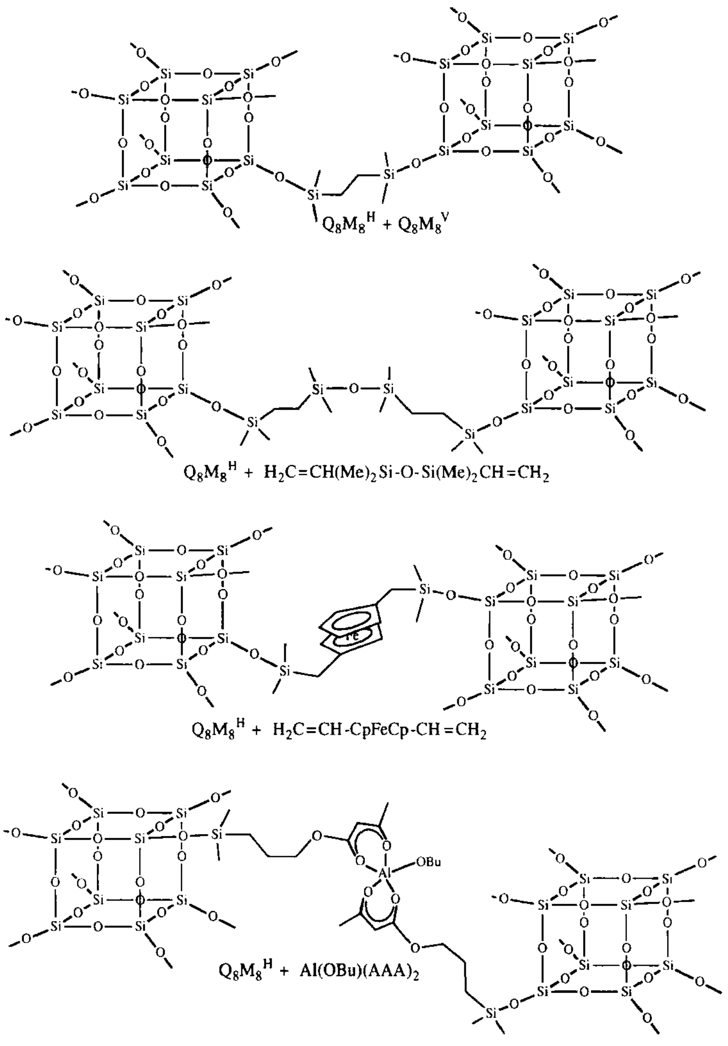


FIGURE 13 Examples of functionalized spherosilicates linked by hydrosilylation

Mixtures of $Q_8M_8{}^H$ and $Q_8M_8{}^V$or $Q_8M_8{}^A$, or spherosilicates simulteously bearing Si-H and Si-CH=CH_2 functions ($Q_8M_4{}^HM_4{}^V$) have also been used without additional links (Fig. 13). In some cases, i.e.,

$Q_8M_8{}^H$ + $Q_8M_8{}^V$, the linking of the nanobuilding blocks causes sterical constraints and results in the absence of reaction for part of the assembling functions.[33] Yet, the generally large number of assembling functions in these nanobuilding blocks allows the hybrid framework to extend tridimensionally, and gels are commonly obtained. After drying, these gels yield solids insoluble in organic solvents.

In a series of materials derived from $(XSiO_{1.5})_8$ cubic nanobricks, Hoebbel *et al.* have studied the influence of the length of the interbrick links.[33] Their results are reported in Table II. Links based on six atoms appear to be the best to develop large surface areas. The decrease of the surface area for longer links was explained by their possible curling, finally making the nanobricks closer to one another than expected. The completeness of hydrosilylation appears to increase steadily with the link length, likely because of larger conformational freedom.

TABLE II Some characteristics of hybrid materials derived from Q_8M_8 nanobuilding blocks (Ref. 33)

Starting Nanobricks	*Number of Atoms in the Links*	*Degre of Polymerization*[a]	*Specific Surface Area (BET) m^2/g*
$Q_8M_8{}^V + T_8{}^H$	4	66 %	2
$Q_8M_8{}^V + Q_8M_8{}^H$	6	78 %	300
$Q_8M_4{}^HM_4{}^V$	6	78 %	200
$Q_8M_8{}^A + Q_8M_8{}^H$	7	86 %	3

[a] Percentage of assembling functions having reacted.

Two other examples where the links exhibit a more complex structure can be mentioned to illustrate the versatility of this route. By assembling $Q_8M_8{}^H$ nanobricks with 1,1′-divinylferrocene (Fig. 13), Moran *et al.* have obtained a material which exhibits red-ox properties and can be used to prepare modified electrodes.[66f] The hydrosilylation of $Al(O^sBu)(AAA)_2$ by $Q_8M_8{}^H$ yields a tridimensional hybrid polymer in which the link assembling the spherosilicates is articulated around an aluminum atom (Fig. 13).[47] Moreover, this aluminum atom still bears an alkoxy group which can be hydrolyzed later to generate Al-O-Al bonds and stiffen the materials.

Hydrosilylation being an addition reaction, the structure of the links is fairly well controlled. The only possible variation is in the relative proportions of the two addition geometries : Markovnikov or anti-Markovnikov (terminal). Therefore, this reaction is well adapted to the synthesis of nanobuilding-block-based hybrid materials with controlled properties. Yet, this assembling strategy is not always applicable, as the metal constituting the nanobricks might interfere with hydrosilylation. Indeed, attempts to link $\{(3\text{-butenylSn})_{12}O_{14}(OH)_6\}^{2+}$ by hydrosilylation with poly(methylhydrosiloxane) resulted in the destruction of the nanobuilding blocks, because of reactions between Si-H groups and Sn-O-Sn bonds.[57]

III.B.2. Polymerization

All the nanobuilding blocks which bear at least one unsaturated function can, a priori, be turned into hybrid materials by polyaddition. This type of reaction has been used for R_7T_8(methacryloxypropyl) and R_7T_8(4-vinylphenyl) (R: c-C_6H_{11} or c-C_5H_9) which have a single assembling function.[40b,c,d] Their homopolymerization, or co-polymerization with methymethacrylate or 4-methylstyrene, respectively, give, under free radical initiation, hybrid polymers whose solubility depends strongly on R. Their structure corresponds to a linear backbone of C-C bonds on which pendent silsesquioxane cubes are hanged (Fig. 14). The building sequence used and the strong covalent links binding the mineral clusters with the organic polymers guarantee a perfect dispersion of the nanoscale filler in the polymer. The materials derived from R_7T_8(methacryloxypropyl) are amorphous and are best described as transparent and brittle plastics.[40d] Moreover, they exhibit a very high thermal stability, decomposing without melting above 380°C.

This assembling strategy has also been used for organically modified polyoxometalates, $[SiW_{11}O_{40}(SiR)_2]^{4-}$ with R : $CH{=}CH_2$, $CH_2CH{=}CH_2$, $(CH_2)_3O_2C(CH_3){=}CH_2$ and 4-$C_6H_4CH{=}CH_2$.[65c,d] The polymers, prepared under free radical initiation, are soluble in polar aprotic solvents. Their hydrodynamic radii, measured by quasi-elastic light scattering, range from 10 to 100 nm depending on the polymerization conditions, what is much larger than the size of the nanobuilding blocks (~ 1 nm). The double functionality borne by these nanobricks makes the structure of the hybrid polymers more complex than in the previous example. They are likely based on short organic polymers cross-linked by polyoxometalates. The cyclic voltamograms of these hybrid polymers, in solution, evidence the reversible reduction of the

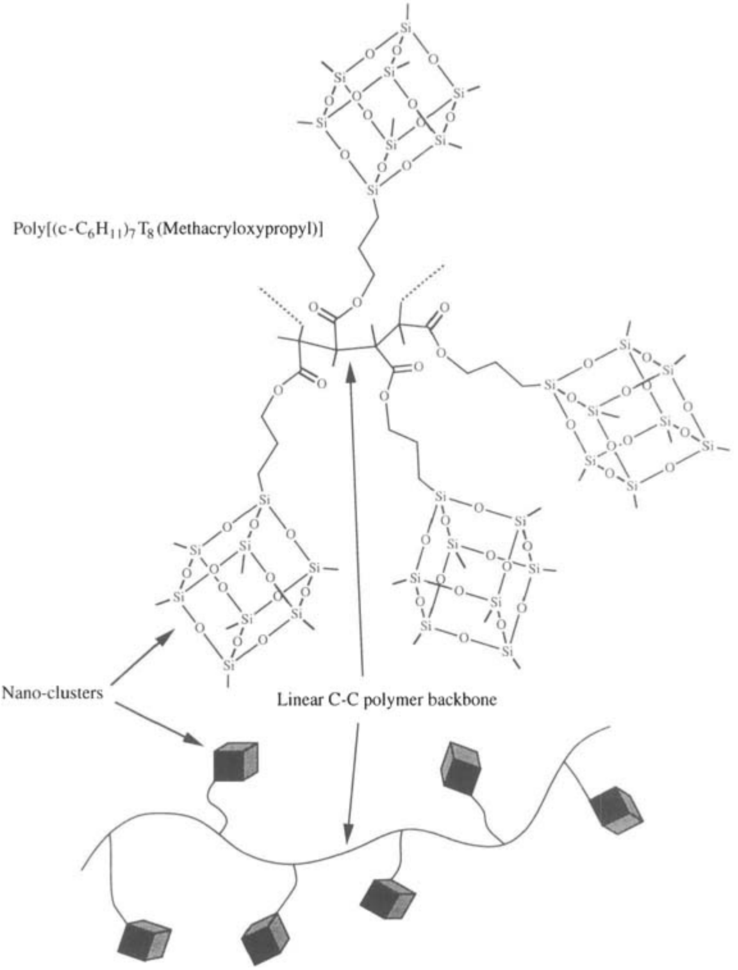


FIGURE 14 Schematic structure, at two different scales, of the hybrid materials prepared by free radical polyaddition of (c-C_6H_{11})$_7$$T_8$(methacryloxypropyl) (cyclohexyl groups have been omitted) (Ref. 40d)

constituting polyoxometalates. Taking advantage of the polymer solubility, transparent films can be deposited onto various substrates (glass, plastic, metal). These films turn reversibly to blue upon UV irradiation or electrochemical reduction.

Yet, the polyaddition of unsaturated assembling functionalities is not always possible. The monofunctionalized nanobuilding blocks $R_7T_8[CH=CH(CH_2)_8CH=CH_2]$ and $R_7T_8[(CH_2)_6CH=CH_2]$ (R: c-C_6H_{11}) remain monomers when treated with free radical initiators or Ziegler-Natta catalyst.[32] The tin-based nanobuilding block $\{(3\text{-butenylSn})_{12}O_{14}(OH)_6\}^{2+}$ also does not polylmerize under free radical initiation, contrary to what was previously observed.[51a]

Other polymerization reactions can also be used. For example, nanobuilding blocks functionalized with epoxy groups have been assembled into hybrid materials by ring opening polymerization, initiated chemically or photochemically.[42i]

In this assembling by polymerization, the organic component obtained by polymerization might be poorly defined, especially for its size. The use of a co-monomer might also introduce some inhomogeneities. Yet, the control of the growth and sequencing of the polymer backbones can probably be achieved with the knowledge of polymers scientists.

III.B.3. Polycondensation

In this part, polycondensation is used with its inorganic acceptation, meaning the formation of M-O-M bonds. The incomplete polyhedral oligosilsesquioxane $(c\text{-}C_6H_{11})_8T_8(OH)_2$ is a nanobuilding which exhibits two Si-OH funtions that can participate in condensation reactions.[67,68] Hybrid polymers have thus been prepared from $(c\text{-}C_6H_{11})_8T_8(OH)_2$ and various short and linear silanes or siloxanes terminated by Si-Cl or Si-NMe_2 functions.[67] The copolymers obtained exhibit a beads structure (Fig. 15) in which 10 to 30 nanobricks are included. They exhibit high solubility in THF or $CHCl_3$. The dry materials have the physical appearance of clear plastics when hot pressed or deposited from solution as films. Their decomposition temperatures, under nitrogen, are quite high (~500°C). Finally, their glass transition temperatures decrease when the length of the silane or siloxane link increases. Similar hybrid materials, but with transition-metal based links, have also been prepared by co-condensing the same nanobuiding blocks with Cp_2ZrCl_2 or $[Cp_2ZrCl]_2O$.[68]

Following a similar approach, Hasegawa *et al.* have assembled $[Si_8O_{20}]^{8-}$ cages by reacting them with dimethyldichlorosilane, Me_2SiCl_2, in dimethoxypropane.[69] The solid obtained are made of

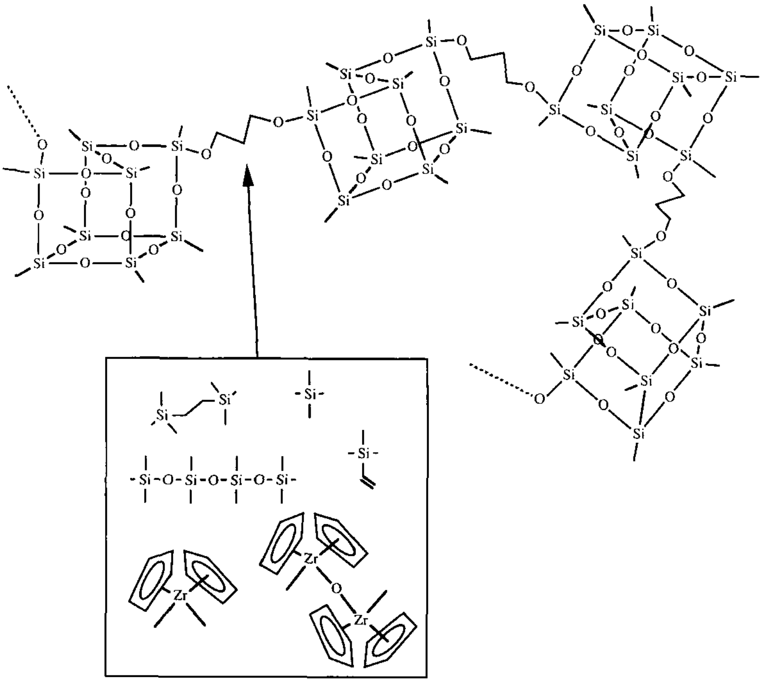


FIGURE 15 Schematic structure of the hybrid materials prepared by condensing $(c\text{-}C_6H_{11})_8T_8(OH)_2$ with various links (cyclohexyl groups have been omitted) (Refs. 67 and 68)

Si_8O_{12} cubes attached by some of their summits through Me_2SiO_2 units. Indeed, solid state ^{29}Si NMR shows $\underline{Si}(OSi\equiv)_4$ and $Me_2\underline{Si}(OSi\equiv)_2$ sites which correspond to the corner of the cubes which have reacted and to the formed links, respectively. NMR also shows $\underline{Si}(OSi\equiv)_3O$ and $Me_2\underline{Si}(OSi\equiv)O$ sites corresponding to unbound cube corners and pending links, respectively. These materials, once dried, exhibit low BET surfaces (~30 m^2/g), but heating them at 350°C under air can raise their specific areas to about 350 m^2/g. Yet, this increase is associated with a partial modification of the structure, as evidenced by ^{29}Si NMR which indicates the formation of $Me\underline{Si}O_3$ sites, likely resulting from the oxydation of some of the links.[69]

Finally, this assembling strategy can also be used for nanobuilding blocks functionalized by $M(OR)_x$ moieties, such as $Q_8M_8^{MPTS}$, $Q_8M_8^{VTMS}$, $Q_8M_8^{AAAAl(OBu)}$, and $Q_8M_8^{AAAZr(OPr)}$ (Table I). Hydrolysing these nanobuilding blocks generates M-OH functions that condense into oxo-polymers (see Section II.A) and connect the nanobricks.[47] Even though the starting spherosilicates are preserved, the inorganic component generated upon hydrolysis-condensation is likely ill-defined, which makes the use of nanobuilding blocks less relevant. Yet, these systems exhibit an interesting feature. Hoebbel *et al.* have shown that the large number of potential assembling sites on $Q_8M_8^{MPTS}$, $Q_8M_8^{VTMS}$ (24 Si-OR per cube) causes important steric effects during condensation. Thus, the so-obtained materials are hydrophilic because many Si-OH groups cannot condense (about 6–7 Si-OH per cube), even after a thermal treatment at 180°C.

III.B.4 Exchange of the charge compensating ions

This strategy has been used for the nanobricks $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$. As previously stated (see Section III.A.2.a), the charge compensating anions of this macrocation are not dissociated in low dielectric constant solvents. Moreover, when the anions are hydroxyls they can be easily exchanged, in solution, for others such as carboxylates. Combining these two characteristics, alternated hybrid co-polymers, exhibiting a bead structure (Fig. 16), have been prepared from $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ and dicarboxylic acids such as adipic acid, $HO_2C(CH_2)_4CO_2H$, or p-terephtalic acid, $HO_2CC_6H_4CO_2H$.[51b] These hybrids are highly insoluble in most organic solvents. Solid state ^{119}Sn NMR confirmed the anion exchange as the spectra of these hybrids are equivalent to that of $\{(BuSn)_{12}O_{14}(OH)_6\}(OAc)_2$. Moreover, FT-IR evidenced a strong network of hydrogen bonds between the bridging hydroxy of the nanobricks and the carboxylates[51b]. Even though the resulting bead structure is similar to that obtained from $(c\text{-}C_6H_{11})_8T_8(OH)_2$, this system is quite different. Here, the assembling is based on electrostatic interactions, reinforced by hydrogen bonds. The organic-inorganic interface is therefore mostly ionic, while it is mainly covalent in the systems discussed previously.

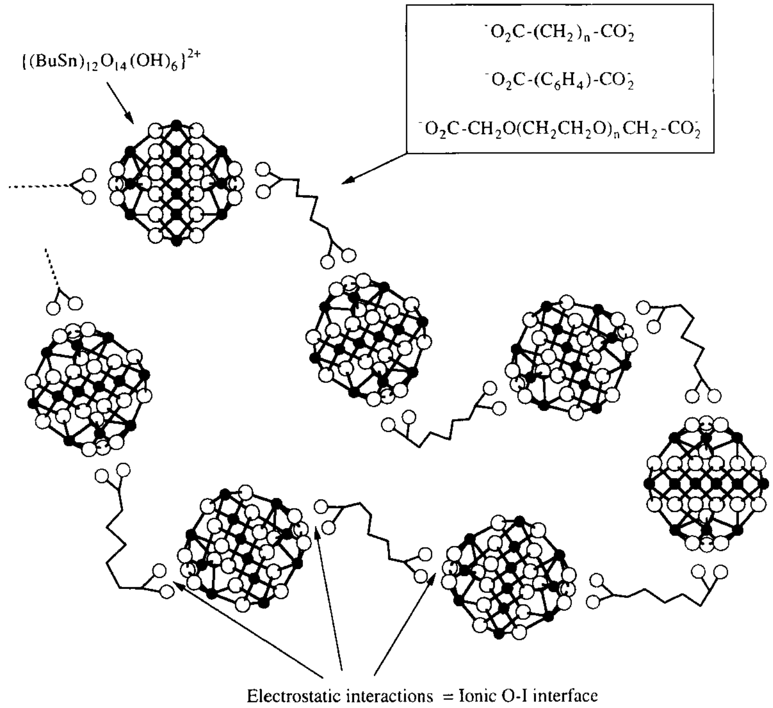


FIGURE 16 Schematic structure of the hybrid materials prepared by assembling $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ with telechelic dicarboxylates (Refs. 51b and 51d)

Insolubility may be an important issue for material processing. Short carboxymethyl terminated poly(ethyleneglycol) chains, $HO_2CCH_2O(CH_2CH_2O)_nCH_2CO_2H$ ($\langle n \rangle \approx 3$ or 11) yield systems with the same bead structure, but soluble (CH_2Cl_2, THF).[51d] This solubility allows the formation of coating by spin coating, for instance. The variation of the average length of the links, obtained by mixing carboxymethyl terminated poly(ethyleneglycol) with 3 and 11 units, results in materials exhibiting very different physical appearances. They change from powder (100% of "3") to tacky wax (100% of "11"). With 50% of "3" and 50% of "11", the material looks like a soft plastic, yet 80% of its weight comes from $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$.

IV. CONCLUSION

Hybrid organic-inorganic materials are more and more developed in the free spaces left between inorganic chemistry, polymer chemistry, organic chemistry, and even biology. The use of the sol-gel process, and more generally the so-called soft chemistry, has allowed to prepare a large number of hybrid materials in the past 10 years. Many new combinations between an inorganic component and an organic or biologic component will likely appear in the future. Yet, a better understanding and control of the local and semi-local structure of these materials is an important issue, especially if tailored properties are sought.

To achieve such control of the material structure, the assembling of well-defined nanobuilding blocks is an interesting approach, but it would be dishonest not to mention some problems. This building game increases the number of synthesis and purification steps, which usually raises the cost tremendously. Heterofunctional nanobuilding blocks, such as $(RMe_2Si)_x(R'Me_2Si)_{8-x}(OSiO_{1.5})_8$, are generally prepared as stastitical mixtures whose distributions are difficult to sharpen. Therefore, improved or new syntheses are needed. The stability of the transition-metals based nanobricks, where a critical size is likely involved, needs also to be better understood and better controlled.

However, the assembling of nanobuilding blocks also exhibits advantages. The inorganic components are nanometric and monodispersed. Their structure is perfectly defined, which likely facilitates the characterization of the final materials. The variety found in the nanobuilding blocks (nature, structure, functionality) and links, associated to different assembling strategies, allow us to build very different types of architectures and organic-inorganic interfaces. Moreover, the step-by-step preparations of the materials usually allows some control over their semi-local structure. One can also combine the nanobuilding block approach with the use of organic templates that self-assemble and allow, through weak forces, control of the assembling step. With the aim of organizing/structuring the nanobuilding blocks prior to their assembling, one can also functionalize them with mesogenic groups and give them self-organizing properties. All these characteristics make these materials interesting models to study the structure-property relationships.

Finally, as far as the elaboration of new materials is concerned, the issue of material processing should also be studied in great detail.

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