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Review

Titanium-Oxo Clusters, Versatile Nanobuilding Blocks for the Design of Advanced Hybrid Materials[#]

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Summary. This review describes the major advances made on titanium-oxo clusters chemistry and their derived hybrid materials. The main synthesis procedures, the cluster structures presented in literature, and the relation between the titanium-oxo clusters condensation degree and poisoning ratio are discussed. The tuned organo-functionalisation of the titanium-oxo based nanobuilding blocks allows to develop a LEGO-like chemistry, able to direct the assembling of a large variety of structurally well defined complex hybrid architectures.

Keywords. Hybrid materials; Nanobuilding blocks; Titanium-oxo clusters; Nanomaterials.

Introduction

One of nature's remarkable features is its ability to combine at the nanoscale (bio)organic and inorganic components allowing the construction of smart natural materials that found a compromise between different properties or functions (mechanics, density, permeability, colour, hydrophobicity, *etc*...). The high level of integration found in many biomaterials and systems is obtained via the association of a maximum of elementary functions in a small volume and hybridisation between inorganic and organic components. The resulting hybrid materials optimize therefore complementary possibilities, functions, and hierarchy [1].

In academic research, hybrid organic–inorganic materials conquer more and more of the free spaces left between inorganic chemistry, polymer chemistry, organic

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[#] In honor of the 60th birthday of Prof. *Ulrich Schubert* chemistry, and biology [2, 3]. The progress in this field depends largely on the core competence of materials chemists, and illustrates the central role of chemistry in the development of advanced materials. An extraordinary amount of research has appeared in the last twenty years in the field of hybrid materials indicating the growing interest of chemists, physicists, and materials researchers to fully exploit this technical opportunity for creating materials and devices benefiting of the best of the three realms: inorganic, organic, and biologic [4]. Moreover, organic–inorganic hybrid materials do not represent only a creative alternative to design new materials and compounds for academic research, but their improved or unusual features allow to develop innovative industrial applications [5–7].

This field of research is based on the numerous possibilities provided by the mild and versatile synthetic conditions of ‘‘Chimie Douce’’ allowing to combine at the nanoscale any organic and inorganic components [8, 4d]. The nanostructure, the degree of organization, and the properties that can be obtained for such hybrid materials certainly depend on the chemical nature of their components, but they also rely on the synergy between these components. Thus, a key point for the design of new hybrids is the tuning of the nature, the extent, and the accessibility of the inner interfaces. As a consequence, the nature of the interface or the nature of the links and interactions exchanged by the organic and inorganic components have been used to categorize these hybrids into two main different classes [4d].

✓ Class I corresponds to all the systems where no covalent or iono-covalent bonds are present between the organic and inorganic components. In such materials, the various components only exchange weak interactions (at least in terms of orbital overlap) such as hydrogen bonding, *van der Waals* contacts, or electrostatic forces.
✓ On the contrary, in class II materials, at least a fraction of the organic and inorganic components are linked through strong chemical bonds (covalent, iono-covalent, or *Lewis* acid-base bonds). The chemical strategy followed for the construction of class II hybrid networks depends of course on the relative stability of the chemical links that associate the different components. The main chemical routes to hybrids and their applications have been extensively described in several review articles [4, 6, 9a].

Recent synthesis pathways of novel hybrid phases are based on the interfacial chemistry between nanobuilding blocks (NBBs: clusters, nanoparticles, colloids...) and the organic species. The use of NBBs as starting units to obtain hybrid organic–inorganic structures is an approach developed with various systems such as oligosilsesquioxanes and derivatives, organotin-oxo clusters, organically functionalized heteropolyoxo-tungstates, transition metal-oxo clusters, and finally, with functionalized nanosized particles (metallic oxides, metals, chalcogenides) [9].

The main NBBs cluster based approaches used to achieve hybrid materials with a high structural control are schematized in Fig. 1.

i) The assembling of NBBs. These NBBs are generally capped with functional ligands, which can be polymerized in a second step or connected through organic spacers, like telechelic molecules or polymers, or functional dendrimers (path A).
ii) Strategies combining the nanobuilding blocks approach with the use of organic templates that self-assemble and allow one to control the assembling step are also

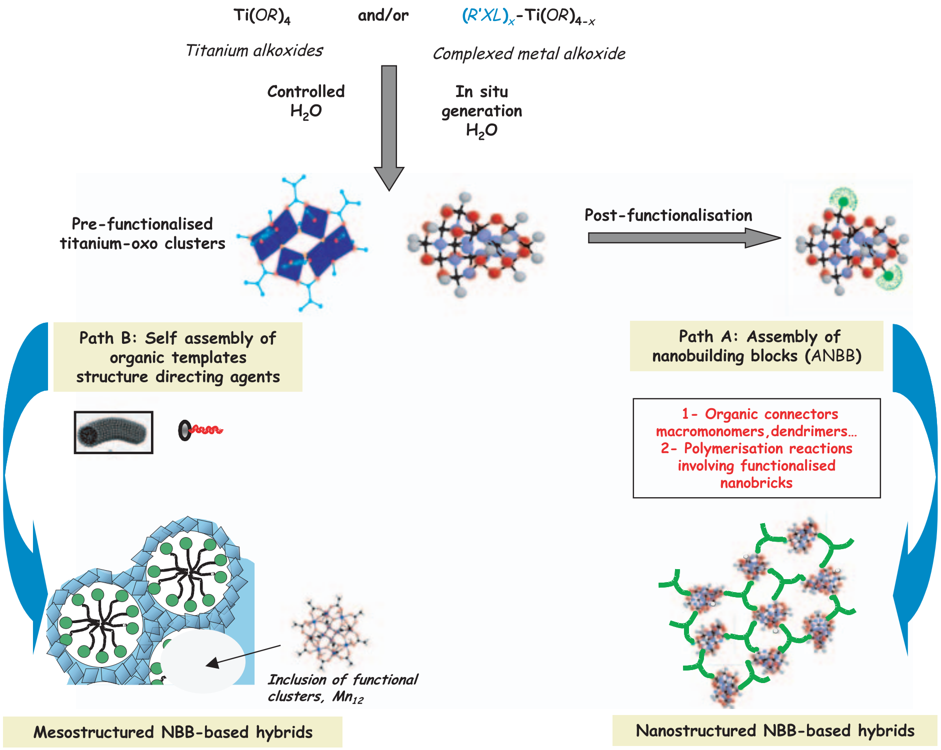


Fig. 1. Different paths to obtain hybrid materials titanium-oxo based NBBs; path A uses already former macromonomers or dendrimers that can react with the cluster surface groups to yield the nanostructured hybrid material; a second strategy consists in using polymerizable ligands (methacrylates, stryryl…) anchored at the cluster surface and driving copolymerization with free monomers; these functional groups can be post-grafted or included *via* complexation within the modified metal alkoxide precursor used to synthesize the metal-oxo cluster; path B involves the self assembly of NBBs in the presence of amphiphilic molecules or structure directing agents (surfactants, amphiphilic block copolymers, double hydrophilic block copolymers…) leading to the formation of a bicontinuous mesostructured hybrid arrangement; the interactions between the template and the inorganic NBB include covalent bonding and *van der Waals* forces (hydrophobic contacts); functional metallic oxo-clusters such as $[Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4]$ can be embedded in mesoporous structure

appearing (Fig. 1, path B). This combination between the "*nanobuilding block approach*" and "*templated assembling*" will have a paramount importance in exploring the theme of "synthesis with construction" of hierarchically organized materials in terms of structure and functions [10]. Moreover, mesostructured materials can immobilize nanobuilding blocks that keep their intrinsic properties in the resulting nanocomposites. As an example, the magnetic clusters $[Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4]$ ($R = CH_3$ or C_6H_5) and $[Mn_4(CH_3COO)_2(pdmH)_6]$ (*pdm*H = 2,6-bis(hydroxymethyl)pyridine) keep their chemical integrity and retain their magnetic properties when they are incorporated in mesoporous silicates [11].

These approaches are very versatile because NBBs exhibit a large variety of interfaces between the organic and the inorganic components (covalent bonding, complexation, electrostatic interactions…). Moreover, NBBs with tuneable

Table 1. Developed formulae, degree of condensation O/Ti, and poisoning ratio *p* of titanium-oxo-alkoxy clusters

Clusters	*R*	*R′*	O/Ti	*p*	Ref.
Titanium-oxo-alkoxy clusters					
$[\mathrm{Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_3(O^{\mathit{i}}\mathit{Pr})_6}]$	H, *Me*, ^{i}Pr		0.33	0.33	[12, 13]
$[\mathrm{Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_3(O^{\mathit{i}}\mathit{Pr})_4}]$	$O_3C_9H_{15}$		0.33	0.22	[14, 15]
$[\mathrm{Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O\mathit{Et})_8(O\mathit{Et})_{12}}]$			0.57	0.29	[16–19]
$[\mathrm{Ti_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_2(\mu_2\text{-}O\mathit{Bz})_8(O\mathit{Bz})_{12}}]$			0.75	0.27	[18]
$[\mathrm{Ti_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O\mathit{Et})_{10}(O\mathit{Et})_{14}}]$			0.8	0.23	[18]
$[\mathrm{Ti_{11}(\mu_3\text{-}O)_{10}(\mu_2\text{-}O)_3(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_7(O^{\mathit{i}}\mathit{Pr})_{11}}]$			1.18	0.18	[15, 20]
$[\mathrm{Ti_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}O)_2(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_4(O^{\mathit{i}}\mathit{Pr})_{12}}]$			1.33	0.18	[20, 21]
$[\mathrm{Ti_{16}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(\mu_2\text{-}O)_4(\mu_2\text{-}O\mathit{Et})_{16}(O\mathit{Et})_{16}}]$			1	0.17	[17, 19, 22, 23]
$[\mathrm{Ti_{17}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_{16}(\mu_2\text{-}O)_4(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_4(O^{\mathit{i}}\mathit{Pr})_{16}}]$			1.41	0.17	[24]
$[\mathrm{Ti_{18}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_{20}(\mu_2\text{-}O)_3(\mu_2\text{-}OH)(O^{\mathit{t}}\mathit{Bu})_{17}}]$			1.55	0.17	[25]
Titanium-oxo-alkoxy-acac clusters					
$[\mathrm{Ti_4(\mu_3\text{-}O)_2(O^{\mathit{i}}\mathit{Pr})_8(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_2(\mathit{acac})_2}]$			0.5	0.54	[26]
$[\mathrm{Ti_{18}(\mu_5\text{-}O)_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{10}(\mu_2\text{-}O)_8(\mu_2\text{-}O^{\mathit{n}}\mathit{Bu})_{14}(O^{\mathit{n}}\mathit{Bu})_{12}(\mathit{acac})_2}]$			1.22	0.15	[27, 28]
Titanium-oxo-alkoxy-carboxylate clusters					
$[\mathrm{Ti_2(\mu_2\text{-}O)(O^{\mathit{i}}\mathit{Pr})_2(HO^{\mathit{i}}\mathit{Pr})_2(\mu_2\text{-}OOCCCl_3)_2(OOCCCl_3)_2}]$			0.5	0.5	[29]
$[\mathrm{Ti_3(\mu_3\text{-}O)(\mu_{??}\text{-}O\mathit{R})_2(O\mathit{R})_6(\mu_2\text{-}OOC\mathit{R}')_2}]$	^{i}Pr	C_6H_5	0.33	0.35	[30]
	$CH_2C\mathit{Me}_3$	H			[31]
		Me			[31]
		$CH_2C\mathit{Me}_3$			[31]
$[\mathrm{Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_2(O^{\mathit{i}}\mathit{Pr})_5(\mu_2\text{-}OOCCCl_3)_3}]$			0.33	0.28	[29]
$[\mathrm{Ti_4(\mu_3\text{-}O)_2(O^{\mathit{i}}\mathit{Pr})_6(\mu_2\text{-}OOC\mathit{R}')_6}]$		$C{=}CH_2$	0.5	0.25	[32, 33]
		$C\mathit{Me}{=}CH_2$	0.5	0.25	[33]
$[\mathrm{Ti_4(\mu_4\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}O^{\mathit{i}}\mathit{Pr})_4(O^{\mathit{i}}\mathit{Pr})_6(\mu_2\text{-}OOC\mathit{R}')_2}]$		H			[34]
		^{i}Pr			[35]
$[\mathrm{Ti_4(\mu_3\text{-}O)_4(O\mathit{R})_4(\mu_2\text{-}OOC\mathit{R}')_4}]$	C_6H_5	$CCo_3(CO)_9$	1	0.17	[36, 37]
	$2,6\text{-}C_6H_3\mathit{Me}_2$	$CCo_3(CO)_9$			[38]
	Et	$CCo_2(CO)_6M^1$			[38]
	^{n}Bu	$CCo_3(CO)_9$			[36, 37]
	^{i}Pr	$CCo_3(CO)_9$			[36, 37]
		$CCo_2(CO)_6M^1$			[38]
$[\mathrm{Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O\mathit{R})_6(O\mathit{R})_6(\mu_2\text{-}OOC\mathit{R}')_4}]$ (Type I)	^{i}Pr	*Me*	0.67	0.17	[21, 39]
	$^{i}Pr\text{-}1,2\text{-}O_2C_6H_4$ (1:1)	$CCo_3(CO)_9$			[36, 37]
$[\mathrm{Ti_6(\mu_3\text{-}O)_4(\mu_2\text{-}O\mathit{Et})_4(O\mathit{Et})_8(\mu_2\text{-}OOC\mathit{R}')_4}]$ (Type II)		$CCo_3(CO)_9$	0.67	0.22	[36, 37]
$[\mathrm{Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O\mathit{R})_2(O\mathit{R})_6(\mu_2\text{-}OOC\mathit{R}')_8}]$	*Et*	*Me*	0.67	0.17	[40]
		$C\mathit{Me}{=}CH_2$			[32, 33, 41]
	^{n}Pr	$CH{=}CH_2$			[33]
		C_6H_5			[42]
	^{n}Bu	*Me*			[43]
	^{n}Pr	*Me*			[44]
		$C\mathit{Me}_2Br$			[45]
$[\mathrm{Ti_6(\mu_3\text{-}O)_6(O\mathit{R})_6(\mu_2\text{-}OOC\mathit{R}')_6}]$	*Et*	$C_6H_4\text{–o–}OC_6H_5$	1	0.17	[46]
	^{i}Pr	H			[34]
		$C_6H_4\text{–o–}OC_6H_5$			[46]

(*continued*)

Table 1 (*continued*)

Clusters	R	R'	O/Ti	p	Ref.
		$\mathrm{CH_2{-}C_6H_5}$			[47]
		$\mathrm{CH_2C}Me_3$			[48]
		$\mathrm{CHCl_2}$			[29]
	$\mathrm{CH_2C}Me_3$	$\mathrm{CH}Me_2$			[31]
		$\mathrm{C_6H_5}$			[42]
$[\mathrm{Ti_6}(\mu_4\text{-O})_2(\mu_2\text{-O})_2(\mu_2\text{-O}Et)_6(\mathrm{O}Et)_8(\mu_2\text{-OOCC}_6\mathrm{H}_5)_2]$			0.67	0.22	[49]
$[\mathrm{Ti_9}(\mu_3\text{-O})_2(\mu_2\text{-O})_6(\mathrm{O}^nPr)_4(\mu_2\text{-OOC}Me{=}\mathrm{CH_2})_{16}]$			0.88	0.07	[50]
Titanium-oxo-alkoxy clusters bearing multidentate ligands					
$[\mathrm{Ti_4}(\mu_3\text{-O})_4(\mathrm{O}^iPr)_4(\mu_2\text{-OOP(C}_6\mathrm{H}_5)_2)_4]$			1	0.17	[51]
$[\mathrm{Ti_4}(\mu_3\text{-O})(\mu_2\text{-O}^iPr)_3(\mathrm{O}^iPr)_5(\mu_3\text{-}R'\mathrm{PO_3})_3]$		$\mathrm{C_6H_5}$	0.25	0.21	[51]
		4-$\mathrm{CNC_6H_5}$			[52]
		Me			[52]
		^tBu			[52]
$[\mathrm{Ti_{10}}(\mu_4\text{-O})_2(\mu_2\text{-O})_4(\mu_2\text{-O}^nBu)_4(\mathrm{O}^nBu)_8(\mathrm{HO}^nBu)_2(\mu_3\text{-}pc)_2(\mu_2\text{-}pc)_6]$			0.6	0.17	[53]
$[\mathrm{Ti_6}(\mu_3\text{-O})_4(\mu_2\text{-O}^iPr)_2(\mathrm{O}^iPr)_2(\mathrm{HO}^iPr)_2(\mu_2\text{-}bph)_6]$					[53]
$\{[\mathrm{Ti_4}(\mu_2\text{-O})(\mathrm{O}^nBu)_7(\mu_2\text{-O}^nBu)(\mu_3\text{-}THMNM)_2]\}_2$					[54]

[1] $M = [\mathrm{Mo(CO)_2}Cp]$ or $[\mathrm{W(CO)_2}Cp]$

functionalities can, through molecular recognition processes, permit the development of a new *vectorial chemistry*. However, depending on the set of chosen experimental conditions, these NBBs will keep or loose their integrity. Therefore, they can be used as true building blocks that can be connected through organic spacers or surface driven condensation reactions, or as a reservoir of inorganic matter, which can be delivered at the hybrid interface to build an extended inorganic network. Moreover, the NBBs approaches provide versatile models to better understand the chemistry and structures of nanohybrids. Indeed, the degree of substitution of NBBs may be changed, thus changing the local symmetry; moreover, the presence of different sites, with different reactivities, will permit the creation of asymmetric hybrid blocks, ready to self-assemble. Each functionalized part can play a defined role directing assembling processes through molecular recognition or/and covalent coupling.

The use of highly pre-condensed NBBs species presents several advantages:

- The use of perfectly calibrated preformed objects, such as clusters, nanoparticles, or nanolayered compounds that keep their integrity in the final material allows to reach a better definition of the inorganic component in the resulting nanohybrid material.
- NBBs exhibit a lower reactivity towards hydrolysis or attack of nucleophilic moieties than metal alkoxides.
- The NBBs components are nanometric and monodispersed, and with perfectly defined structures, which facilitates the characterization of the final materials.

These NBBs based stategies can provide larger concentrations of active dots, better defined systems, minimize coalescence into larger ill-defined aggregates and provide improved mechanical properties. Numerous recent reports already have emphasized the specific magnetic, optical, electrochemical, chemical, mechanical, and catalytic properties of nanostructured hybrid materials built from molecular clusters.

Among the numerous metallic oxo-clusters [9], titanium-oxo clusters are good candidates to model and therefore to understand the chemistry and structures of NBBs based hybrids. They have been extensively studied by *Schubert*'s, *Klemperer*'s, and by *Sanchez*'s groups (see Table 1). This review describes the major advances made on titanium-oxo clusters chemistry and their derived hybrid nanomaterials. The main synthetic procedures, the cluster structures presented in literature, and the relation between the titanium-oxo clusters condensation degree and poisoning ratio are discussed. The tuned organo-functionalisation of the Ti-oxo based nano-building blocks, allows to develop novel hybrid architectures. These resulting hybrid networks are discussed in the light of several striking examples and some of their properties are presented.

Titanium-Oxo Clusters

The titanium-oxo clusters $[M_xO_y(OR)_z(L)_w]$ are polynuclear titanium complexes which size is between 5 and 25 Å. Their perfectly defined structures were characterized by single crystal X-ray diffraction and the resulting developed formulae of these titanium-oxo clusters reported so far are gathered in Table 1. The titanium-oxo clusters exhibit a rich variation in structural types characterized by different

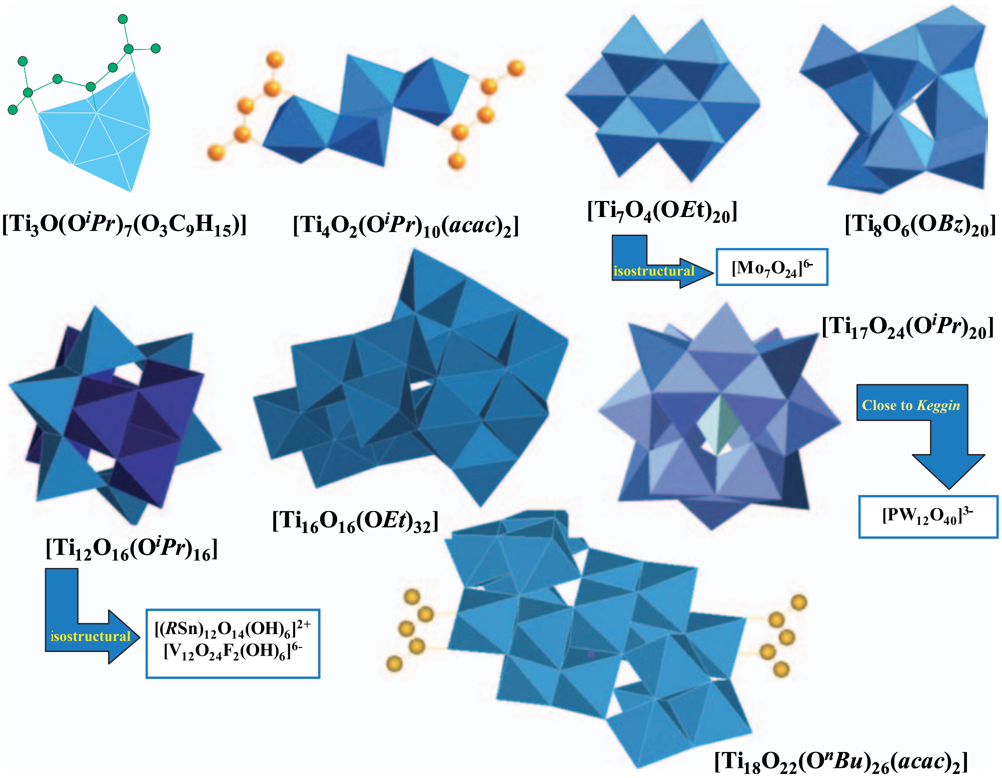
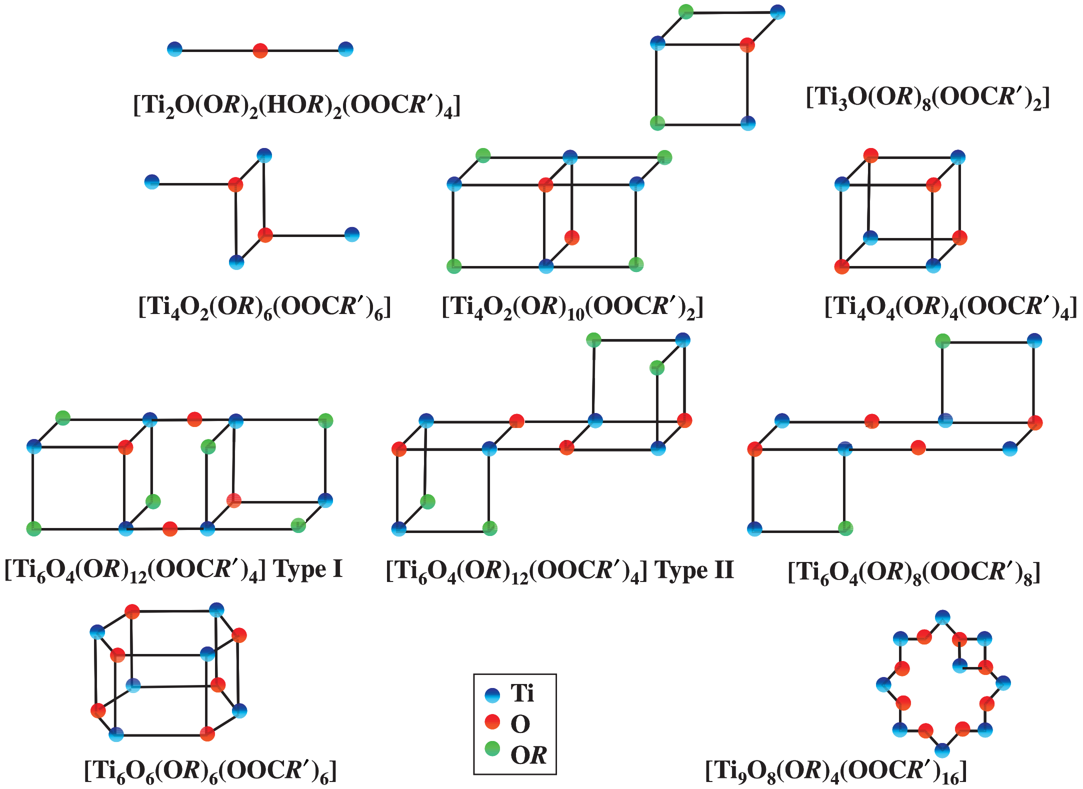


Fig. 2. Polyhedral representations of a few titanium-oxo-alkoxy clusters

coordination modes of the ligands (O, O*R*, and *L*), variations in linkages of the coordination polyhedra, degree of condensation O/Ti, and coordination number of Ti atoms. Today, their nuclearity (number of titanium atoms, *x*) varies from two to eighteen. The metallic centers that exhibit coordination numbers between four and six are coordinated to bridging oxo ligands and terminal or bridging alkoxy, O*R*, groups. A large variety of oxo bridges can be present in the clusters from μ_2-O to μ_5-O. Furthermore, numerous titanium-oxo clusters bear strongly complexing ligands *L* (β-diketone, carboxylic acid, phosphonates...) on their surfaces with a chelating or a bridging coordination mode. The attachment of organic groups that carry organic functionalities, such as polymerizable double bonds, may be the key issue for the preparation of organically modified titanium-oxo clusters.

In the following part of this review, the main polyhedral arrangements of the titanium-oxo framework will be described (see Figs. 2 and 3). Some of these structures are commonly observed in the polyanions chemistry since associations of edge-shared octahedra M_3O_{13} units are typically observed in both families of compounds (see Scheme 1). Moreover, the titanium-oxo cores depend strongly on the steric hindrance of the ligands and on their coordination requirement (bridging and chelating coordination modes). First, titanium polyoxoalkoxy structures will be described, and secondly, the compounds that bear multidentate ligands in addition to oxo and alkoxy groups. This article is restricted to compounds still having alkoxy groups in the coordination sphere of titanium.


$[Ti_2O(OR)_2(HOR)_2(OOCR')_4]$

$[Ti_3O(OR)_8(OOCR')_2]$

$[Ti_4O_2(OR)_6(OOCR')_6]$

$[Ti_4O_2(OR)_{10}(OOCR')_2]$

$[Ti_4O_4(OR)_4(OOCR')_4]$

$[Ti_6O_4(OR)_{12}(OOCR')_4]$ Type I

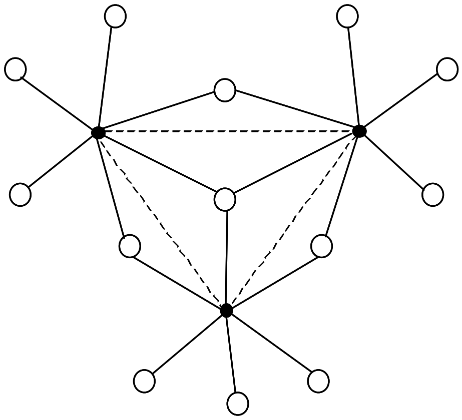
$[Ti_6O_4(OR)_{12}(OOCR')_4]$ Type II

$[Ti_6O_4(OR)_8(OOCR')_8]$

$[Ti_6O_6(OR)_6(OOCR')_6]$

$[Ti_9O_8(OR)_4(OOCR')_{16}]$

Fig. 3. Schematic representations of the skeletal arrangements of oxo-alkoxy-carboxylate clusters



Scheme 1

Structures of Titanium-Oxo-Alkoxy Clusters

The titanium-oxo-alkoxy clusters (Fig. 2) were mainly obtained by the controlled hydrolysis (small $h = H_2O/Ti$ ratio) and condensation of $Ti(OR)_4$ ($R = Et$, ${}^iPr$, ${}^tBu$, Bz). The condensation degree (O/Ti) of a cluster is mainly determined by the hydrolysis ratio h, and the reactivity of O*R* groups. It lies in the relatively narrow range of 0.33 (for $[Ti_3O(OR)_{10}]$) to 1.55 (for $[Ti_{18}O_{28}H(O^tBu)_{17}]$) (see Table 1).

Three titanium-oxo-ethoxy clusters $[Ti_7O_4(OEt)_{20}]$ [16–19], $[Ti_{10}O_8(OEt)_{24}]$ [18] and $[Ti_{16}O_{16}(OEt)_{32}]$ [17, 19, 22, 23] exhibit particularly compact structures based on μ_4-oxo, μ_3-oxo, and μ_2-oxo ligands connected to octahedral titanium centers. These compact arrangements of polyhedra are probably due to the low steric hindrance of ethoxy groups that have terminal or bridging coordination modes in those structures. They are synthesized from the $Ti(OEt)_4$ precursor which exhibits different oligomeric structures (dimer, trimer in pure benzene, or tetramer in solid state) that are in equilibrium in solution [55]. These oligomers are built from alkoxy bridging between Ti centers, thereby favouring a coordination expansion of the Ti center to five (dimer, trimer) or six (tetramer). This aggregation of the titanium alkoxide, which is mainly due to the *Lewis* acidity of the Ti atoms and the *Lewis* basicity of the O*R* group contributes to a decrease of the Ti alkoxide reactivity. Therefore, the titanium-oxo frameworks of $[Ti_7O_4(OEt)_{20}]$, $[Ti_{10}O_8(OEt)_{24}]$, and $[Ti_{16}O_{16}(OEt)_{16}]$ may also be influenced by the aggregation state of the parental $Ti(OEt)_4$ precursor. These complexes result from edge-shared octahedral M_3O_{13} associations. The $[Ti_7O_4(OEt)_{20}]$ cluster exhibits a structure of seven octahedrally coordinated titanium centers. This arrangement of polyhedra is isostructural to the polyanion $[Mo_7O_{24}]^{6-}$. It is based on a central octahedron that shares six of its twelve edges with the other TiO_6 octahedra. A more condensed titanium-oxo-ethoxy cluster $[Ti_{10}O_8(OEt)_{24}]$ is derived from the titanium-oxo framework of $[Ti_7O_4(OEt)_{20}]$. Actually, the $\{Ti_{10}O_8\}$ skeleton of this cluster can be described by two interpenetrating $\{Ti_7O_4\}$ cores resulting in a centrosymmetric $[Ti_{10}O_8(OEt)_{24}]$ molecule. The titanium-oxo core of the $[Ti_{16}O_{16}(OEt)_{16}]$ cluster is built up of two orthogonal blocks of eight TiO_6 octahedra. In each block, six octahedra form a layer with a NiAs-type structure, with the remaining two lying either side of the layer.

Numerous titanium-oxo clusters have been obtained from a $Ti(OR)_4$ precursor with a bulky alkoxy group ($R={}^iPr$, ${}^tBu$, Bz). The titanium-oxo-alkoxy clusters exhibit more open structural frameworks that prevent steric repulsions between O*R* groups. Their composition is also dependent on the reactivity of the parental alkoxide $Ti(OR)_4$. Indeed in contrast to $Ti(OEt)_4$, $Ti(OR)_4$ ($R={}^iPr$, ${}^tBu$, Bz) is monomeric and its reactivity towards hydrolysis is quite high since the titanium atom is still four-coordinate and can not extend its coordinence environment to six.

The $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(O^iPr)_9]$ ($R=H$, Me, ${}^iPr$) [12, 13] cluster is the first hydrolysis compound of $Ti(O^iPr)_4$ in the presence of $HO^iPr/HOMe$. This trinuclear unit can be described by a M_3O_{13} unit of octahedra sharing edges that is capped by an additional μ_3-O*R* ligand replacing three terminal O*R* groups. Therefore, a highly compact arrangement is built since each octahedron shares two of its adjacent octahedral faces with the two neighbouring octahedra. Such cluster topology is quite exceptional among titanium-oxo clusters since to our knowledge, it is the only cluster that exhibits a μ_3-O*R* ligand and an arrangement of face-sharing between octahedra presumably because this arrangement promotes strong repulsions between the metallic centers. This cluster is one of the least stable of the known titanium-oxo clusters in hydrocarbon solvents and this is certainly related to its low degree of condensation. However, the relative stability of a cluster might in general be strongly influenced by the steric repulsions between the ligands. Indeed, only the clusters $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(O^iPr)_9]$ ($R=H$, Me) could be isolated as single crystals while the sterically crowded analogue $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}O^iPr)(O^iPr)_9]$ was much more unstable. Accordingly, this μ_3-O*R* group may also be occupied by a large tridentate ligand resulting in the formation of a less constrained structure $[Ti_3(\mu_3\text{-}O)(O^iPr)_7(Me_2C(O)CH{=}C(O)CH_2C(O)Me_2)]$ [14, 15]. Substitution of the μ_3-O*R* and μ_2-O*R* groups in the $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(O^iPr)_9]$ cluster can also be expected due to the high basicity of these groups. Such a substitution is expected to proceed without structural changes if both the number of the occupied coordination sites and the charges of the entering ligands are the same as those of the leaving groups. By this approach, the $[Ti_3(\mu_3\text{-}O)(OOCPh)_2(O^iPr)_8]$ [30] was obtained by the reaction of benzoic acid with $[Ti_3O(O^iPr)_{10}]$ and $[Ti_3(OMe)(O^iPr)_9]$. The resulting substitution of two O^iPr by two HOOC*Ph* groups preserves almost entirely the titanium-oxo core of the titanate cluster. The only structural change is the decrease of one Ti coordination number to five in order to balance the substitution of one μ_3-O*R* ligand by a bridging benzoate.

$[Ti_8O_6(OBz)_{20}]$ ($Bz=CH_2\text{–}C_6H_5$) [18] molecule has a crystallographic C_2 symmetry in the solid state and therefore, the asymmetric unit is constituted by a half-molecule. In this cluster two isostructural groups of two TiO_6 octahedra are connected to two TiO_5 square pyramids by edge-sharing through four μ_3-oxo and eight bridging O*Bz*. These two groups are linked by the octahedra sharing corners through two μ_2-oxo bridges. The $[Ti_7O_4(OEt)_{20}]$ [16–19] cluster presents a close nuclearity. However, in contrast to the $[Ti_7O_4(OEt)_{20}]$ cluster where all Ti atoms are six-coordinate, half of the Ti atoms are five-coordinate in $[Ti_8O_6(OBz)_{20}]$ [18], presumably to accommodate bulkier bridging and terminal O*Bz* in the framework.

The $[Ti_{12}O_{16}(O^iPr)_{16}]$ [20, 21] and $[Ti_{11}O_{13}(O^iPr)_{18}]$ [15, 20] clusters exhibit close titanium-oxo frameworks in which five- and six-coordinate Ti atoms are connected to μ_3-oxo and μ_2-oxo bridges. Their titanium-oxo core forms a nearly spherical cage that is large enough to reduce the steric repulsions between bulky O^iPr groups. The $[Ti_{12}O_{16}(O^iPr)_{16}]$ cluster is isostructural to the organostannate framework $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ ($R = {}^iPr$, ${}^nBu$) [56–58] and the fluorovanadate framework $[V_{12}O_{24}F_2(OH)_6]^{6-}$ [59]. This oxo-cluster can be described by three subunits: the first one is a hexameric crown which contains only five-coordinate titanium atoms. The two others are trimers M_3O_{13}, based on edge-shared titanium octahedra. The complete oxo-cluster framework is obtained by capping each side of the crown by a trimer. The titanium-oxo skeleton of $[Ti_{11}O_{13}(OR)_{18}]$ is derived from that of $[Ti_{12}O_{16}(OR)_{16}]$ by removal of a five-coordinate titanium atom of the crown.

Two large clusters $[Ti_{18}O_{28}H(O^tBu)_{17}]$ [24] and $[Ti_{17}O_{24}(O^iPr)_{20}]$ [25] join the group of polyoxometalate complexes that display the *Keggin* structure. This structure was first described for the heteropolyanion $[PW_{12}O_{40}]^{3-}$ and reported for a variety of polyoxo-tungstate and -molybdate compounds [60]. This compact arrangement has a great importance in the construction of metal-oxo cores in heteropolyanion chemistry. The metal-oxo core of the *Keggin* structure consists of a central tetrahedron XO_4 ($X = P$, Si, transition metal) which is encapsulated in a metal-oxygen cage of twelve MO_6 octahedra. These octahedra constitute four trinuclear M_3O_{13} units of octahedra sharing edges. The trinuclear units are corner-linked to the central tetrahedron. Much more compact arrangements (*i.e.* super *Keggin* structures) can be derived from the *Keggin* structure since some square faces between trimeric M_3O_{13} units can be capped by other polyhedra. Therefore, the structure of the $[Ti_{18}O_{28}H(O^tBu)_{17}]$ and $[Ti_{17}O_{24}(O^iPr)_{20}]$ clusters can be viewed as a $[Ti_{13}O_{40}]^{28-}$ *Keggin* complex capped by five and four TiO^{2+} units in a trigonal-bipyramidal environment. In both structures, titanium atoms are connected through μ_4-oxo, μ_3-oxo, and μ_2-oxo bridges and terminal/bridging OR groups.

Structures of acac-Substituted Titanium-Oxo-Alkoxy Clusters

A few *acac*-substituted titanium-oxo clusters were obtained upon hydrolysis of modified $Ti(OR)_{4-c}(acac)_c$ precursors (*acac*: acetylacetonate). The condensation degree of these clusters is mainly governed by the complexing ratio, $c = acac\mathrm{H}/\mathrm{Ti}$ and the hydrolysis ratio h. Indeed, acetylacetonate groups (*acac*) are rather strong chelating ligands in such a way that *M-acac* bonds are less hydrolysable than M–OR bonds and then prevent condensation [4d, 9b]. Therefore, these groups protect the polyoxotitanium species from growing by blocking condensation sites (*vide supra*). Two *acac*-substituted titanium-oxo clusters $[Ti_4O_2(O^iPr)_{10}(acac)_2]$ [26] and $[Ti_{18}O_{22}(O^nBu)_{26}(acac)_2]$ [27, 28] were obtained with a low complexing ratio, $c = 0.5$ and 0.1, respectively.

The titanium-oxo core of $[Ti_4O_2(O^iPr)_{10}(acac)_2]$ is isostructural to that of $[Ti_4O_2(O^iPr)_8(HYDBINO)_2]$ (*HYDBINO* = 5,5′,6,6′,7,7′,8,8′-octahydrobinaphtho) [61]. In this structure, the Ti atoms that bear *acac* groups are six-coordinate while the two remaining are five-coordinate. The $\{Ti_4O_2\}$ skeleton consists of a structural unit of two square pyramids sharing an edge. The octahedra are connected to this edge *via* two μ_3-oxo and two μ_2-O^iPr. $[Ti_{18}O_{22}(O^nBu)_{26}(acac)_2]$ [27, 28] is one of the highest condensed clusters with $[Ti_{18}O_{28}H(O^tBu)_{17}]$ [25]. One structural feature of this cluster is the presence of all kinds of oxo bridges from μ_2-oxo to

μ_5-oxo. Interestingly, it is the only cluster that contains two μ_5-oxo bridges. The highly compact framework of this cluster is built from a central unit consisting of ten octahedra linked through edges. Six of these octahedra lead to the formation of a sheet, while the four others are located on both sides of this sheet. Two other groups of four octahedra are then linked to this compact unit, *via* corner sharing. The orientation of these two groups, with respect to the central unit is 90°. Such an orthogonal molecular assembling is also present in the structure of $[Ti_{16}O_{16}(OEt)_{32}]$ [17, 22] cluster. The titanium-oxo core of $\{Ti_{18}O_{22}\}$ is surrounded by 26 butoxide groups (14 bridging and 12 terminal) and two *acac* groups in a chelating coordination mode.

Structures of Carboxylate-Substituted Titanium-Oxo-Alkoxy Clusters

The carboxylate-substituted titanium polyoxoalkoxy clusters constitute an important subclass of titanium-oxo clusters whose nuclearity varies from two $[Ti_2O(O^iPr)_2(HO^iPr)_2(OOCCCl_3)_4]$ [29] to nine $[Ti_9O_8(OR)_4(OOCR')_{16}]$ [50]. The main frameworks of carboxylate substituted titanium-oxo clusters are presented in Fig. 3. In those structures, the degree of condensation ($0.33 < O/Ti < 1$) is often more limited due to the increased coordination requirement of the carboxylate ligands that are always bridging (exception for chlorocarboxylates in $[Ti_2O(O^iPr)_2(HO^iPr)_2(OOCCCl_3)_4]$ [29] with two terminal carboxylates). In all titanium-oxo clusters, the Ti centers are six-fold coordinated with only one exception (one Ti atom in $[Ti_3O(OR)_8(OOCR')_2]$ [30, 31] is five-fold coordinated). This coordination number restricts the maximum carboxylate/Ti ratio of Ti-oxo clusters to 2, *i.e.* to the composition of the titanium-oxo-carboxy polymer $TiO(OOCR')_2$ (provided that all carboxylate ligands are bidentate) [62]. This ratio is consequently lower than 2 in polyoxo-carboxylate-titanium clusters in order to accommodate additional O*R* groups. The Ti atoms are connected by μ_2-oxo and μ_3-oxo bridges (μ_4-oxo in $[Ti_4O_2(O^iPr)_{10}(OOCR)_2]$ ($R = H, {}^iPr$) [34, 35]). The presence of at least one μ_3-oxo in those structures allows the description of most carboxylate-substituted Ti-oxo clusters as sub-structures of the cubic $\{Ti_4O_4\}$ motif [41] (see Fig. 3).

$[Ti_2O(O^iPr)_2(HO^iPr)_2(OOCCCl_3)_4]$ [29] is the least condensed titanium-oxo-alkoxy-carboxylate cluster. It consists of two symmetrical octahedral titanium centers with a common μ_2-oxo. The two octahedra are connected by two bridging trichloroacetate groups. Three terminal groups complete the coordinence of Ti: an O^iPr, an HO^iPr molecule, and a trichlorocarboxylate. The monodentate coordination mode of the trichloroacetate is a structural feature of this cluster since carboxylates are generally bridging in the titanium-oxo clusters. It may be explained by the electro-attractive behavior and steric bulk of *trichloro*-carboxylates compared to *alkyl*-carboxylates. Moreover, this compound is also the first isolated titanium-oxo-alkoxy-carboxylate complex with an alcohol solvating the Ti atom.

The clusters $[Ti_3O(OR)_8(OOCR')_2]$ ($R = OCH_2CMe_3$, $R' = H$, Me, or CH_2CMe_3) [31] consist of two six-coordinate Ti atoms and one five-coordinate Ti atoms assembled by a μ_3-oxo bridge. The $[Ti_3O(OR)_8(OOCR')_2]$ ($R = OCH_2CMe_3$, $R' = H$ or CH_2CMe_3) clusters, which are isostructural to $[Ti_3(\mu_3\text{-}O)(OOCPh)_2(O^iPr)_8]$ [30] described above, display an asymmetrical distribution of ligands. In contrast, in the $[Ti_3O(OR)_8(OOCR')_2]$ [31] ($R = OCH_2CMe_3$, $R' = Me$) cluster the two carboxylate groups bridge the same Ti atoms leading to a symmetric arrangement of bridging and terminal ligands. The $\{Ti_3O\}$ skeleton of $[Ti_3O(O^iPr)_7(OOCCCl_3)_3]$ [29] is quite close to that of $[Ti_3O(OR)_8(OOCR')_2]$ with an additional carboxylate group and a subsequent change in the distribution of bridging/terminal O*R* groups at the surface of the cluster. In contrast to the structure of $[Ti_3O(OR)_8(OOCR')_2]$, the three titanium atoms are six-coordinate.

Three different structures of tetramers were reported:

- The titanium-oxo core of $[Ti_4O_2(O^iPr)_6(OOCR')_2]$ [32, 33] (Table 1) is based on a structural motif of two octahedra sharing an edge. The corners of two octahedra are connected to this edge by two μ_3-oxo.
- The titanium-oxo framework of $[Ti_4O_2(OR)_{10}(OOCR')_2]$ [34, 35] (Table 1) is best described as a sub-structure of a cubic $\{Ti_4O_4\}$ core. It can be viewed as two face shared $\{Ti_4O_4\}$ cubes, which have one of the non-shared, mirror-related titanium atoms removed from each cube. The four six-coordinate titanium atoms are linked by a μ_2-oxo and a single μ_4-oxo group which is the peculiar feature of this structure.
- The titanium-oxo core of $[Ti_4O_4(OR)_4(OOCR')_4]$ [36–38] (Table 1) consists of a distorted $\{Ti_4O_4\}$ cube with Ti centers and μ_3-oxo occupying alternate vertices. Each Ti atom lies in the center of a distorted octahedron of O atoms with three derived from μ_3-oxo ligands, two from bridging cobalt carbonyl ligands, and one from a terminal alkoxy ligand. The cobalt carbonyl carboxylates bridge four of the six edges of the Ti_4 tetrahedron.

Among the family of hexanuclear titanium-oxo clusters (see Table 1), four structural types of the titanium-oxo cores can be described. They all involve six-coordinate Ti atoms:

- The structure of $[Ti_6O_4(OR)_8(OOCR')_8]$ [32, 33, 40–45] can be described by two $\{Ti_2O_{10}\}$ (two edge-sharing octahedra) units linked by two corner-sharing octahedra.
- Two structural types were reported for the developed formulae $[Ti_6O_4(OR)_{12}(OOCR')_4]$:
  - ✓ The basic structural motif of $[Ti_6O_4(OR)_{12}(OOCR')_4]$ ($R = {}^iPr$, $R' = Me$ and $R = {}^iPr$-1,2-$O_2C_6H_4$, $R' = CCo_3(CO)_9$) [21, 26, 36–39] (Type I) is the typical M_3O_{13} unit made of edge-sharing Ti octahedra. The cluster is constructed from two trioctahedral units that are connected by sharing corners through two μ_2-oxo bridges.
  - ✓ The structure of $[Ti_6O_4(OR)_{12}(OOCR')_4]$ ($R = Et$, $R' = CCo_3(CO)_9$) [36, 37] (Type II) consists of two identical units. Each of these units contains a $\{Ti_3O_4\}$ core fragment which can be derived from the $\{Ti_4O_4\}$ cube by removing one Ti vertex.
- The $[Ti_6O_4(OEt)_{14}(OOCPh)_2]$ [49] cluster is formed by addition of benzoic acid to the $[Ti_7O_4(OEt)_{20}]$ cluster. The substitution of two monodentate O*Et* groups by two bidentate benzoate groups and the removal of one $Ti(OEt)_4$ unit is accompanied by an extensive rearrangement of the cluster structure despite the fact that all the Ti atoms are still octahedrally coordinated. This structure can be

presented as an association of two uncomplete distorted $\{Ti_4O_4\}$ cubes with one missing corner in each cube. The Ti centers, μ_4-(oxo/OR), and μ_3-oxo occupy alternate vertices of the cubes that are connected to each other by two μ_4-oxo groups and two bridging OR groups.

- The structure of $[Ti_6O_6(OR)_6(OOCR')_6]$ [46] consists of two six membered rings of alternating Ti and O atoms $[Ti\text{-}(\mu_3\text{-}O)]_3$ that are stacked, offset to each other. Each titanium atom possesses a terminal alkoxide and two OOCR' ligands, forming an up-down chain of OOCR' ligands.

$[Ti_9O_8(O^nPr)_4(OMc)_{16}]$ [50] is the cluster having the highest average number of carboxylate ligands per Ti atom (1.78) known today. This large value leads to a quite open structure which consists of a ring with six octahedra linked by corners and two octahedra sharing an edge. Therefore, only two oxo bridges are μ_3-oxo while the six remaining are μ_2-oxo. This macrocycle is not symmetric with regard to the distribution of bridging methacrylate and bridging OR groups.

Structures of Titanium-Oxo-Alkoxy Clusters Bearing Other Multidentate Ligands

The partial hydrolysis and condensation of modified titanium alkoxide precursor was extended to other bidentate or even tridentate ligands. In particular, promising results were obtained with bidentate diorgano phosphinic acids R'_2PO_2H and tridentate organophosphonic acids $R'PO_3H_2$. The cluster $[Ti_4O_4(O^iPr)_4(OOPPh_2)_4]$ [51] which was obtained by reaction of $Ti(O^iPr)_4$ with $Ph_2P(O)OH$ ($c = Ph_2PO_2H/Ti = 1$) is isostructural to the carboxylate analogue, *i.e.* the $[Ti_4O_4(OR)_4(OOCR')_4]$ cluster discussed above. This is not surprising since phosphinate and carboxylate groups are bidentate ligands with similar coordination properties. However, a large variety of coordination modes may be accessible to tridentate ligands (organophosphonic acid $R'PO_3H_2$, catechol ligands) so that their introduction may expand the structural chemistry of titanium-oxo cores giving rise to novel arrangements of polyhedra. Moreover, by substituting bidentate by tridentate ligands, a decrease of the condensation degree of the clusters may be expected. Reaction of $Ti(O^iPr)_4$ with different organophosphonic acids $R'PO_3H_2$ ($R' = Ph$, 4-CNPh, Me, ^tBu) and small amounts of water led to the formation of the cluster $[Ti_4O(O^iPr)_8(R'PO_3)_3] \cdot DMSO$ [52]. The Ti–O–P core can be described as a six-membered $\{Ti_3(\mu\text{-}O^iPr)_3\}$ ring adopting a chair conformation with alternating isopropoxy groups and six-coordinate Ti atoms. The Ti atoms of this trinuclear unit present a highly distorted octahedral environment and are connected through a μ_3-oxo bridge. In this structure, the phosphonato groups act as tridentate bridging ligands: each phosphonato group bridges two Ti atoms of this trinuclear unit to a fourth six-coordinate Ti atom. It is noteworthy that the condensation degree of this cluster ($O/Ti = 0.25$) is quite small compared to other carboxylate titanium-oxo tetramers. It is in agreement with the presence of strong tridentate ligands in the structure. In contrast to this cluster, all Ti atoms of carboxylate-substituted clusters are connected with each other by at least one bridging oxygen.

The $[Ti_{10}O_6(O^nBu)_{12}(HO^nBu)_2(pc)_8]$ [53] with (pc = pyrocatechol = 1,2-dihydroxybenzene) was obtained by the reaction of $Ti(O^nBu)_4$ with pc (complexation ratio $c = pc/\mathrm{Ti} = 0.75$). Its molecular structure can be described as two tetrahedral $\{Ti_4(\mu_4\text{-}O)\}$ building block sharing corners with one central edge-sharing dioctahedral unit. The tetrahedral unit is similar to the titanium-oxo core of $[Ti_4O_2(OR)_{10}(OOCR')_2]$ described above. In this cluster, the pyrocatechol ligands exhibit two kinds of coordination modes: a singly bridging chelate μ_2-(O, O′, O′) mode (*i.e.*, one oxygen bridges two Ti centers and the other one is linked to Ti in a terminal fashion) and a doubly bridging chelate μ_3-(O,O′O,O′) mode (two oxygen atoms bridge two Ti atoms). Since a wide range of coordination modes may be accessible to the catechol ligands, these ligands are certainly very attractive for the design of new titanium-oxo frameworks. By the same approach, the $[Ti_6O_4(O^iPr)_4(HO^iPr)_2(bph)_6]$ [53] (*bph* = 2,2′-biphenol) was obtained by the reaction of $Ti(O^iPr)_4$ with *bph* ($c = 2$). This cluster exhibits a quasi ladder-like hexameric core based on four μ_3-oxo groups. The metal-oxo core may arise from hydrolysis of O*R* by residual water in the reaction medium since no water was added to the modified precursor ($h = 0$). The *bph* ligands present two different coordination modes: a μ_2-(O, O′) bridging mode and a μ_2-(O, O, O′) chelating-bridging mode. In a similar approach, the tripodal ligands 2,6-bis(hydroxymethyl)-*p*-cresol (*BHMPC*H$_3$) and tris(hydroxymethyl)nitromethane (*THMNM*H$_3$) were also used to yield the $[Ti_4(\mu_3\text{-}O)_2(BHMPC)_2(HBHMPC)_2(H_2BHMPC)_2]$ and $[Ti_4O(O^nBu)_8(THMNM)_2]_2$ clusters. These two clusters display the same basic tetraoctahedral motif of the parental tetrameric alkoxide $Ti_4(OR)_{16}$ ($R = Et$, ^nBu). Two such units are fused through two μ_2-oxo groups in the octameric complex $[Ti_4O(O^nBu)_8(THMNM)_2]_2$. All edges of the tetraoctahedral unit initially occupied by μ-O*R* groups in the tetramers $Ti_4(OR)_{16}$ are substituted by tripodal ligands in both clusters. Indeed, bridging O*R* groups are expected to be more reactive towards hydrolysis and complexation than terminal ones and are sites of preferential attack for substitution by OH/O*X* groups. No water was added for the synthesis of both clusters. Therefore, their titanium-oxo cores result presumably from partial hydrolysis of O*R* groups by residual water present as traces in the synthetic medium. The preservation of the $\{Ti_4O_{16}\}$ core upon hydrolysis arises probably from the presence of large tripodal ligands that protect titanium atoms against hydrolysis. This $\{Ti_4O_{16}\}$ oxo-core can therefore be used as a building block in various supramolecular networks. This strategy of using multidentate ligands to stabilize new titanium-oxo skeletons was extended to ligands such as citric acid or aminoalcohols: we may finally report the polynuclear titanium-oxo complexes $[Ti_8O_{10}(\text{citrate})_4(H_2O)_{12}]$ [63] and $[Ti_6O_6(N\text{-methyldiethoxoamine})_6]$ [64] in which all O^nPr groups of the parental alkoxide $Ti(O^nPr)_4$ were replaced by the multidentate ligands.

General Synthetic Routes for Preparing Titanium-Oxo Clusters

The titanium-oxo-alkoxy clusters are usually prepared from the controlled hydrolysis (low H_2O/Ti ratio ≤ 1) of the corresponding titanium alkoxide in solution [4d, 9b]. They are formed at the early stages of the titanium alkoxide polycondensation and may be reaction intermediates in the polycondensation of titanium alkoxides. They could also constitute some dead ends in the polymerization pathway or a reservoir of matter. These clusters are isolated by crystallization, frequently resulting in low yields, from the ill-defined oxo polymers concurrently formed. The simultaneous formation of large titanium-oxo polymers and small clusters arises from the high reactivity of titanium alkoxide towards hydrolysis [4d]. Therefore, numerous titanium-oxo clusters were obtained by hydrolysis (with a low H_2O/Ti ratio ≤ 1) of complexed alkoxides $M(OR)_{n\text{-}c}(L)_c$ ($L = \beta$-diketone, organophosphinic acids, organophosphonic acids, catechols…) [4d, 9b]. Indeed, it is quite known that the control of the transition metal polycondensation reactions can be performed through the use of inhibitors such as protons, or complexing ligands, that act as "poison" towards the growth of oxo-polymers [4d, 9b]. Due to the bidentate character of these ligands, the complexation of the titanium alkoxides will cause an increase of the metal coordination. Moreover, the formation for many of these ligands of a metallo-cycle containing five or six bonds considerably increases the strength of the *M–L* link towards hydrolysis. The hydrolysis of these new modified precursors will mostly, if not exclusively, involve the alkoxy groups. Therefore, these ligands can reduce the functionality of the titanium precursors. The condensation degree of the clusters depends strongly on the complexing ratio $c = L/\mathrm{Ti}$ and the hydrolysis ratio $h = \mathrm{H_2O/Ti}$: more condensed species are obtained as c decreases and h increases [4d]. As an example the controlled hydrolysis of $\mathrm{Ti(O}R)_{4\text{-}c}(acac)_c$ leads to $[\mathrm{Ti_4O_2(O}^iPr)_{10}(acac)_2]$ [26] for $c = 0.5$ while $[\mathrm{Ti_{18}O_{22}(O}^nBu)_{26}(acac)_2]$ [27, 28] is obtained for $c = 0.1$. These complexes show the striking dependence of the condensation degree of a cluster and the complexing ratio. It should be interesting to establish a general correlation between this complexing ratio and the condensation degree of a metal polyoxoalkoxide. However, no straightforward relation exists between these two parameters if one considers different metal alkoxides. Indeed, the reactivity of the corresponding alkoxide depends on the electronegativity and the size of the metal. As an example with $c = 2$, a dimer $[\mathrm{Ti_2O_2}(acac)_4]$ is obtained while for a similar complexing ratio, a hexamer $[\mathrm{Ce_6O_4(OH)_4}(acac)_{12}]$ is formed with cerium(IV). Therefore, in an attempt to relate the chemical composition to the degree of condensation of transition metal polyoxoalkoxides, a new parameter p called the poisoning ratio was recently introduced [65]. This poisoning ratio can be defined as the proportion of the metal coordination sphere occupied by terminal ligands that have reacted neither by hydrolysis/condensation nor by coordination polymerization. Any non-bridging ligand must actually be considered as poison. Moreover, a chelating ligand such as *acac* has certainly to be considered more poisoning than a terminal alkoxy ligand. By this approach, a poisoning ratio defined as $p = \sum C_{\text{poison}} / \sum_N C_{\text{metal}}$ could be calculated for each titanium polyoxoalkoxy cluster. C_{poison} is the number of donor atoms in the poisoning ligand (1 for a terminal O*R* and 2 for a bidentate chelating ligand). C_{metal} is the coordination number of the metal centre. $[\mathrm{Ti_{16}O_{16}(O}Et)_{16}]$ and $[\mathrm{Ti_2O_2}(acac)_4]$ clusters have the same condensation degree ($\mathrm{O/Ti} = 1$) while they exhibit a different poisoning ratio $p = 1/6$ and $2/3$. These two clusters show that a relation between the condensation degree and the nuclearity x is rather weak while the one between p and x is much better. The p dependence of x is presented in Fig. 4 in which the monomeric $\mathrm{Ti(O}^iPr)_4$ precursor is included ($p = 1$). For compact titanium-oxo-alkoxy clusters, the experimental curve can be well approximated by the following power law: $x = p^{-3/2}$ (Eq. A). However, some titanium-oxo clusters ($x = 3$, 4, and 6) and particularly those that

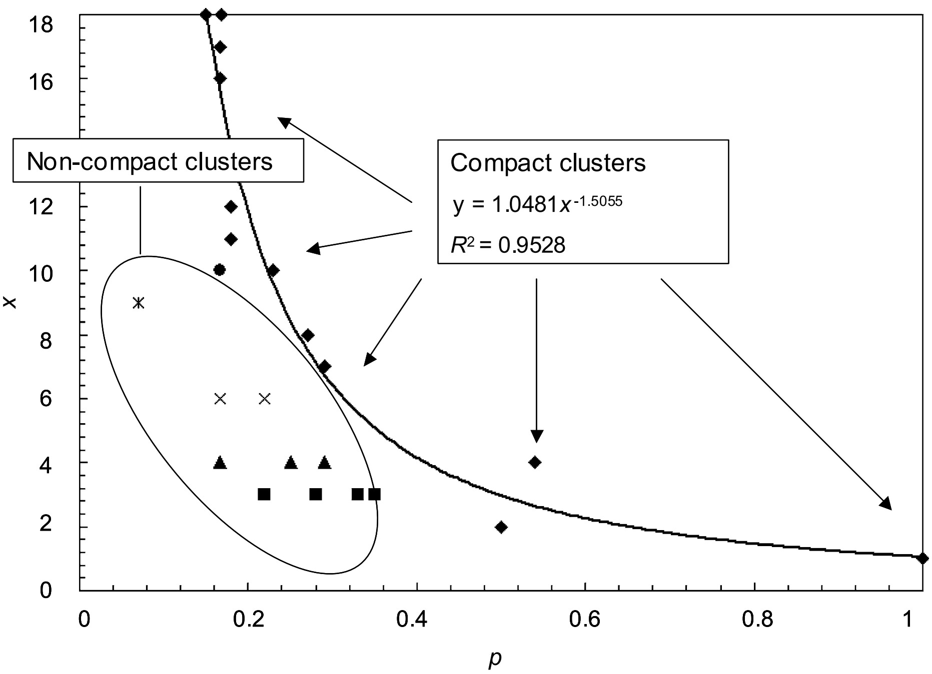


Fig. 4. Nuclearity *x versus* poisoning ratio *p* for titanium-oxo-alkoxy clusters

bear carboxylate ligands do not lie on this idealized curve. These clusters exhibit quite open structures and therefore, it seems that Eq. A is relevant to compact clusters whose octahedra are mainly assembled by edges. That is why the relation between N and p depends presumably on the geometry of the polyoxoalkoxy clusters. It was previously reported that the exponent of $x = p^{-3/2}$ could be related to the one that relates the surface area A and the volume V of the aggregates ($A \propto V^{1/3}$) assuming also that the poisoning ratio is proportional to the specific surface ($p \propto A/V$) and that the nuclearity of a cluster is proportional to the volume ($x \propto V$). Similar equations were also reported for larger zirconium polyoxoalkoxides which means that this approach may be generalized to other transition metal alkoxides.

For numerous titanium-oxo clusters, the source of oxolation was water generated *in-situ* in the reaction medium. In fact, direct addition of water to the titanium alkoxide precursors may lead to local surconcentrations of water, which are not favourable for the stability of these clusters upon ageing. Titanium-oxo-carboxylate clusters were prepared by the modification of titanium alkoxide with carboxylic acids for $c = R'\text{COOH}/\text{Ti} \geq 1$ [21, 32, 33, 41, 43, 54]. The titanium-oxo core of these clusters arises from water produced *in-situ* through esterification reactions. For $R'\text{COOH}/\text{Ti} \geq 1$, the substitution reaction (Eq. (1)) is competing to an esterification reaction between the free carboxylic acid in excess and the released alcohol (Eq. (2)).

$$\mathrm{Ti}(\mathrm{O}R)_4 + R'\mathrm{COOH} \leftrightarrows [\mathrm{Ti}(\mathrm{O}R)_3(\mathrm{OOC}R')] + R\mathrm{OH} \qquad (1)$$

$$R'\mathrm{COOH} + R\mathrm{OH} \leftrightarrows R'\mathrm{COOR} + \mathrm{H_2O} \qquad (2)$$

However, titanium-oxo-carboxylate clusters are also found for $R'\mathrm{COOH}/\mathrm{Ti} = 1$. Different chemical processes may be taken into account to explain this observation. First, if the equilibrium constant for the formation of $[\mathrm{Ti(O}R)_3(\mathrm{OOC}R')]$ is quite small, ester formation may result from the free carboxylic acid in equilibrium with $[\mathrm{Ti(O}R)_3(\mathrm{OOC}R')]$. Intramolecular reactions may also take place inside the modified precursor between carboxylate and alkoxy ligands. Similarly, it has been shown that ketones (acetone, acetylacetone, diacetone alcohol) can be used through condensation-dehydration reactions as oxolation sources for the formation of titanium-oxo clusters ($[\mathrm{Ti}_3(\mu_3\text{-O})(\mathrm{O}^i Pr)_7(Me_2\mathrm{C(O)CH{=}C(O)CH_2C(O)}Me_2)]$ and $[\mathrm{Ti}_{11}\mathrm{O}_{13}(\mathrm{O}^i Pr)_{18}]$) [15]. Another approach for the synthesis of titanium-oxo clusters consists in heating the titanium alkoxide precursors by reflux or in a hydrothermal autoclave [17]. In absence of any organic entities, titanium may condense presumably through a non-hydrolytic route which implies etherification reactions (Eq. (3)):

$$2\mathrm{Ti(O}R)_4 \leftrightarrows (R\mathrm{O})_3\mathrm{Ti{-}O{-}Ti(O}R)_3 + R\mathrm{O}R \tag{3}$$

This synthesis route is expected to give rise to the $[\mathrm{Ti}_{16}\mathrm{O}_{16}(\mathrm{O}Et)_{16}]$ cluster, although no ether could be detected in the reaction mixture. In the presence of carboxylic acid, the esterification-polycondensation reactions are kinetically and thermodynamically favoured by increasing the temperature. This chemical approach was used to prepare titanium-oxo-alkoxy clusters ($[\mathrm{Ti}_6(\mu_3\text{-O})_6(\mathrm{O}Et)_6(\mu_2\text{-OOCC}_6\mathrm{H}_4\text{–}o\text{–}\mathrm{OC}_6\mathrm{H}_5)_6]$, $[\mathrm{Ti}_6\mathrm{O}_4(\mathrm{O}^i Pr)_{12}(\mathrm{OOC}Me)_4]$ $[\mathrm{Ti}_{12}\mathrm{O}_{16}(\mathrm{O}^i Pr)_{16}]$, $[\mathrm{Ti}_{17}\mathrm{O}_{24}(\mathrm{O}^i Pr)_{20}]$) [24, 46]. An increase of the cluster nuclearity was evidenced by increasing the temperature and the $c = R'\mathrm{COOH}/\mathrm{Ti}$ ratio. Indeed, for $c = 1.2$ an hexameric compound $[\mathrm{Ti}_6\mathrm{O}_4(\mathrm{O}R)_{12}(\mathrm{OOC}R')_4]$ that still bears acetate ligands is obtained at room temperature. The presence of acetate ligands in the complex means that the acetic acid added to the titanium precursor was not completely converted to ester and water. In contrast, $[\mathrm{Ti}_{12}\mathrm{O}_{16}(\mathrm{O}^i Pr)_{16}]$ and $[\mathrm{Ti}_{17}\mathrm{O}_{24}(\mathrm{O}^i Pr)_{20}]$ were obtained for $c = 1.2$ and $c = 1.3$, respectively, and at temperatures of 80 and 150°C [66]. Since these complexes do not contain any acetate ligands, it means that most of the acetic acid molecules have been transformed into isopropylester and water by increasing the temperature. A larger conversion of the esterification process is obtained and consequently a higher hydrolysis ratio h [24, 62]. Finally, another chemical route implies preformed titanium-oxo clusters that can be used as a reservoir of matter to produce other species. The reaction of $[\mathrm{Ti}_7\mathrm{O}_4(\mathrm{O}Et)_{20}]$ with benzoic acid results in $[\mathrm{Ti}_6\mathrm{O}_4(\mathrm{O}Et)_{14}(\mathrm{OOC}Ph)_2]$ with concomitant rearrangement of the cluster structure [30]. The formation of this complex is certainly related to the strong reactivity of the $[\mathrm{Ti}_7\mathrm{O}_4(\mathrm{O}Et)_{20}]$ clusters towards nucleophilic additives (benzoic acid) due to the small size of its titanium-oxo core [15].

Hybrid Materials Based on Titanium-Oxo Clusters

When can properly functionalized perfectly defined inorganic nanobuilding blocks, such as metal-oxo-alkoxy clusters, be assembled without damage to create new hybrid materials? Despite the successes of elaboration of hybrid materials by the sol–gel processes, amorphous materials are generally obtained that exhibit some polydispersity in the size and composition of the components of the hybrids. A suitable approach to achieve a better definition of the inorganic component is based on the assembling of well-defined nanobuilding blocks [9] that are defined as perfectly calibrated, nanometric, and monodispersed preformed objects. Metallic oxo-clusters, by the perfect control of the nature of their surface are good candidates to have a better understanding and a better control of the local and semi-local structure of the resulting nanocomposites. Because the study of the structure-property relationships is an important issue, especially if tailored properties are sought, these versatile nano bricks can be considered as good models to gain better knowledge of the properties of hybrid materials. Indeed, the characterization of materials based on well defined species is facilated, the nature, the extent, and the accessibility of the hybrid interface is better controlled, and the phase segregation usually encountered in the preparation of nanocomposites can be reduced. Moreover, by the tuning of the structure, the nature of the functionalities and links, associated to different assembling strategies, the NBBs approach allows to build very different types of architectures.

Literature reports a large number of metal-oxo clusters with sizes ranging from 5 to 25 Å based on silicon, tin, or transition metal chemistries that are potential nanobuilding blocks for the elaboration of hybrid materials [9]. The high ionic strength of the M–C bond, when M is a transition metal makes it very sensitive to hydrolysis or nucleophilic attacks. Therefore, the route of functionalizing transition-metal-based nanobricks with M–C bonds cannot be used contrary to silicon or tin precursors. Different strategies have been described in the literature to overcome this problem, including functionalization of the surface clusters by complexing ligands or the formation of stable M–O–Si–R bonds [4d, 9]. The presence of appropriate functional groups on the organic shell of the inorganic cluster allow the formation of covalent bonds with an organic polymer to give nanobuilding blocks-based hybrid material. The following part of this review will be focused on nanocomposites based on titanium-oxo clusters. Except few examples [67, 68] the work reported in the literature is essentially performed by *Schubert*'s and *Sanchez*'s group.

There are two possibilities to functionalize metal-oxo clusters by organic groups. Whether by *in situ* functionalization of the clusters during their formation, which allows the elaboration of structurally well defined transition metal-oxide clusters with polymerizable surface ligands by the carefully controlled hydrolysis and condensation of metal alkoxides in the presence of unsatured carboxylate ligands. Whether, by grafting functional organic groups onto the surface of preformed oxometallic clusters, which allows a perfect control of the shape of the inorganic oxo-core and the number of functional ligands at the surface of the nanobricks and their localization on the structure.

In situ Functionalization of Titanium-Oxo Clusters

In the *in situ* functionalization method, the oxo-clusters are formed in the presence of functional molecules which serve to cap the cluster surface. The incorporation of the organic groups on the cluster's surface is controlled by the chemical reactions by which the cluster is formed. This process is based on a self-assembly of the organic and inorganic units.

Organically substituted titanium-oxo clusters (or other transition metal-oxo based clusters such as Zr, Ta...) can be prepared by the reaction of metal alkoxides $M(OR)_4$ with a defined excess of acrylic or methacrylic acid. Crystalline clusters of the general composition $M_xO_y(OH/OR)_z(OCR')_w$ of differing size and shape are obtained. Structurally characterized $Ti_6O_4(OEt)_8(OR)_8$ [32, 33], $Ti_4O_2(O^nPr)_8(OR)_8$ [33], $Ti_4O_2(O^iPr)_6(OR)_6$ [32, 33], and $Ti_9O_8(O^nPr)_4(OR)_{16}$ [30] ($OR =$ methacrylate and/or acrylate) have been reported and the synthetic route of elaboration of these oxo-clusters was already presented in this review.

The molecular structures of the clusters show that double bonds of the (meth)acrylate ligands are fully accessible for further chemical reactions. The proportion of reactive ligands on the cluster surface can be modulated with a variable and controllable ratio of non-polymerizable (OR) and polymerizable (OR') ligands [69]. Two approaches can be followed and have been reported. The first approach consists on the preparation of metal-oxo cluster by the use of a mixture of methacrylic and *iso*-butyric acid. The second approach consists on the partial exchange of the polymerizable ligands for non-polymerizable ones which can also be performed on the preformed functionalized oxo-cluster without modification of the size and shape of the oxo-core. Although, in the latter case the reactive/non reactive ligands ratio can not yet be controlled in a rational way.

The pre-formed carboxylate-substituted clusters are then polymerized in the presence of organic co-monomers. In the resulting hybrid polymers, the clusters crosslink the organic polymer chains very efficiently [33]. The properties of the cluster-crosslinked hybrid polymers are distinctly different to those of the parent polymers and are influenced by (i) the cluster proportion, (ii) the kind of cluster, (iii) the ratio of functional and non-functional capping ligands, and (iv) the polymerization conditions [70]. The variation of these parameters allows modifying the materials properties of the hybrid materials. Varying the cluster proportion in the polymer or the proportion of reactive ligands on the cluster surface affects the cross-linking density and all the properties associated with that. For an example, depolymerization of undoped polymer *PMMA* is strongly reduced and even suppressed by the increase of the cross-linking density. The thermal degradation behavior is improved as the cluster proportion and thus the crosslinking degree increases [33].

Copolymerization of the clusters with methyl methacrylate (*MMA*) or methacrylic acid (*MA*) in ratios between 1:50 and 1:2000 resulted in hybrid polymers in which the polymer chains are efficiently cross-linked by the oxo-metallate clusters. Glassy, insoluble materials were typically obtained upon copolymerization with *MMA*, and insoluble powders with *MA*. The specific surface area of the doped *PMA* depends on the amount of cluster incorporated and increased with an increasing cluster proportion. The cluster crosslinked *PMMA* hybrids were insoluble in common organic solvents but swelled. The solvent uptake upon swelling increased with increasing the comonomer/cluster ratio [33].

More recently, the organic polymerization conditions have been modified in order to improve the conversion of organic monomers and to get a narrower molecular mass distribution. The optimization of the polymerization conditions by the use of a pre-polymerization step, leads to an improvement of the thermal stability of the hybrids probably due to a better polydispersity of the organic phase and a better consumption of the vinylic groups [69]. Polymerization of appropriately substituted clusters with organic co-monomers is also possible with other polymerization techniques than free radical polymerizations. The prerequisite is that the organic ligands of the employed clusters bear suitable functionalities, such as 2-bromopropianate groups for atom transfer radical polymerization (ATRP) [45], and 5-norbornene-2-carboxylate ligands on zirconium-oxo cluster $[Zr_6O_4(OH)_4(5\text{-norbornene-2-carboxylate})_{12}]$ give an alternative to obtain oxo-cluster crosslinked polymers by ring opening metathesis polymerization (ROMP) [70]. As an example, $Ti_6O_4(O^iPr)_8(OOCCBrMe_2)_8$ was used as a macroinitiator to produce inorganic–organic core-shell nanoparticles. The core is built up of connected titanium polyhedra and the shell is built up from the growth of organic polymers in a well controlled manner. The diameters of the resulting nanoparticles are in the nanometer range as studied by light scattering and AFM [45].

Post-Functionalization of Titanium-Oxo Clusters

The advantage of the post-functionalisation of oxo-clusters is that the cluster cores can be prepared by well-established techniques. However, for a covalent modification of the cluster surface, reactive groups must be available, and sometimes the modification by organic groups may require a rearrangement of the cluster to accommodate multidentate ligands. Since such clusters are very stable, their rearrangement is generally not thermodynamically favored, and therefore the substitution of the cluster surface by organic groups may be difficult to achieve. The attachment of organic groups yielding thereby ionic interactions is also possible. In this case, the charge of the cluster should be spatially located because delocalized charges result in weak interactions which can be broken during further reactions. The tendency of metal alkoxides to support transalcoholysis or transesterification reactions can be advantageously used with the aim to post-functionalized metallic oxo-clusters. In the post-functionalization of titanium-oxo clusters, the alkoxy-oxo cluster $[Ti_{16}O_{16}(OEt)_{32}]$ seems to be a relevant example.

The $[Ti_{16}O_{16}(OEt)_{32}]$ [17, 22] presents a good compromise with the yield (more than 70%) and the stability of its oxo-core towards nucleophilic species [23, 71]. This oxo-cluster is synthesized by the controlled hydrolysis of $Ti(OEt)_4$. Its structure consists of two orthogonal blocks of eight TiO_6 octahedra with an organic shell constituted by 32 ethoxy groups. The 16 titanium atoms of the inorganic core are interconnected through three different types of oxygen bridges. Four oxygen atoms are doubly bridging (μ_2-oxo), eight are triply bridging (μ_3-oxo), and four are quadruply bridging (μ_4-oxo). There are two kinds of ethoxy groups: 16 ethoxides are bonded to one titanium atom (μ_2-oxo: terminal ethoxy groups) and the other 16 ethoxides are linked to two titanium atoms (μ_3-oxo: bridging ethoxy groups). The geometry of the structure presents a 2 axis and a pseudo -4 axis, so that the 32 organic groups can be divided into 8 groups of 4 pseudo-equivalent ethoxy groups. The characterization of the metallic oxo-core can be performed by ^{17}O NMR [18, 72] (after the enrichment of the cluster by $H_2{}^{17}O$ during its synthesis) while the organic alkoxy groups are usually characterized by ^1H and ^{13}C NMR [23]. A complete spectroscopic assignment of each ethoxy group was proposed after combining crystallographic data, ^{13}C NMR T_1 measurements, and ^1H-^1H, ^1H-^{13}C 2D NMR experiments [23, 73].

A complete study of the surface reactivity of the cluster towards nucleophilic species was recently reported [23] in order to control the number of accessible functionalities, their exact location correlated with their spectroscopic assignment, and to control the kinetic parameters of the cluster modification. A better understanding of the reactivity of the organic shell of the cluster allows having a better tuning of the affinities and compatibility between substituents and polymeric dispersion media. This understanding allows to increase the homogeneity of the resulting hybrid material.

$[Ti_{16}O_{16}(OEt)_{32}]$ is stable in solution (toluene and ethanol) and the ethoxy groups present at the surface are labile, with the ability to be selectively exchanged by transalcoholysis reactions with preservation of the titanium-oxo core, leading to new oxo-alcoxy clusters $Ti_{16}O_{16}(OEt)_{32-x}(OR)_x$ ($R =$ alkyl, phenyl, styrenic... groups). The reactivity of the $Ti_{16}O_{16}(OEt)_{32}$ cluster towards aliphatic and aromatic alcohols was investigated by *in situ* ^{13}C NMR in solution and the use of the molecular structures established by single-crystal X-ray diffraction of two clusters, $Ti_{16}O_{16}(OEt)_{28}(O^nPr)_4$ and $Ti_{16}O_{16}(OEt)_{24}(O^nPr)_8$, as references [23]. The kinetics of the substitution reaction and the degree of substitution can be adjusted by tuning the nature of the alcoholic reagent. With linear aliphatic alcohols (such as *n*-propanol and *n*-butanol), only 8 ethoxy groups can be exchanged even with a large excess of such alcohols [19, 23]. When the pK of the alcohol is lower (methanol), the degree of substitution increases. For sterically hindered alcohols (*i*-propanol) the substitution is less effective. In the case of more acidic reactants (phenol), all the terminal ethoxy groups are exchanged by phenoxy ligands, yielding to a new $Ti_{16}O_{16}(OEt)_{16}(OPh)_{16}$ cluster. The intermediate clusters ($[Ti_{16}O_{16}(OEt)_{28}(O^nPr)_4]$, $[Ti_{16}O_{16}(OEt)_{24}(O^nPr)_8]$, $[Ti_{16}O_{16}(OEt)_{28}(OPh)_4]$, and $[Ti_{16}O_{16}(OEt)_{24}(OPh)_8]$) have been isolated and characterized by ^{13}C and ^1H NMR and for some of them by single-crystal X-ray diffraction. Thus, the $[Ti_{16}O_{16}(OEt)_{32}]$ nanobuilding unit can be substituted in a controlled fashion by four, eight, or sixteen new ligands. The post-functionalization by transalcoholysis reactions can be also extending to transesterification reactions [23].

The lability of the ethoxide groups and the possibility to introduce new ligands at the surface of the cluster were used in order to create functional NBBs. By the use of appropriate alcohols or acetate derivates, clusters bearing styrenic or methacrylate groups have been synthesized. The modification of the cluster was carried out by treatment of the $[Ti_{16}O_{16}(OEt)_{32}]$ in a toluene solution with different ratio of 4-acetoxystyrene [74] or hydroxyethyl methacrylate (*HEMA*) [75, 76]. The transalcoholysis or the transesterification reactions proceeded as expected with the introduction of styrenic or methacrylate groups producing the functional clusters ($[Ti_{16}O_{16}(OEt)_{32-x}(OPhCH{=}CH_2)_x$, $x = 4$, 8, or 16 and $[Ti_{16}O_{16}(OEt)_{24}(OEMA)_8]$). Hybrid organic-inorganic networks were then obtained by copolymerization of the functional cluster with an organic monomer (stryrene, hydroxyethyl methacrylate, or a thermoset methacrylate precursor). These new hybrid materials can be described as transparent 3D networks in which inorganic nano-fillers are covalently linked to the host organic matrix (Fig. 5).

The composition of the hybrids can be adjusted and the structure of the resulting nanocomposites was determined by TEM and SAXS. The mechanical and thermal properties were investigated by DMTA and TGA. The presence of this kind of inorganic phases enhances significantly the thermal stability and the

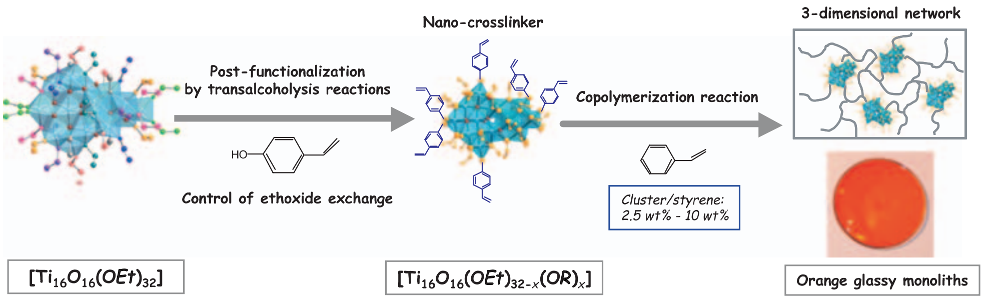


Fig. 5. Schematic route of the elaboration of polystyrene reinforced by covalently bonded titanium-oxo clusters; step 1: functionalization of the oxo-cluster $[Ti_{16}O_{16}(OEt)_{32}]$ by transalcoholysis reaction; step 2: copolymerization of $[Ti_{16}O_{16}(OEt)_{32-x}(OPhCH{=}CH_2)_x]$ ($x = 4$, 8, or 16) with styrene

mechanical properties of the polymers by increasing the titanium-oxo cluster content and a strong reinforcement is observed in the rubbery regimes with only an amount of 2.5 wt%. SAXS measurements show the presence of three different levels of structure, a large structure composed by aggregates of size in order of 120 nm, an intermediate structure with aggregates of size in order of 30 nm, and the sub-unit structure which corresponds to the primary clusters. Nevertheless, only few clusters are involved in the building of aggregates and the oxo-clusters can be considered as well-distributed in the nanocomposites.

The hybrid materials based on the titanium-oxo clusters $[Ti_{16}O_{16}(OEt)_{32}]$ are also good models to understand the optical behaviors encountered in titanate composites. We recently reported that interpenetrating networks based on titanium-oxo-poly(hydroxyethyl methacrylate) lead to a strong laser-induced darkening activity [77]. These materials are obtained through one-pot synthesis from modified titanium alkoxides $(Ti(OEMA)_{4-x}(O^iPr)_x)$ copolymerized with *HEMA*. The high photonic activity, inherent to the titanium oxide phases, has been assigned to electrons trapped at Ti^{3+} sites as a result of sample irradiation by UV photons. When the inorganic phase is constituted by $[Ti_{16}O_{16}(OEt)_{24}(OEMA)_8]$, the same behavior is observed, nevertheless, the intensity of coloration is lower (for the same ratio of titanium oxide phase) due to a better dispersion of the clusters in the organic media: we showed that it is necessary to have more extended inorganic domains with a extended hybrid interface to display a strong optical activity [78].

Nanotextured Materials Based on Titanium-Oxo Clusters

By combining the nanobuilding block approach with the use of organic templates that self-assemble, organizing/structuring nanocomposites have been performed. Indeed, the surface reactivity of the titanium-oxo cluster, $[Ti_{16}O_{16}(OEt)_{32}]$, towards nucleophilic molecules can be advantageously used with the aim of designing nanostructured hybrid materials. The alkoxy-oxo clusters used without further modification, act as the inorganic precursor, which can be assembled with dendrimers [79, 80] or amphiphilic block copolymers [81–83].

First, the assembly of preformed inorganic entities permits to circumvent the high reactivity of metal alkoxides towards hydrolysis of the Ti(IV) metal center and makes it easier to obtain long-range ordered phases. It is well known that clusters opposite to the more reactive titanium alkoxides, can be organized and hydrolysed under controlled conditions. On the other hand, the use of functionalized dendrimers or block copolymers permits to control the reactivity at the surface of the cluster, giving birth to novel architectures.

$[Ti_{16}O_{16}(OEt)_{32}]$ molecules are dissolved in a texturing medium formed by arrangements of block copolymers, or attached to ordering agents, such as dendrimeric molecules. The mixing of the clusters and the templating agents or dendrimers in dry *THF* or toluene leads to yellow to orange glassy solids upon solvent evaporation under nitrogen flow or by placing the solution in *Petri* dishes open to the atmosphere. Water from atmospheric moisture diffuses into these solutions and likely link the pre-condensed bricks by hydrolysis-condensation reactions.

Dendrimers combine their highly controlled size and shape with the versatility of their functional tips [84] permitting to control the interactions of the hybrid interface and this combination permits formation of tailored phases. Two different dendrimers with alcohol and acid functions have been studied [79, 80]. In the case of benzyl alcohol-dendrimers transalcoholysis reactions occur, covalent bonding between dendrimers and clusters was shown by ^{13}C CP MAS NMR, and the integrity of the titanium-oxo core was checked trough solid state ^{17}O NMR. The shape of the organic blocks dictates a pyramidal local symmetry, which is repeated to form a larger range ordered texture leading to the formation of a continuous inorganic phase (investigated by DRX). On the other hand, in the case of acid-capped dendrimers, the bridging behavior of the carboxylate was observed by FTIR. Nevertheless, ^{17}O and ^{13}C NMR show a partial destruction of the titanium-oxo core due to the bidentate chelating behavior of the carboxylate when increasing the cluster content (Fig. 6).

The control of the growth and the morphology of mesotextured materials can be achieved by the use of organic templates which self-organise into complex structures, patterning inorganic architectures built from nanobuilding blocks pre-

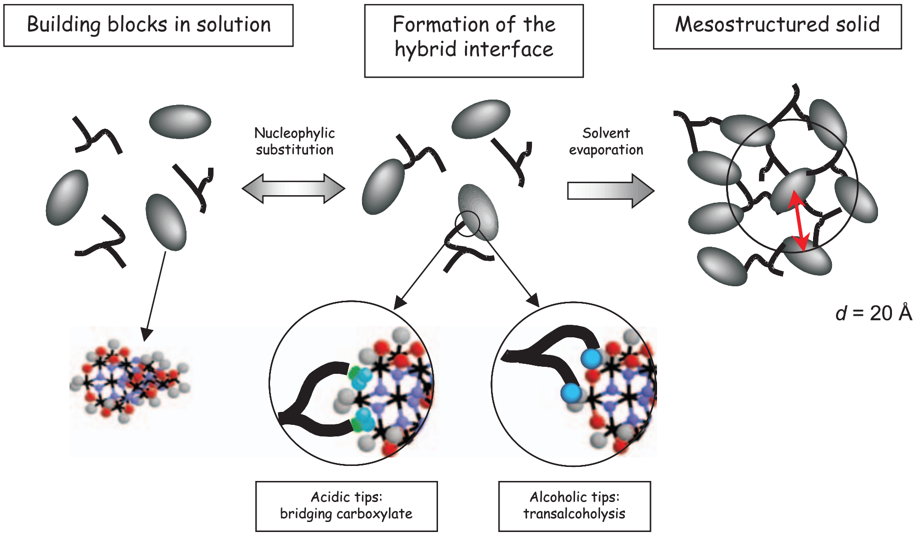


Fig. 6. Schematic route of the elaboration of nanostructured hybrid materials based on the assembly of the titanium-oxo clusters $[Ti_{16}O_{16}(OEt)_{32}]$ and dendrimers

cursors. The titanium-oxo cluster [$Ti_{16}O_{16}(OEt)_{32}$] was used also as precondensed building block for the sol–gel synthesis of titanium oxide nanostructures in the presence of an amphiphilic block copolymer *PEO-b-PPO* [hydrophilic poly(ethylene oxide), *PEO*, and hydrophobic poly(propylene oxide), *PPO*] as a structure directing agent [81]. Amphiphilic block copolymers consisting of hydrophilic and hydrophobic blocks can through their incompatibility give rise to their self-assembly into particulate structures such as spherical and cylindrical micelles and also liquid crystalline phases. In the construction of the mesostructured hybrid network, the interactions between the surface of the inorganic precursor and the organic texturing agent are of paramount importance. There are two essential interactions that lead to unfolding of the polymer; transalcoholysis of the $-CH_2-CH_2-OH$ tips of the texturing agent on the oxo-cluster moieties and chelation of titanium(IV) ions or oligomers by *PEO* or *PPO* blocks. Thus, strong chelation between hydrophobic clusters and non ionic polar heads leads to polymer unfolding and thus to worm-like phases. Reactions were carried out in low water content media (moisture as the only water source), that allow the connection of the clusters without cleaving the titanium-oxo core to form the inorganic network.

The elaboration of nanostructured titanium oxide from the assembly of the titanium-oxo cluster [$Ti_{16}O_{16}(OEt)_{32}$] and another amphiphilic block copolymer, *PS-b-PMAA*, have been reported [82, 83]. The copolymers used consist of one polystyrene block and one poly(methacrylic acid) block. In contrast to the previously used triblock copolymers poly(ethylene oxide)-poly(propylene oxide), the solubility difference between the blocks is more pronounced in the case of *PS-b-PMAA*. As a consequence, this copolymer is expected to make the template more stable against structural changes occurring throughout the reaction. In addition, the carboxylate groups induce a strong chemical binding to the oxo-clusters by ligand exchange (Fig. 7).

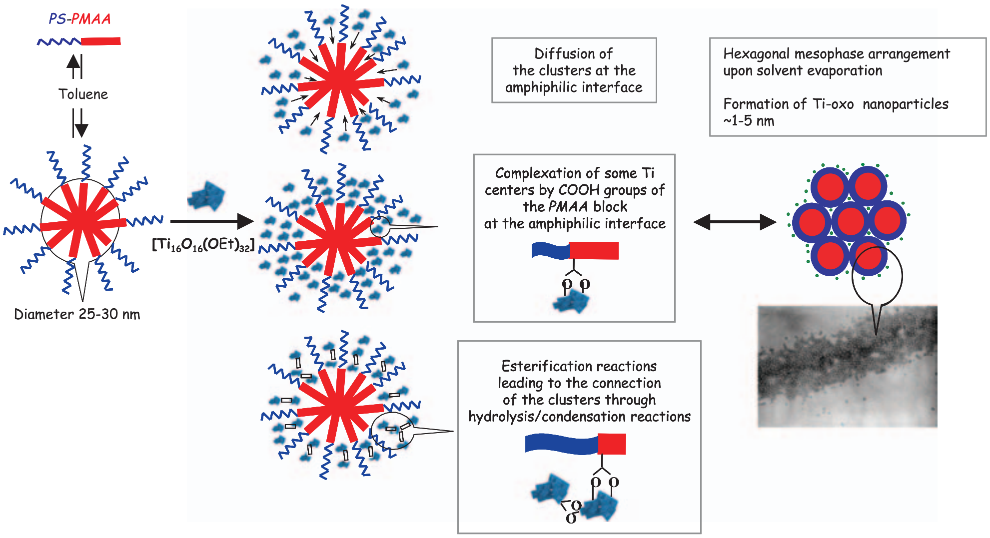


Fig. 7. Schematic route of the elaboration of mesostructured hybrid materials from the assembly of the titanium-oxo cluster [$Ti_{16}O_{16}(OEt)_{32}$] and amphiphilic block copolymer *PS-b-PMAA*

The resulting polymer-titanium oxide nanocomposites structures were characterized by TEM and SAXS. Titanium oxide nanoparticle-block copolymer composites with different topologies can be obtained under the structure directing influence of block copolymer micelles. The morphology of the materials is strongly dependent on the polarity of the solvent used to dissolve the block copolymer.

In this study, two organic solvents that selectively dissolve one of the two blocks were used. In a selective solvent, the diblock copolymers form micelles with a core consisting of the insoluble block and a corona of the soluble blocks. In the case of symmetric diblock copolymers the resulting structures are spherical micelles. In non-polar solvent such as toluene, the polystyrene block is pointing outside the micelle core. Titanium-oxo based nanoparticles are formed and are located in the corona of micelles arranged in a hexagonal mesophase upon evaporation of the solvent. The hydrophobic behavior of the $[Ti_{16}O_{16}(OEt)_{32}]$ due to the presence of the alkoxy groups at the surface leads to their localization in the hydrophobic regions. Moreover, some titanium clusters are covalently bound to the carboxylate of the *PMAA* blocks, presumably those which are in direct proximity to the polystyrene regions. These complexation reactions are accompanied by esterification reactions between released alcohol and carboxylic acid groups. The small quantities of released water lead to the formation of titanium-oxo based nanoparticles through the hydrolysis-condensation of some alkoxy groups, thereby forming bridges between $[Ti_{16}O_{16}(OEt)_{32}]$ clusters. The inorganic framework that is covalently linked to the polymer matrix enhances the stability of the aggregate structures and changes the interface curvatures.

On the other hand, in polar solvent such as ethanol, reverse micelles are formed and the *PMAA* block is pointing outside the micelle core. Thus, titanium-oxo-based nanoparticles are incorporated in the micelle cores. Moreover, the solubilisation of the *PMAA* block in ethanol may favor esterification reaction, which leads to the release of a large amount of water in the micellar solution. As a consequence, larger titanium oxide aggregates are formed and no specific ordered phases were observed. In all cases, the titanium-oxo cores have been characterized by ^{17}O MAS NMR and the oxo-core of the clusters was still preserved during the assembly, the complexation, and the condensation processes.

Conclusions

An extraordinary amount of research has appeared in the two last decades in the field of hybrid materials, indicating the growing interest of chemists, physicists, and materials researchers to fully exploit this technical opportunity for creating materials and devices benefiting of the best of the three realms: inorganic, organic, and biologic. This field of research initially grew out of the sol–gel community, and it is at present thriving with the appearance of a new class of mesoscopic hybrid structures engineered at the molecular or nanometer scales to satisfy the requirements for a variety of applications from biological and chemical sensing, catalysis, selective separation, to optical communications. Among the different strategies used to design nanostructured hybrids, nanobuilding blocks (NBBs) based ones present numerous advantages already emphasized in more general feature articles [9].

The present review emphasizes that the chemistry of titanium-oxo clusters is rich, varied, and versatile. Today more than fifty structures have been already reported and about twenty articles deal with the assembly of such nanobuilding blocks to form new hybrid organic–inorganic materials. Literature demonstrates that indeed these titanium-oxo based NBBs are good models to allow the designed construction of new hybrid organic–inorganic nanocomposites. The NBBs approach allows a better understanding of the stability, lability of the hybrid, and a better control of hybrid interfaces. Such understanding can then be transferred to the construction of more complex hybrid materials which exhibit many interesting properties and applications [6].

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