Chem. Mater. **2001,** *13,* 3061−3083

Reviews

Designed Hybrid Organic−Inorganic Nanocomposites from Functional Nanobuilding Blocks

C. Sanchez,*,† G. J. de A. A. Soler-Illia,† F. Ribot,† T. Lalot,‡ C. R. Mayer,§ and V. Cabuil§

Chimie de la Matière Condensée, UMR CNRS 7574, Laboratoire de Synthèse Macromoléculaire, UMR CNRS 7610, and Laboratoire des Liquides Ioniques et Interfaces Chargées, UMR CNRS 7612, Equipe Colloïdes Magnétiques, Université Pierre et Marie Curie 4, place Jussieu, 75252 Paris, France

Received February 12, 2001. Revised Manuscript Received July 20, 2001

This article describes hybrid materials and systems in which the core integrity of inorganic nanobuilding blocks (NBBs) is preserved and reviews the main synthetic procedures presented in the literature. The relation between the NBB and the resulting hybrid networks is discussed for several striking examples: silicon and tin oxo clusters, polyoxometalates, and transition metal−oxo-based clusters. This approach is extended to nanoparticule-based hybrids. The chemical strategies offered by the coupling of soft chemistry processes and this approach based on functional NBBs allows, through an intelligent and tuned coding, to develop a new *vectorial chemistry* that is able to direct the assembly of a large variety of structurally well-defined clusters or nanoparticles into complex architectures.

1. Introduction

The possibility of combining properties of organic and inorganic components in a unique composite material is an old challenge starting with the beginning of the industrial era. Some of the earliest and most well-known organic−inorganic representatives are certainly derived from the paint and polymer industries, where inorganic pigments or fillers are dispersed in organic components (solvents, surfactants, polymers, etc.) to yield or improve optical and mechanical properties. However, the concept of “hybrid organic−inorganic” materials exploded only very recently with the birth of soft inorganic chemistry processes (“Chimie Douce”), where mild synthetic conditions allow versatile access to chemically designed hybrid organic−inorganic materials.[1,2] Afterward, the research shifted toward more sophisticated nanocomposites with higher added value.[3,4] Numerous new applications in the field of advanced materials science are related to matter for which the surface-to-volume ratio is very high. Therefore, the combination at the nanosize level of inorganic and organic or even bioactive components in a single material has made accessible an immense new area of materials science that has extraordinary implications in the development of multifunctional materials.[1−4] These are considered as innovative advanced materials, and promising applications are expected in many fields, including optics, electronics, ionics, mechanics, membranes, protective coatings, catalysis, sensors, biology, and others.[1−10] Many interesting new materials have already been prepared with mechanical properties that can be tuned between those of glasses and those of polymers to achieve improved optical properties or improved catalytic or membrane-based properties.[3,4] For example, hybrid materials having excellent laser efficiencies and good photostabilities,[5] very fast photochromic responses,[6] very high and stable second-order nonlinear optical responses,[7] or acting as original pH sensors[8] and electroluminescent diodes[9] have been reported in the past five years. Some hybrid products have already entered the applied fields. Examples include the one million TV sets sold annually by Toshiba, the screens of which are coated with hybrids made of indigo dyes embedded in a silica−zirconia matrix;[10a] organically doped sol−gel glassware sold by Spiegelau;[10b] and sol−gel-entrapped enzymes sold by Fluka.[10c]

The nanostructure, degree of organization, and properties that can be obtained for such materials certainly depend on the chemical natures 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, extent, and accessibility of the inner interfaces. As a consequence, the nature of the interface or of the links and interactions exchanged by the organic and inorganic components has been used to categorize these hybrids into two main classes.[2e,h,i]

---

[*] Corresponding author. E-mail: clems @ccr.jussieu.fr.

[†] Chimie de la Matière Condensée, UMR CNRS 7574.

[‡] Laboratoire de Synthèse Macromoléculaire, UMR CNRS 7610.

[§] Laboratoire des Liquides Ioniques et Interfaces Chargées, UMR CNRS 7612.

10.1021/cm011061e CCC: $20.00

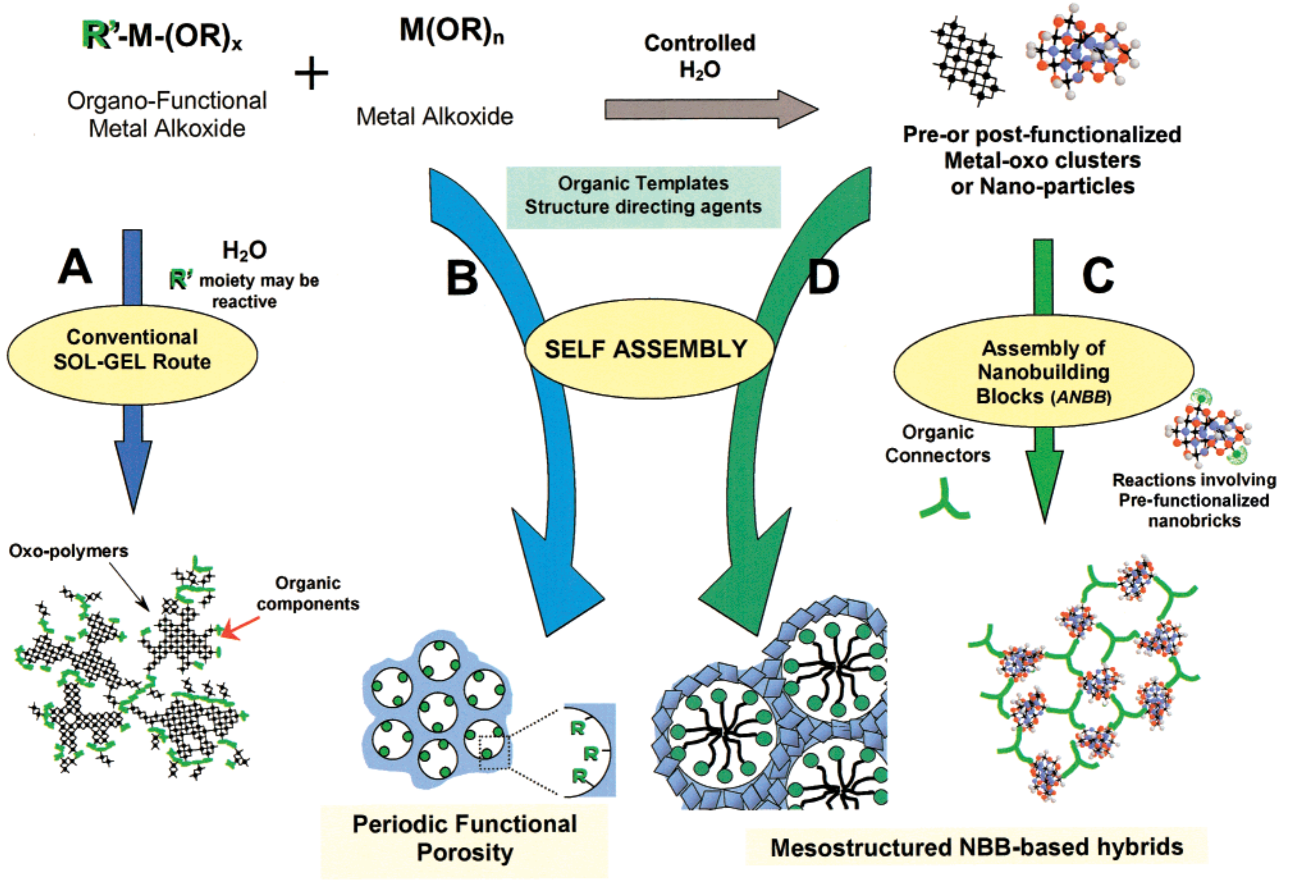

Figure 1. Different paths for obtaining hybrid materials. A conventional sol−gel route (path A) leads to “ordinary” hybrids. Routes B and D involve the use of templates capable of self-assembly, giving rise to meso-organized phases. Paths C and D involve the assembly of nanobuilding blocks (ANBB).

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 exchange only weak interactions (at least in terms of orbital overlap) such as hydrogen bonding, van der Waals contacts, or electrostatic forces. In contrast, 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.

Siloxane- or stannane-based class II hybrids[2e] can be easily synthesized because $Si-C_{sp^3}$ and $Sn-C_{sp^3}$ bonds are rather covalent and therefore quite stable toward attack by nucleophilic species such as water, alcohols, hydroxylated ligands, etc. The precursors of these compounds are organo-substituted silicic acid esters of general formula $R'_nSi(OR)_{4-n}$, bridged precursors of silesquioxanes $X_3Si-R'-SiX_3$ (X = Cl, Br, OR) or organostannanes, $R'_nSn(X)_{4-n}$ (X = OR, Cl, or C≡CH), where R′ can be any organofunctional group and n is usually 1 or 2. Organic R′ groups can be bonded to an inorganic network with two different goals in mind: as *network modifiers* or as *network formers*.[1e] If R′ is a simple nonhydrolyzable group, it will have a network-modifying effect (e.g., R′ containing an alkyl group or an organic dye). On the other hand, if R′ bears any reactive group that can, for example, polymerize or copolymerize (e.g., methacryloyl, epoxy, or styryl groups) or undergo hydrolysis−condensation (trialkoxysilyl groups), it will act as a network former.

This approach is no longer valid with transition metals for which the more ionic M−C bond (M can be, for example, Ti^{IV}, Zr^{IV}, V^{V}, or Al^{III}) is easily cleaved by water and by many nucleophilic species.[11,12] Consequently, two strategies can be envisaged to incorporate transition metals within class II hybrid materials: (i) the formation of stable $M-O-Si-C_{sp^3}$ bonds, such as in many siloxane−metal oxide hybrids[2e,13] or in modified polyoxotungstates,[14] or (ii) the use of complexing organic ligands HLZ (L being an anchoring function and Z a general organic group) such as carboxylic acids, phosphonic acids, hydroxyacids, polyols, or betadiketones and allied derivatives[2e,11,12] which leads to the formation of modified metallic alkoxides $M(OR)_{m-n}(LZ)_n$ and open a wide range of possibilities. When the Z group carries a polymerizable function, organic−inorganic copolymers can be obtained.[15] Complexation of metallic centers is also an interesting way to design new layered hybrid materials that exhibit magnetic[16] or liquid-crystal properties[17] or both.

Independent of the nature of the interface between the organic and inorganic components, a second important feature in tailoring hybrid networks concerns the chemical pathways that are used to design a given hybrid material. These main chemical routes are schematically represented in Figure 1.

Path A corresponds to conventional sol–gel chemistry. Hybrid networks are obtained through the hydrolysis of organically modified metal alkoxides ($R'_nSi(OR)_{4-n}$,[1,2] $X_3Si-R'-SiX_3$,[2g,2k,2m,18] $R'_nSn(X)_{4-n}$,[19] $M(OR)_{m-n}(LZ)_n$,[15] vide supra) condensed with or without simple metallic alkoxides. The solvent might or might not contain a specific organic molecule, a biocomponent, or a polyfunctional cross-linkable polymer (telechelic polymers for example). This strategy is simple and low-cost, and it yields amorphous hybrid materials. These materials that exhibit an infinity of microstructures can be transparent and easily shaped as films or bulks. However, they are generally polydisperse in size and locally heterogeneous in chemical composition.

A better understanding and control of the local and semilocal structures of these materials and their degrees of organization are important issues, especially if tailored properties are sought. Organization usually involves controlled segregation at the nanoscopic level. Three main approaches can be conceived to achieve such control of the materials structure, as schematized in Figure 1: self-assembly procedures (route B), assembly of well-defined nanobuilding blocks (NBBs, route C), and a combination of the two (route D).

In the past 10 years, a new field has been explored that corresponds to the organization or texturing of growing inorganic or hybrid networks, templated by organic structure-directing agents (Figure 1, routes B and D).[20−25] The success of this strategy is also clearly related to the ability that materials scientists have to control and tune hybrid interfaces. In this field, hybrid organic–inorganic phases are very interesting because of the versatility they demonstrate in building a continuous range of nanocomposites, from ordered dispersions of inorganic bricks in hybrid matrixes to highly controlled nanosegregations of organic polymers within inorganic matrixes. In the latter case, one of the most striking examples is the synthesis of mesostructured hybrid networks (routes B and D).[23−25]

A suitable method for achieving a better definition of the inorganic component consists of the use of perfectly calibrated preformed objects, such as clusters, nanoparticles, or nanolayered compounds that keep their integrity in the final material. These NBBs are generally capped with polymerizable ligands or connected through organic spacers, such as telechelic molecules or polymers, or through functional dendrimers (Figure 1, route C).[2m,25] The use of highly precondensed species presents several advantages: (1) They exhibit a lower reactivity toward hydrolysis or attack of nucleophilic moieties than metal alkoxides. (2) The nanobuilding components are nanometric and monodispersed, with perfectly defined structures, which facilitates the characterization of the final materials.

The variety found in the nanobuilding blocks (nature, structure, and functionality) and links allows one to build an amazing range of different architectures and organic–inorganic interfaces, associated with different assembling strategies. Moreover, the step-by-step preparation of these materials usually allows for tight control over their semilocal structures.

Strategies combining the nanobuilding block approach with the use of organic templates that self-assemble and allow one to control the assembly step are also appearing (Figure 1, route D). This combination between the nanobuilding block approach and templated assembly will have paramount importance in exploring the theme of "synthesis with construction" of hierarchically organized materials in terms of structure and functions.

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,[26] organotin–oxo clusters,[19,27] organically functionalized heteropolyoxo–tungstates,[14] transition metal–oxo clusters,[25] and finally functionalized nanosized particles (metallic oxides, metals, and chalcogenides). We thus focus on these type of NBBs.

Such nanobuilding units are very versatile. Indeed, they exhibit a large variety of interfaces between the organic and the inorganic components (covalent bonding, complexation, electrostatic interactions, etc.). These NBBs with tunable 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 lose 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 that can be delivered at the hybrid interface to build an extended inorganic network. This article describes only hybrid materials and systems in which the core integrity of the NBB is preserved and reviews the synthetic approaches summarized by pathways C and D in Figure 1.

2. Relation between the NBBs and the Resulting Hybrid Networks.

Some typical examples of organically functionalized nanobuilding units, the synthesis of which has already been described in several articles,[2e,2m,14,15c,26−28] are presented in Figure 2.

These NBBs belong to polysilsesquioxane,[26] organotin,[19,27] polyoxometalates,[14] and metal–oxo cluster[28] chemistry and contain several organic functionalities connected to the inorganic core through different interfaces. As previously discussed, the nature of the interface between the organic and inorganic components, together with the connectivity and functionality of the NBB, are of paramount importance in determining the final structures of the hybrid materials. Consequently, the relation between the NBBs and the possible resulting hybrid networks will be described first.

General features of polymer science can be applied to some extent to the synthesis of hybrid materials. For convenience, a simplified description is given according to the functionality of the precursor (functionality, ***f***, is defined as the number of reactive functions or anchoring sites per monomeric unit).

(i) As a prerequisite to the formation of macromolecules, the functionality of the precursor must be equal to 2, such as in vinyl, styryl, or methacryl moieties. Without further specifications, linear chains are obtained regardless of the polymerization mode. Generally speaking, macrocycles and linear chains equilibrate when the concentration of the reactive function is low (high dilution).

(ii) When the functionality of the monomer or of a mixture of monomers is greater than 2, branched chains

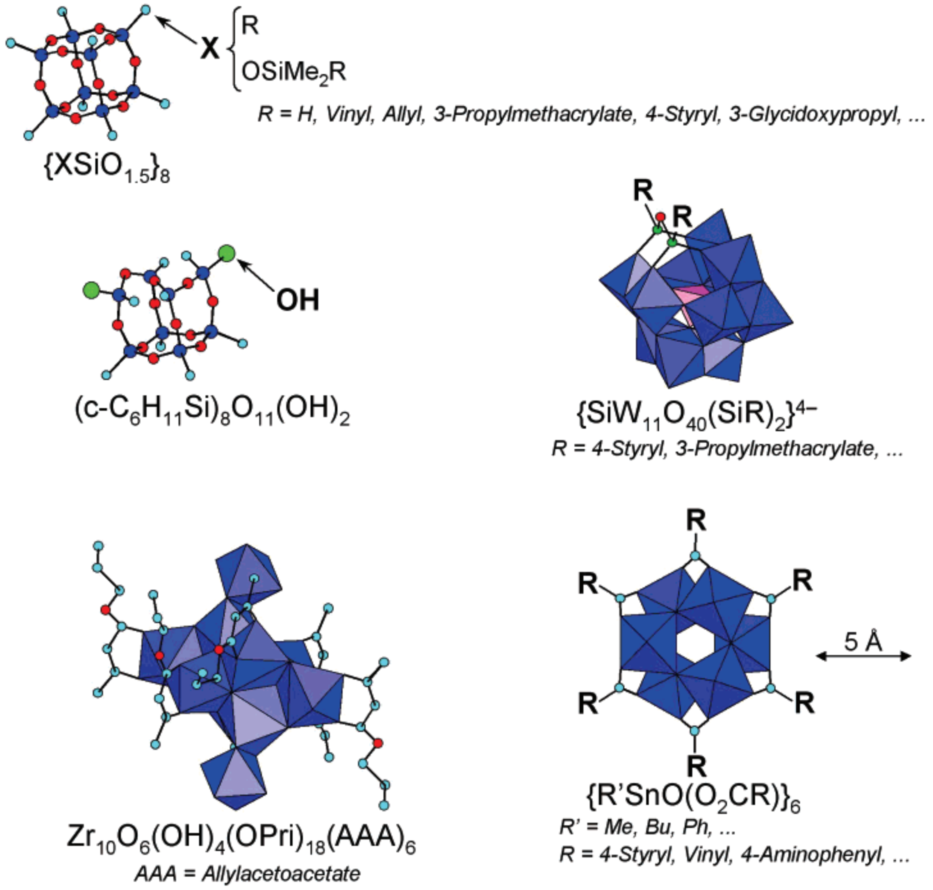

Figure 2. Various examples of oxo clusters that can be used as NBBs. The references are summarized in Table 1.

appear first, leading to the formation of a network in most classical cases.

On the other hand, numerous synthetic pathways allow for hybrid materials with various structures to be obtained.[2h] Focusing on NBBs with organic functionalities, the construction of macromolecular species obeys the above-mentioned classical rules. However, several possibilities emerge according to the polymerization mode, the nature of the connection between the organic and inorganic parts (class I- or II-type interactions), the functionality of the precursor ($f = 2$ or $f > 2$), and the moiety that effectively bears the functionalities.

Interestingly, the mode of polymerization defines the type of participation of the NBBs in the structure of the hybrid material. When step-growth polymerization and related modes are employed, the NBB is an integral part of the macromolecular backbone (Figure 3a and b). It is incorporated into the chain regardless of its initial functionality. When chain polymerization is performed, the inorganic part of the organically functionalized NBB plays the role of a side group or a cross-linking knot (Figure 3c and d, respectively). It does not participate in the chain construction.

Depending on the chemical nature of the functionalities, the choice of synthesis mode definitively turns the expected structure and properties of the hybrid material toward the those of polycondensates and related macrostructures or toward those of vinyl-type polymers.

2.1. Step-Growth Polymerization and Related Processes. The assembly of $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ and aliphatic or aromatic dicarboxylates illustrates how macromolecular species can be obtained by electrostatic interactions of difunctional monomers.[27a,29] Covalently built macromolecules were synthesized by condensing $(c\text{-}C_6H_{11}Si)_8O_{11}(OH)_2$ with various links.[30−33] The preparations of class I or II hybrid materials were successfully achieved because of the presence of two well-defined reacting or interacting groups.

For class I and II networks, metal alkoxides are pertinent precursors for the inorganic component. For instance, silica−oxo polymers and poly(2-methyl-2-oxazoline) interact by hydrogen bonds to form a physical gel.[34] The hybrid material is the result of weak interactions and belongs to class I. Classical sol−gel chemistry presents several difficulties linked to the fact that hydrolysis of the alkoxy group is first required. The effective functionality cannot be defined by the initial number of alkoxy groups. As hydrolysis proceeds, the functionality in terms of hydroxy groups indeed increases. In addition, when two hydroxy groups condense, the functionality of the resulting dimer is higher than that of its precursor. As a consequence, the effective functionalities of the molecules present in the reaction medium are functions of time and depend on the rates of hydrolysis, oxolation, and olation. This is very probably the reason why materials obtained by sol−gel chemistry (Figure 1, route A) exhibit heterogeneous domains. The control of the actual functionality is an interesting challenge for the design of well-defined networks by sol−gel chemistry.

The expected properties of linear hybrid materials are greatly influenced by the average molecular weight

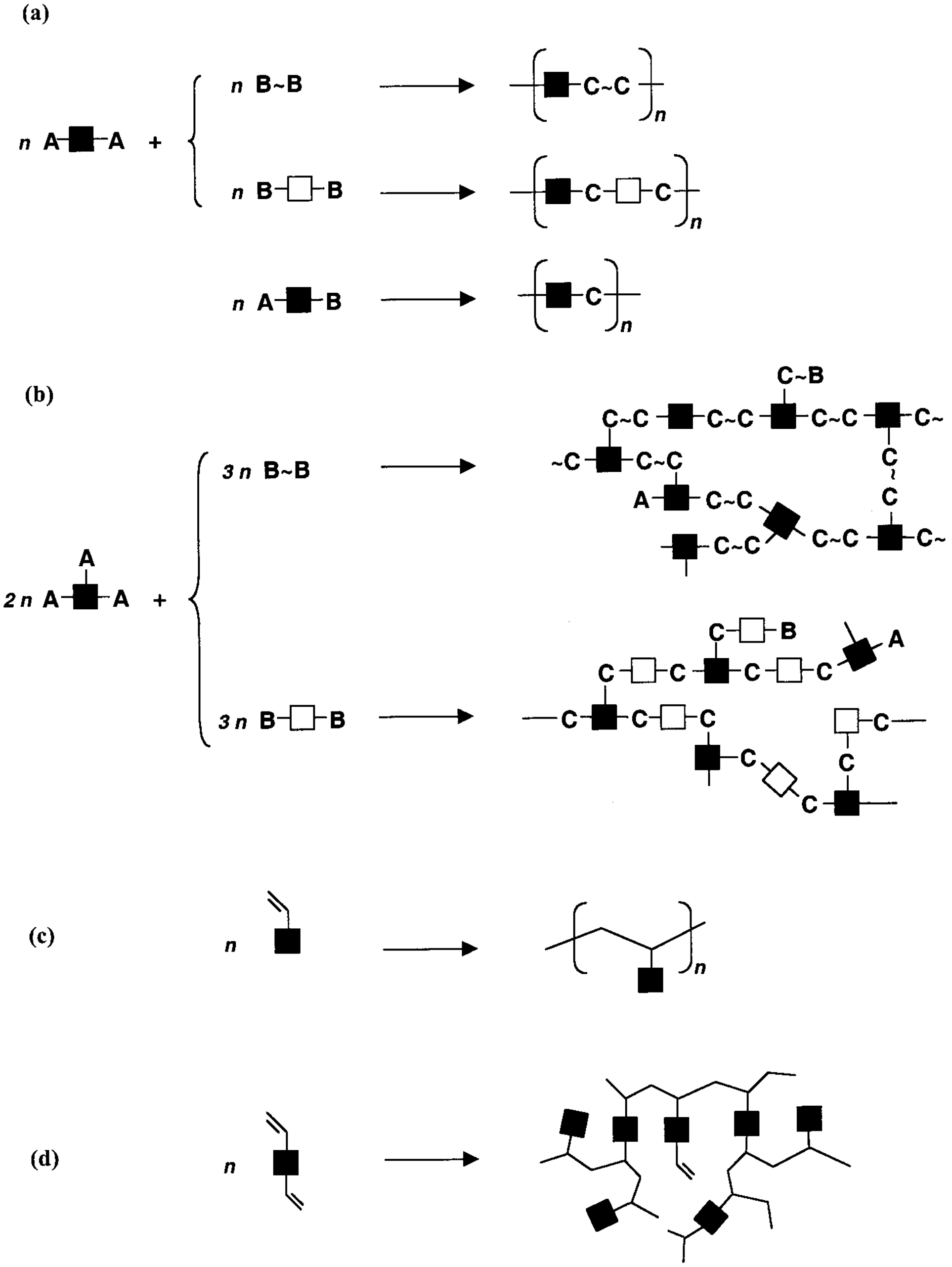

Figure 3. Schematic structure, at a macromolecular scale, of the hybrid materials prepared by (a) polycondensation of bifunctional precursors, (b) polycondensation of one multifunctional and one difunctional precursor, (c) chain homopolymerization of a bifunctional precursor, and (d) chain homopolymerization of a multifunctional precursor. A and B represent the reacting or interacting groups; C arises from the reaction or interaction between A and B. Black and white squares, −, and ∼ symbolize various inorganic cores; organic links between functions A, B, or C and the inorganic moiety; and organic links between organic functions, respectively.

(MW). For polycondensates, the MW is controlled by the extent of reaction between the functional groups, whereas their degree of "assembly" is the key parameter for chains of class I. Concerning networks, the cross-linking density should be considered first.

2.2. Chain Polymerization. The functionalization of inorganic cores by double bonds opens up the possibility of chain polymerization. It can occur by means of weak or strong interactions, and a wide range of precursors can be prepared according to various strategies.[2h,m] However, a precise definition of the number of grafted double bonds is important. If one function has been grafted, the functionality of the hybrid precursor is equal to 2, and its polymerization leads to linear chains.[35] As an example, the free-radical polymerization of (c-$C_6H_{11}Si)_7O_{12}Si$(3-propyl methacrylate) leads to a polymer schematically drawn as a polymethacrylate-type backbone with pendant inorganic cubes.[35a]

Networks have also been obtained by polymerization of at least tetrafunctional (two double bonds) polyoxometalates[14a] or by its copolymerization with organic monomers.[14e,f] In the latter case, the structure of the resulting hybrid material can be described in terms of cross-linking degree, swelling ratio, or average number of chain segments between two cross-links, among other properties.

Homopolymerization seems to be a useful tool for obtaining materials in which properties reflect those of the precursor, whereas copolymerization broadens the field of possible structures with potential synergies between the organic backbone and inorganic side groups.

3. Silicon-Based Nanobuilding Blocks and the Resulting Hybrid Structures

3.1. Silicon-Based Nanobuilding Blocks. As for sol−gel and the other types of hybrid materials, silicon is likely the most studied element in NBB-based hybrid materials.[2m,26] As stated before, because of the stability of the Si−C bond, silicon offers a very large variety of organic functionalizations.[2m,26] Several types of silicon-based building blocks have been described in the literature and used to elaborate hybrid materials. Most of these "nanobricks" correspond to cage compounds of the general formula $[XSiO_{1.5}]_n$, where n is an even number ranging from 6 to 18.[36] The most common case is an octamer ($n = 8$), which results in an almost cubic shape with one silicon atom at each corner.[37] This oligomer has a size of ca. 10 Å and can be thought as the smallest existing part of silica.[36b] Depending on X, a distinction can be made between polyhedral oligohydridosilsesquioxanes (POHSSs) when X is H (generally abbreviated as T_n^{H}), polyhedral oligosilsesquioxanes (POSSs) when X represents organic groups linked to silicon through Si−C bounds, and spherosilicates when X corresponds to siloxy groups (−O−SiRR′R″, with R′ = R″ = Me being the most common case). Polyhedral oligosilsesquioxanes with uncompleted Si−O−Si frameworks, such as $(c\text{-}C_6H_{11}Si)_8O_{11}(OH)_2$[38] and $(RSi)_7O_9(OH)_3$ (R = $c\text{-}C_5H_9$, $c\text{-}C_6H_{11}$, ^{i}Bu),[39] also offer interesting possibilities, either directly as building blocks[30−33] or as precursors to POSSs of controlled functionality.[26p,40,41] The latter case is well exemplified by the large number of POSSs bearing a single functional group obtained by capping the missing corner of $(c\text{-}C_6H_{11}Si)_7O_9(OH)_3$ with various trichlorosilanes ($RSiCl_3$, R = H, vinyl, allyl, styryl, norbornyl, 3-propyl methacrylate, etc.).[26p,40,42]

The syntheses of POHSSs, POSSs, and incomplete POSSs are based on the hydrolysis−condensation of $RSiX_3$ derivatives (X = Cl, OMe, OEt).[2m,36,43,44] Yet, such reactions also yield large and ill-defined tridimensional oxo polymers (T resins),[45] and much attention should be paid to the operating conditions to favor the formation of the nanobricks, which have been generally isolated by crystallization. The spherosilicates are commonly prepared from the polyanions $[OSiO_{1.5}]_n^{n-}$, which are formed in good yield upon hydrolysis of $Si(OMe)_4$ in the presence of a quaternary ammonium hydroxide.[2m,26l,46] The silylation of the cage corners involves reagents such as RMe_2SiCl or $(RMe_2Si)_2O$ and HCl (R = H, vinyl, allyl, etc.).[2m,47] The modification of the functions borne by the Si−O−Si framework can also offer access to particular organic groups on the surface of the nanobrick. Hydrosilylation is commonly used to graft functions onto POHSSs or spherosilicates covered by $-OSiMe_2H$ moieties.[2m,48,49] Reaction with *m*-chloroperbenzoic acid has also been used to turn alkene-functionalized silicon-based nanobricks into epoxy-functionalized nanobricks.[26p,50]

3.2. Structures and Materials Derived from Silicon-Based Nanobuilding Blocks. As discussed in section 2, the types of architectures that can be achieved depend on the nanobrick functionality. Nanobuilding blocks, such as $RSi(c\text{-}C_6H_{11}Si)_7O_{12}$ with R = styryl, 3-propyl methacrylate, or 2-ethylnorbornyl, which all bear a single double bond, yield upon polymerization (with or without a comonomer) linear polymeric backbones with pendant silsesquioxane cubes.[26b,26c,35,42] The polymerization can be performed using standard free-radical polymerization,[26b,26c,35] ring-opening polymerization (norbornyl),[42] or atomic-transfer radical polymerization.[51] The latter conditions offer better control over the composition, topology, and molecular weight of the polymers. Such functional nanobricks allow for good dispersion of the nanoscale inorganic filler in the polymer and, moreover, for covalent anchoring of the inorganic filler. Increases in the glass transition temperature as large as 200 °C have been observed in several copolymers made of butyl methacrylate and cyclopentyl-POSS-methacrylate $[H_2C{=}C(CH_3)C(O)O(CH_2)_3)(c\text{-}C_5H_9)_7Si_8O_{12}]$.[40] The mechanical relaxation behavior of poly(norbornene) containing pendant $((CH_2)_2C_7H_9)R_7Si_8O_{12}$ moieties (R = $c\text{-}C_5H_9$ or $c\text{-}C_6H_{11}$) was also shown to be greatly influenced by the weight fraction of POSS.[42]

The sole presence of a double bond might be insufficient to permit polymerization. Indeed, the nanobricks $(CH_2{=}CH{-}(CH_2)_6{-})R_7Si_8O_{12}$ (R = $c\text{-}C_5H_9$ or $c\text{-}C_6H_{11}$) could not be polymerized or copolymerized with Ziegler−Natta-type catalysts,[26p] whereas the $(CH_2{=}CH{-}(CH_2)_8{-})(Et)_7Si_8O_{12}$ nanobrick, which contains less bulky corner-capping groups, was copolymerized with ethene or propene to afford polymers with improved thermal stabilities.[48]

Pendant POSS can also be introduced through polycondensation reactions as shown for segmented polyurethane-based elastomers.[52] The nanobrick $(HMe_2SiO)(c\text{-}C_6H_{11})_7Si_8O_{12}$ was first grafted by hydrosilylation of 3,3′-diallylbisphenol A and then copolycondensed with poly(tetramethyleneglycol) and 4,4′-methylenebis(phenylisocyanate). With such an elaboration sequence, the inorganic nanobuilding blocks are attached to the hard segments and greatly enhance the tensile modulus and strength of the elastomer.[52a]

Linear hybrid polymers containing silicon-based nanobuilding blocks in their backbones can be prepared from the incomplete POSS $(c\text{-}C_6H_{11}Si)_8O_{11}(OH)_2$, which exhibits a functionality of 2 through its Si−OH moieties. Its polycondensation with various short and linear silanes or siloxanes, terminated by Si−Cl or $Si{-}NMe_2$ groups, results in polymers that incorporate 10−30 nanobricks in a bead structure, showing a decrease in the glass transition temperature when the length of the spacer increases.[30−32] Similar systems, but with zirconocene-based spacers, have also been obtained upon reacting difunctional incomplete POSSs with Cp_2ZrCl_2 or $[Cp_2ZrCl]_2O$.[33] More recently, linear and soluble, and therefore processable, hybrid polymers incorporating the nanobuilding blocks in their backbones were prepared from the multifunctional nanobrick $[HSiO_{1.5}]_8$ but hydrosilylating sterically hindered diynes (e.g., 1,3-phenylethynylbenzene)[53] or vinyl-terminated poly(dimethylsiloxane) short chains under carefully controlled operating conditions.[54] An interesting point in these last systems is the possible use, later in the process, of the remaining unreacted Si−H moieties.

Except for some peculiar cases, as discussed above, hybrid systems made from multifunctional NBBs form insoluble, three-dimensional networks. The first reported hybrid material based on the NBB approach was of this type when Agaskar, in 1989, assembled $[\text{vinyl}(\text{Me})_2\text{SiOSiO}_{1.5}]_{10}$ decamers by hydrosilylation with $[\text{HMe}_2\text{SiC}_6\text{H}_4]_2\text{O}$.[55] This material was hard, clear, resilient, and thermally stable up to 350 °C, and it could absorb more than 50% of its weight of THF. Hoebbel et al. and Zhang et al. have investigated the materials obtained by the hydrosilylation of $[\text{vinylSiO}_{1.5}]_8$ or $[\text{vinyl}(\text{Me})_2\text{SiOSiO}_{1.5}]_8$ with $[\text{HSiO}_{1.5}]_8$ or $[\text{H}(\text{Me})_2\text{SiOSiO}_{1.5}]_8$.[26a,f] They observed that varying the length of the spacer that connects two cube corners greatly affects the degree of reaction and the porosity of the materials, which can exhibit specific surface areas as high as 500 m^2/g. The spacer used to connect the nanobuilding blocks can also bring a particular property, as demonstrated by Morán et al. who assembled $[\text{H}(\text{Me})_2\text{SiOSiO}_{1.5}]_8$ with 1,1′-divinylferrocene to produce a material that exhibits redox properties and can be used to prepare modified electrodes.[26k,56] Recently, Laine et al. prepared well-defined nanocomposites from the epoxidic precursors $[(\text{CH}_2\text{OCH}-\text{CH}_2-\text{O}-(\text{CH}_2)_2)(\text{Me})_2\text{SiOSiO}_{1.5}]_8$ or $[(\text{ethylcyclohexenyl epoxide})(\text{Me})_2\text{SiOSiO}_{1.5}]_8$; slight differences in the molecular structure affect the mechanical properties of the resulting hybrids.[57] Finally, purely inorganic cages, such as $[\text{Si}_8\text{O}_{20}]^{8-}$, can also be assembled into three-dimensional networks by reaction with Me_2SiCl_2.[26l,m]

All of the examples presented above correspond to class II hybrid materials, but POSSs have also been simply blended with polymers to afford class I hybrids.[58] In such systems, the dispersability of the POSS appears to be related to the organic side groups.

4. Tin-Based Nanobuilding Blocks and Related Structures

Tin shares with silicon a $\text{M}-\text{C}_{\text{sp}^3}$ bond stability with respect to nucleophilic agents such as water. These bonds offer strong covalent links between tin–oxo polymers/oligomers and functional organic moieties, but they can also reduce the inorganic functionality of tin and favor the formation of oxo clusters, which can be used as nanobuilding blocks to design new hybrid materials.[2m,19,27]

Tin oxo–carboxylate clusters, such as $\{\text{RSnO}(\text{O}_2\text{CR}')\}_6$ (R = methyl, phenyl, or butyl and R′ = any organic function),[27e] abbreviated tin-6, represent a family of nanobuilding blocks in which the carboxylate groups can be used to provide the assembling functions.[19,59] The tin-6 molecular structure (Figure 2), in which all tin atoms are six-coordinate (distorted octahedra), exhibits a hexagonal prismatic or "drum" shape with the bridging carboxylate groups located on the six square faces of the drum.[27e] The resulting shape is fairly anisotropic as the six carbon atoms of the carboxylates are almost coplanar, while the organic moieties bound to the tin point outside the two basal hexagonal faces of the drum. The tin-6 cluster $\{\text{BuSnO}(\text{O}_2\text{CC}_6\text{H}_4\text{NH}_2)\}_6$, prepared from 4-aminobenzoic acid and butyltin hydroxide oxide, exhibits on its periphery six amino groups amenable to subsequent reactions.[59] It can be functionalized, via reaction with $\text{OCN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, to yield quantitatively a dendrimer-like compound with 18 peripheral ethoxy functions amenable to hydrolysis–condensation.[59] It was also assembled via reaction with 1,4-phenylene diisocyanate or 1,6-diisocyanatohexane.[19] Because of the high functionality of such a NBB, the resulting products are insoluble, even though some of the amino functions remain unreacted.

Another interesting nanobuilding block is the oxo cluster $\{(\text{RSn})_{12}(\mu_3-\text{O})_{14}(\mu_2-\text{OH})_6\}^{2+}$, abbreviated tin-12.[27] It can be prepared through several chemical pathways, including hydrolysis of organotin trichlorides,[27f,h] trialkoxides,[27d] or trialkynides[27g] or refluxing in toluene butyltin hydroxide oxide and sulfonic acids.[27b,i] Depending of the synthesis conditions the +2 charge is balanced by different anions (e.g., OH^-,Cl^-, $\text{R}'\text{SO}_3^-$, $\text{R}'\text{CO}_2^-$). These charge-compensating anions are located at both cage poles, close to the hydroxy groups that bridge the six-coordinate tin atoms. In solvents of low dielectric constant, no ionic dissociation is observed, but it does occur in solvents such as DMSO.[27i]

Tin-12 clusters are versatile nanobuilding blocks for the synthesis of well-defined tin–oxo-based hybrid materials that can be used as models; possible synthesis strategies associated with this cluster are depicted in Figure 4.[19,27] These clusters can be assembled through organic networks by using the covalent interface provided by the Sn–C bond, by using the ionic interface associated to the charge compensating anions X^-, or even by using both. In the first case, the organic moiety bound to tin should be polymerizable (e.g., R = butenyl, propyl methacrylate, propylcrotonate, 4-styryl).[60] In the second case, charge-compensating organic dianions can be used to bridge the clusters.[27a,29] This was achieved by reacting $\{(\text{BuSn})_{12}\text{O}_{14}\text{OH}_6\}(\text{OH})_2$ with carboxymethyl-terminated PEG macromonomers, in THF.[27a]

The use of polymerizable anions offers an alternative synthesis strategy.[27c,61] By a simple acid–base reaction, the oxo–hydroxo butyltin macrocation $\{(\text{BuSn})_{12}\text{O}_{14}\text{OH}_6\}^{2+}$ can be functionalized with 2-acrylamido-2-methyl-1-propanesulfonate (AMPS), affording nanobuilding blocks with two highly polymerizable groups.[27c] For the first time, the direct homopolymerization of such functionalized oxo–hydroxo butyltin nanoclusters was successfully performed, providing hybrid materials in which the nanosized tin-based component is perfectly defined. $\{(\text{BuSn})_{12}\text{O}_{14}\text{OH}_6\}(\text{AMPS})_2$ can also be copolymerized with methylacrylate in toluene to produce gels. In line with the electrostatic interactions that are responsible for the cross-linking, these gels are soluble in DMSO.[27i,62]

5. Transition Metal–Oxo-Based NBBs and the Resulting Hybrid Structures

The syntheses and structures of many high-valence metals (Ti^{IV}, Zr^{IV}, Ce^{IV}, Nb^{V}) or even heterometallic oxo clusters have been described in the literature.[15c,28,63–73] Such species are usually prepared through the controlled substoichiometric hydrolysis of the metallic alkoxides $\text{M}(\text{OR})_n$ or the corresponding complexed alkoxides $\text{M}(\text{OR})_{n-x}(\text{LZ})_x$, (where LZ is a complexing ligand, vide supra) in solution. Alternative strategies using in situ generation of water (through esterification or aldolisation reactions) or nonhydrolytic sol–gel processes can also be developed to avoid stability problems

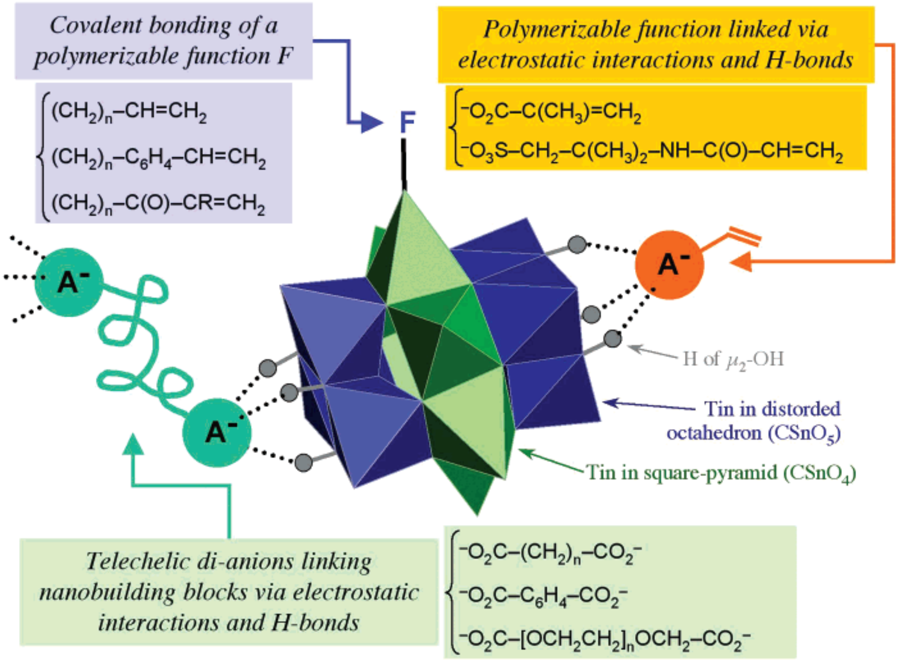

Figure 4. Schematic representation of the various possible strategies that can be used to assemble functionalized $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$ clusters into hybrid materials.

arising from local overconcentrations of water or the presence of residual water in the synthetic medium.[28c,64c,74,75] These clusters are isolated from the ill-defined oxo polymers concurrently formed by crystallization, frequently resulting in low yields. 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. This is made possible by the chelating or bridging character of the organic ligands (including any protecting group, μ_2–OR, and μ_3–OR bridges) but also by the existence of μ_3–O, μ_4–O, μ_5–O, or even μ_6–O[76] bridges. Moreover, the full characterization performed by crossing XRD and FTIR and multinuclear NMR spectroscopies allows one to separately analyze the modifications of the metal–oxo core or the surface.

5.1. Hybrids from Prefunctionalized Transition Metal–Oxo Clusters. Some examples of metal–oxo clusters functionalized for organic reactions are reported in Table 1. These clusters consist of a metal–oxo core with polymerizable complexing ligands located at the periphery. These groups can be used to extend the cluster network to form a hybrid organic–inorganic polymer composed of an assembly of attached well-defined NBBs. The use of ligands containing an assembling function, such as a polymerizable one, allylacetoacetate (aaa), methacrylate (OMc), or acrylate (OAcr), allows access to a great variety of clusters, such as $Ti_6O_4(OEt)_8(OMc)_8$, $Ti_3O_2(OPr^i)_5(OCMe{=}CH_2)_3(Pr^iOH)$, $Ti_4O_2(OPr^i)_6(OAcr)_6$, $Zr_{10}O_6(OH)_4(OPr^i)_{18}(aaa)_6$, $Nb_4O_4(OPr^i)_8(OMc)_4$, $Zr_6(OH)_4O_4(OMc)_{12}$, and $Zr_4O_2(OMc)_{12}$ (see references in Table 1). Yet, because of their small sizes and the presence of several alkoxy groups on their surfaces, these functionalized nanobuilding blocks exhibit rather poor stabilities toward water or nucleophiles. Consequently, their assembly through radical-initiated polymerization must be performed in nonprotic solvents such as toluene, benzene, or THF. Following this pathway, some interesting studies have been performed by several research groups, generating new hybrid materials.[77,78] However, the integrity of the metal–oxo core was not checked in a straightforward manner in the final hybrid materials. In some cases, such as $Nb_4O_4(OPr^i)_8(OMc)_4$, the accessibility of the double bonds for organic homo- and copolymerization reactions can be hindered for steric reasons.[28a]

However, such compounds can be used for organic microcellular doped solids. Indeed, polystyrene foams have already been produced by copolymerization of styrene with $Ti_3O_2(OPr^i)_5(OCMe{=}CH_2)_3(Pr^iOH)$.[77] An interesting piece of work concerning the copolymerization of functional transition metal–oxo clusters was recently reported by Schubert et al.[78] Inorganic–organic hybrid polymers were produced by the radical polymerization, initiated by dibenzoylperoxide in toluene or benzene, of methacrylic acid or methyl methacrylate with (meth)acrylate-substituted oxozirconium and oxotitanium clusters $Zr_6(OH)_4O_4(OMc)_{12}$, $Zr_4O_2(OMc)_{12}$ $Ti_6O_4(OEt)_8(OMc)_8$, and $Ti_4O_2(OPr^i)_6(OAcr)_6$.[78] It was shown that a very small amount of the cluster is sufficient for efficient cross-linking of the polymer chains. Small-angle X-ray scattering experiments indicate that the cluster size is retained in the polymers and that the microstructure of the cluster cross-linked hybrid materials can be described as a dispersion of identical spherical or disk-shaped clusters in polymers. The resulting hybrid polymers exhibit higher thermal stability because depolymerization reactions are inhibited. Contrary to undoped poly(methyl methacrylate), the cluster cross-linked copolymers are insoluble but swell in organic solvents. The solvent uptake upon swelling decreases with increasing amounts of polymerized cluster.[78]

5.2. Hybrid Assemblies of Postfunctionalized Transition Metal–Oxo Clusters. A large number of

Table 1. Some Examples of Metal−Oxo Clusters

precursor[a]	cluster	ref
	Polymerizable Clusters	
$\mathrm{HOMc\backslash[Nb(OPr^{i})_5]_2 = 12}$	$\mathrm{[Nb_4O_4(OPr^{i})_8(OMc)_4]}$	28a
$\mathrm{HOMc\backslash Zr(OPr^{n})_4 = 12}$	$\mathrm{[Zr_4O_2(OMc)_{12}]}$	28b
$\mathrm{MeOMc\backslash Zr(OPr^{n})_4 = 4}$	$\mathrm{[Zr_6O_4(OH)_4(OMc)_{12}(HOPr^{n})]}$	28b
$\mathrm{aaa\backslash Zr(OPr^{n})_4 = 0.6}$	$\mathrm{[Zr_{10}O_6(OH)_4(OPr^{n})_{18}(aaa)_6]}$	28d
$\mathrm{acetone\backslash Ti(OPr^{i})_4 = 2}$	$\mathrm{[Ti_3O_2(OPr^{i})_5(OC(CH_3){=}CH_2)_3(HOPr^{i})]}$	77
	$\mathrm{[Ti_4O_2(OPr^{i})_6(OAcr)_6]}$	78
$\mathrm{HOMc\backslash Ti(OPr^{i})_4 = 2}$	$\mathrm{[Ti_6O_4(OEt)_8(OMc)_8]}$	70
$\mathrm{HOMc\backslash Ti(OPr^{n})_4 = 4}$	$\mathrm{[Ti_9O_8(OPr^{n})_4(OMc)_{16}]}$	65
	Nonpolymerizable Clusters	
$\mathrm{Hacac\backslash Zr(OPr^{n})_4 = 1}$	$\mathrm{[Zr_4O(OPr^{n})_{10}(acac)_4]}$	66a
$\mathrm{Zr(OMe)_4}$	$\mathrm{[Zr_{13}O_8(OMe)_{36}]}$	67
$\mathrm{Ti(OPr^{i})_4}$	$\mathrm{[Ti_3O(OPr^{i})_9(OMe)]}$	71c
$\mathrm{Ti(OPr^{i})_4}$	$\mathrm{[Ti_3O(OPr^{i})_7(O_3C_9H_{15})]}$	69, 75a
$\mathrm{[Ti(\mu\text{-}ONep)(ONep)_3]_2}$	$\mathrm{Ti_3(\mu_3\text{-}O)(ORc)_2(ONep)_8}$ (Rc = Ac, Fc)	72a
$\mathrm{HOAc\backslash Ti(OPr^{i})_4 = 1}$	$\mathrm{[Ti_6O_4(OPr^{i})_{12}(OAc)_4]}$	64b,c
$\mathrm{HOAc\backslash Ti(OR)_4 = 2}$	$\mathrm{[Ti_6O_4(OR')_8(O_2CR)_8]}$ $\mathrm{(R = CH_3, R' = Et, Pr^{i}, Bu^{n})}$	15c, 63c, 64a
$\mathrm{HORc\backslash[Ti(\mu\text{-}ONep)(ONep)_3]_2}$	$\mathrm{Ti_6(\mu_3\text{-}O)_6(O_2CCHMe_2)_6(ONep)_6}$,	72a
$\mathrm{Ti(OEt)_4}$	$\mathrm{[Ti_7O_4(OEt)_{20}]}$	63b, 68
$\mathrm{Ti(O\text{-}CH_2\text{-}C_6H_5)_4}$	$\mathrm{[Ti_8O_4(O\text{-}CH_2\text{-}C_6H_5)_{20}]}$	71b
$\mathrm{Ti(OEt)_4}$	$\mathrm{[Ti_{10}O_8(OEt)_{24}]}$	71b
$\mathrm{Ti(OPr^{i})_4}$	$\mathrm{[Ti_{11}O_{13}(OPr^{i})_{13}(OEt)_5]}$	71a
$\mathrm{Ti(OPr^{i})_4}$	$\mathrm{[Ti_{12}O_{16}(OPr^{i})_{16}]}$	64c, 71a
$\mathrm{Ti(OEt)_4}$	$\mathrm{[Ti_{16}O_{16}(OEt)_{32}]}$	71d
$\mathrm{Ti(OBu^{t})_4}$	$\mathrm{[Ti_{18}O_{27}(OBu^{t})_{17}(OH)]}$	71d
$\mathrm{Hacac\backslash Ti(OBu^{n})_4 = 0.1}$	$\mathrm{[Ti_{18}O_{22}(OBu^{n})_{26}(acac)_2]}$	66b

[a] OMc = methacrylate, OAcr = acrylate, aaa = allylacetoacetate, acac = acetylacetonate, OAc = acetate, OFc = formiate.

oxo−alkoxo clusters, $M_nO_m(OR)_z$, have also been prepared from metal alkoxides as precursors, especially for Ti(IV) and Zr(IV). A large set of selected titanium and zirconium oxo clusters whose structures have been reported in the literature are gathered in Table 1. They can be used as model systems to understand the construction of hybrid materials, particularly at the inorganic−organic interface. There are two major synthetic challenges related to these clusters: (1) postfunctionalization of their surfaces by complexation of metallic atoms and (2) the use of these clusters in protic (even in the presence of water) or nonprotic solvents, with preservation of the metal−oxo core.

Solution NMR spectroscopy is an efficient tool for probing the molecular environments of these clusters. Therefore, ^{17}O and ^{13}C solution NMR spectra were collected to assess the stability of the oxo−metallic core and the lability of the organic surface ligands, respectively.[71a,79−82] In the presence of water, only the larger titanium−oxo clusters can preserve their oxo core. Under the same mild hydrolysis conditions, $Ti_{16}O_{16}(OEt)_{32}$ starts to react slowly via its surface ethoxy groups, whereas $Ti_7O_4(OEt)_{20}$ is quickly destroyed to yield oxo polymers and other oligomers.[71a,80−82] It has also been suggested that $Ti_{12}O_{16}(OPr^{i})_{16}$ clusters do not react with water, provided that the reaction is conducted in the parent alcohol and in the presence of low quantities of water (4 equiv of water per cluster). On the contrary, in nonalcoholic media (toluene−acetonitrile mixtures), white amorphous Ti−oxo−alcoxo precipitates are readily obtained.[71a]

The stability of titanium(IV) oxo−alkoxo clusters toward nucleophilic organic reagents (alcohols, complexing ligands) was shown to depend on their alkoxo/M and oxo/M ratios, as evidenced by ^{13}C and ^{17}O NMR spectroscopy.[82] Larger clusters are generally more stable. Small titanium−oxo clusters, such as $Ti_7O_4(OEt)_{20}$, are generally destroyed by alcohol nucleophilic attack.[80] In contrast, the titanium−oxo cores of $Ti_{11}O_{13}(OPr^{i})_{18}$, $Ti_{12}O_{16}(OPr^{i})_{16}$, $Ti_{16}O_{16}(OEt)_{32}$, and $Ti_{18}O_{22}(OBu^{n})_{26}(Acac)_2$ are stable toward ethanol, propanol, and diols.[79,82] Some of the alkoxide groups are exchanged by alcohol molecules R′OH through transalcoholysis reactions, giving rise to new $Ti_nO_m(OR)_{z-x}(OR')_x$ species such as $Ti_{16}O_{16}(OEt)_{24}(OPr^{n})_8$[80] or $Ti_{12}O_{16}(O^{i}Pr)_{10}(OEt)_6$.[71a] This stability of high nuclearity clusters toward alcohols or diols can thus be used to establish connections between clusters.[82]

Ethoxide groups of $Ti_{16}O_{16}(OEt)_{32}$ can be exchanged by propanediolate ligands, which bind to the clusters by one or both extremities.[82] Similar behavior has been reported previously in the reaction of $Ti_{11}O_{13}(OPr^{i})_{18}$ with diols.[79] Both clusters in the presence of polyols generate hybrid materials that can be described as aggregates of titanium−oxo clusters connected by diolate bridges.

The stability of large clusters such as $Ti_{12}O_{16}(OPr^{i})_{16}$, $Ti_{16}O_{16}(OEt)_{32}$, and $Ti_{18}O_{22}(OBu^{n})_{26}(Acac)_2$ toward acacH and related nucleophiles such as acetoacetylethyl methacrylate (AAEM), dibenzoylmethane (DBM), and carboxylic acids has also been investigated. Nucleophiles bearing chelating functions (carboxy, acetoacetoxy, etc.) can modify the cluster surface by chelation of the metal centers. However, higher quantities of complexing ligands can also destroy the clusters. The effectiveness of the cleavage follows the sequence $Ti_{18}O_{22}(OBu^{n})_{26}(Acac)_2 < Ti_{16}O_{16}(OEt)_{32} \ll Ti_{12}O_{16}(OPr^{i})_{16}$.[82] The observed differences between these titanium−oxo clusters have been assigned to three main causes. First is the unsatisfied coordination over a fraction of the titanium atoms. Whereas all titanium atoms are octahedrally coordinated in $Ti_{18}O_{22}(OBu^{n})_{26}(Acac)_2$ and $Ti_{16}O_{16}(OEt)_{32}$, a corona of 6 out of 12 Ti(IV) atoms are pentacoordinated in $Ti_{12}O_{16}(OPr^{i})_{16}$, making this oxo core more labile

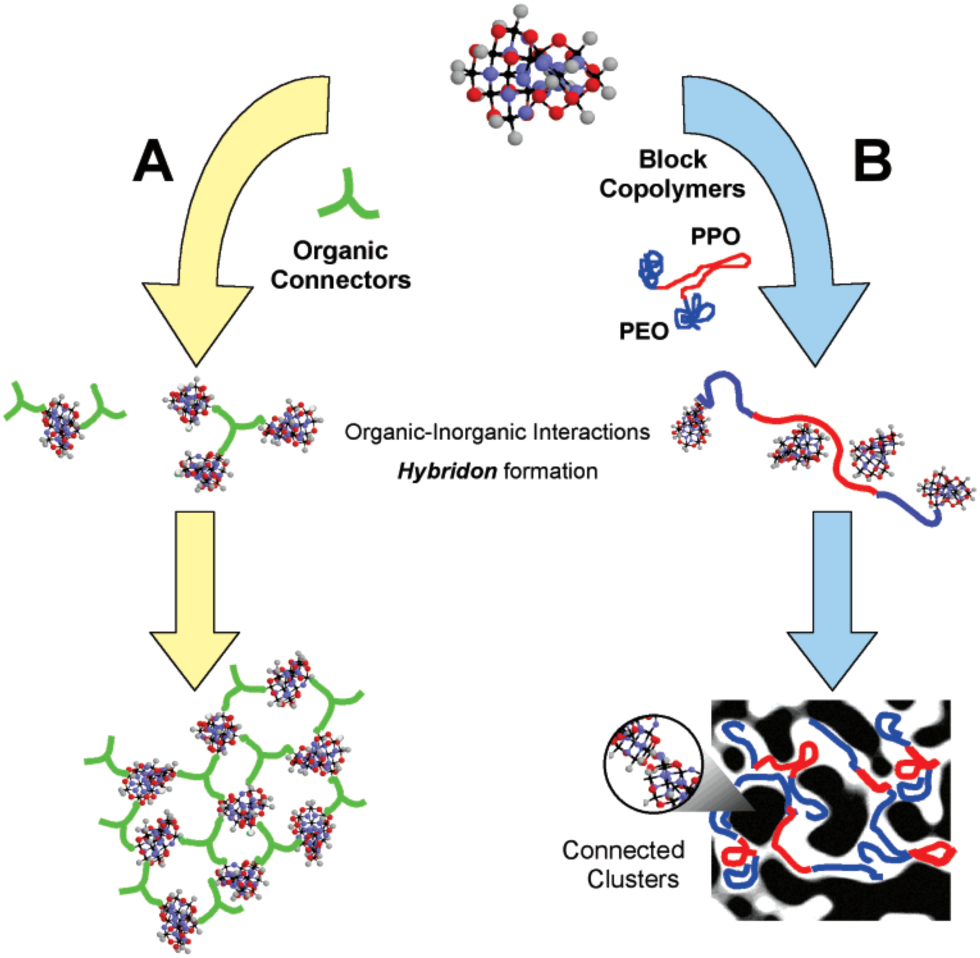

Figure 5. Different ANBB approaches involving clusters and different connectors. (A) Ordered cluster dispersions based on the covalent linkage of complementary organic and inorganic NBBs. (B) Creation of a bicontinuous mesostructured hybrid arrangement. Interactions between the template and the inorganic NBB include covalent bonding and van der Waals forces (hydrophobic contacts).

toward nucleophilic substitution. The stability of the titanium–oxo core also depends on the number of "bulk" oxo bridges, i.e., those with high coordination to Ti (IV) (μ_3-O, μ_4-O, and μ_5-O). Therefore, clusters bearing highly coordinated O bridges are more stable toward hydrolysis. Following this approach, the $Ti_{18}O_{22}(OBu^n)_{26}(Acac)_2$ and $Ti_{16}O_{16}(OEt)_{32}$ oxo cores are more compact than that of $Ti_{12}O_{16}(OPr^i)_{16}$; interestingly, this stability seems not to depend only on the Ti/O ratio. Finally, the presence of strong chelating ligands at the surface might hinder the attack of nucleophilic species. The improved stability of $Ti_{18}O_{22}(OBu^n)_{26}(Acac)_2$ clusters provides an example of this additional kinetic stability.

Once controlled, the reactivity of titanium–oxo clusters can be used advantageously with the aim of designing new hybrid materials with tailored textures. Two main strategies concerning their assembly have recently been reported in the literature.[25,83] They are based on the use of dendrimeric connectors or amphiphilic block copolymers (ABC) as templates.

$Ti_{16}O_{16}$–Dendrimer Hybrids. Glassy yellow transparent xerogels can be obtained from a THF solution of $Ti_{16}O_{16}(OEt)_{32}$ (TS) and first-generation dendrimers after solvent removal under an inert gas atmosphere. The dendrimers bear six acidic $[G'_1(COOH)_6]$ or alcoholic $[G'_1(OH)_6]$ tips. The covalent bonds forming the hybrid interface between the dendrimers tips and the clusters was evidenced through ^{13}C MAS NMR and FTIR spectra, and the integrity of the titanium–oxo core in the final hybrid solid was verified through solid-state ^{17}O NMR measurements.[25] The obtained bicontinuous phases are, in fact, locally ordered dispersions of TS cores with correlation distances of about 2 nm and coherent scattering domains of 5–6 nm. The path to these $Ti_{16}O_{16}$–dendrimer hybrids is sketched in Figure 5 (route A) and can be separated in three steps: (a) "Snap-on" (i.e., quick and selective) reactions take place at the cluster surface (in dilute solution), leading to hybrid bricks ("hybricks"). (b) Upon solvent evaporation, a cross-linking of these hybrid moieties gives rise to higher-weight species. (c) Finally, a bicontinuous hybrid nanocomposite is formed, in which TS clusters are regularly spaced by the polymers. The adequate combination of simple chemistry at the cluster surface and the intrinsic symmetry granted by the dendrimer provides access to these new mesotextured hybrid materials.[25] This strategy can be pushed further; the complementary tuning of the functions of the dendrimeric tips and the inorganic surface can expand this Lego-like chemistry to higher-generation dendrimers and beyond clusters, aiming at organized arrays of nanoparticles.

$Ti_{16}O_{16}$–ABC Hybrid Assemblies. Since the discovery that micellar and lyotropic liquid-crystal phases can act as templates for creating periodic hybrid organic–

inorganic materials, a new class of materials with hierarchical structures and complex forms was born.[20-23] Amphiphilic block copolymers (ABC) consist of hydrophilic and hydrophobic blocks; the most widely used for templating purposes[22c,82] are based on poly(ethylene oxide) and poly(propylene oxide) blocks (PEO−PPO). These species are able to self-assemble into micellar structures (spherical or cylindrical micelles) or lyotropic liquid-crystalline phases (cubic, hexagonal, lamellar, etc.).[84] $Ti_{16}O_{16}(OEt)_{32}$ clusters have been used as nanobuilding bricks to create mesoscopically ordered phases using PEO−PPO−PEO triblock copolymers (for example, Pluronics) as templates.[25b,c] A complex sequence of processes, involving the template, the solvent, and incoming water, drastically affects the self-assembly and thus the mesostructuring of the hybrid phases. The route to $Ti_{16}O_{16}$−Pluronics hybrids is sketched in Figure 5 (route B). In THF or butanol, in the presence of low amounts of water, hydrolysis−condensation reactions between the metallic centers take place in parallel with transalcoholysis reactions of the ethoxy groups of $Ti_{16}O_{16}(OEt)_{32}$ by the PEO terminal functions.[85]

The interaction between the template and TS induces drastic modifications in the folding behavior of the templating agent. The connection of the hydrophilic PEO ends to hydrophobic TS permits the formation of $Ti_{16}O_{16}(OEt)_{32-x}(PEO)_x$ moieties. This leads to a decrease in the solubility difference between the copolymer blocks and promotes polymer unfolding. The hydrophobic TS bricks can loosely attach to the hydrophobic PPO block, hindering an adequate segregation of the amphiphilic blocks. The overall effect is the unfolding of the polymers. The templates also act to inhibit inorganic polymerization, avoiding the massive segregation of a nonporous dense oxidic phase. Further linking between the inorganic bricks can be accomplished through gentle hydrolysis−condensation reactions promoted by residual water or air moisture. The obtained hybrid phases present bicontinuous locally ordered wormlike structures. Upon thermal treatment of these hybrid phases, high-surface-area wormlike amorphous titania (specific surface area > 250 $m^2\ g^{-1}$) is obtained.[25b,c]

In contrast, hexagonal hybrid phases are obtained when PS-*b*-PMAA block copolymers and TS are used as NBBs in toluene. The templating agent consists of one polystyrene block (PS) and one poly(methacrylic acid) block (PMAA) with equal chain lengths (105 monomer units).[83] The solvent plays a major role in this case by selectively dissolving the PS block; spherical micelles are thus formed, with the hydrophilic block PMAA forming the insoluble core. Once the titanium−oxo clusters are added to the micellar solution, their hydrophobicity leads to their incorporation in the PS corona. Some of them can diffuse into the amphiphilic interface between the PS block and the PMAA block, where complexation reactions between the carboxylate ligands and titanium centers take place, generating a covalent hybrid interface. This, in turn, creates a driving force for cluster diffusion to the amphiphilic interface. As a large excess of the block copolymer is added, only a fraction of the carboxylate groups belonging to the PMAA blocks are bound to the titanium atoms. In addition, the EtOH molecules released by the cluster upon complexation might react with the neighboring −COOH groups, leading to esterification. Water can thus be locally produced in a controlled way. This chain reaction might promote further hydrolysis and condensation of the titanium−oxo clusters. In this way, the hexagonal mesophase obtained upon solvent evaporation is frozen. It seems that the addition of a controlled amount of titanium−oxo clusters to the micellar solution does not disrupt the structures of the block copolymer micelles. Moreover, the structures of the micelles and those of the hexagonal phase might be assisted by the addition of the titanium−oxo clusters. The formation of an inorganic framework covalently linked to the polymer matrix might enhance the stability of the aggregated structures.[83]

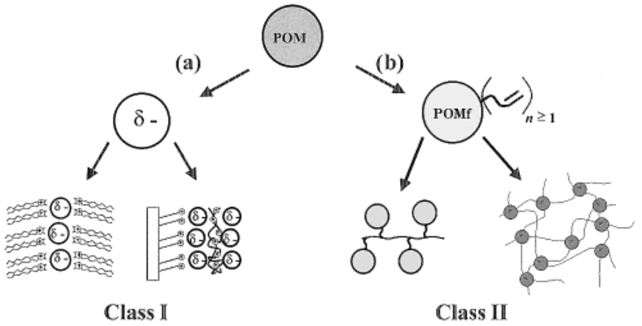

Figure 6. Both classes of organic−inorganic hybrids based on POMs. (a) Electrostatic embedding of POMs in differently charged organic matrixes (class I). (b) Class II hybrids obtained by preliminary functionalization of POMs and subsequent covalent grafting of the NBB into the organic matrix.

6. Polyoxometalate-Based NBBs and the Resulting Hybrid Structures

Polyoxometalate (POM) species based on Mo, W, or V constitute a full class of nanobuilding blocks. These metallic oxo clusters play a great role in areas such as catalysis,[86] medicine (anti-HIV activity),[87] electro- and photochemically active phases,[88] and magnetic materials.[89] The practical applications of polyanions are based on combinations of value-added properties (large sizes of 6−25 Å, anions, fully oxidized/(photo)reducible compounds, etc.).[90] Recently, much attention has been paid to the development of ordered assemblies of POMs within hybrid organic−inorganic materials. These composite materials exhibit a variety of interesting electronic, magnetic, redox, and photonic properties.[91]

POM-based class I materials are based on weak interactions as a result of the anionic charge carried by the POM. Indeed, the anionic character of POM allows its incorporation into materials possessing cationic groups, to yield the first type of hybrid materials described in the literature. On the other hand, obtaining class II hybrid materials requires prior covalent functionalization of the POM species, allowing for the anchoring of the organic moiety. These groups will subsequently ensure the covalent interactions with the organic matrix, as depicted in Figure 6.

6.1. Class I Hybrid Materials Based on POMs.

Most of the composite materials of this class correspond to Keggin heteropolyanions of general formula $[XM_{12}O_{40}]^{n-}$ (M = W, Mo; for X = Si^{IV}, $n = 4$; for X = P^{V} or As^{V}, $n = 3$; for X = Co^{II}, $n = 6$). The following sections describe different materials for which the POMs are embedded in organic matrixes for various applications (e.g., dopants in polymers; toners; materials for magnetic, electrochemical, or electrooptics applications).[91]

POMs in Polymeric Matrixes. The first hybrid materials described in the literature concern the immobilization of POMs in a conducting polymer matrix. The POMs are embedded in conducting polymers such as polypyrrole, polyaniline, polythiophene, or poly(1-naphthol) and used as conductive electrodes.[92] The POM-doped polymers exhibit redox properties inherent to both components of the hybrid. For example, polypyrrole doped with $[PMo_{12}O_{40}]^{3-}$ can be used for the electrocatalytic reduction of O_2 and ClO_3^-.[92a] The incorporation process is based on the chemical or electrochemical oxidation of a polymerizable monomer in the presence of POM solutions. The same process permits one to obtain hybrid films exhibiting both magnetic properties and conductivity from the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion and pyrrole.[93] The incorporation of POM into a polymer matrix can be extended to applications in nonconducting polymers, dyes, pigments, or inks. In addition, POMs form stable precipitates with cationic dyes.[91] Thus, complexes of POMs with tri- or tetracationic polymethinine dyes have been used as pigment in paints, printing inks, and plastics.[94]

POMs in Inorganic Sol−Gel Matrixes. Various devices for optics, electrochromism, and photochromism resulting from the synergy between the POMs and an inorganic sol−gel matrix have been reported.[95] Silica and titania are the most studied inorganic matrixes. These composite materials are synthesized via sol−gel techniques. POM-doped titania exhibits electrochromic behavior and ionic conductivity.[95] Silica−POM hybrids have been described as interesting photochromic recording materials.[95] Other POM−gel systems are of interest for use in optoelectronic devices and for their proton conductive properties,[91] or even for use as precursors to mesoporous ordered materials. In the latter case,[96] a two-step “salt gel” synthesis has been developed. Organized POM−surfactant mesoscopic phases based on electrostatic interactions are initially obtained. Subsequently, phosphate or silicate linkers are added, which generate a continuous gel phase by embedding and connecting the clusters. Surfactant removal by anion exchange or thermal treatment yields high-porosity ($200-600\ m^2\ g^{-1}$), albeit weakly ordered, phases.

POMs in Langmuir−Blodgett or Multilayer Films. In the past few years, different ultrathin mono- and multilayers containing POMs have been described. Well-organized layers of Keggin polyoxoanions have been obtained by means of Langmuir−Blodgett (LB) techniques.[97] By using the anion $[CoW_{12}O_{40}]^{6-}$ and the dimethyldioctadecylammonium cation (DODA), LB films with magnetic properties have been obtained.[97a] Because of their anionic charge, the polyanions are adsorbed onto a positively charged monolayer of DODA, leading to an organic−inorganic superlattice.

The construction of multilayer films involves layer-by-layer (LBL) stepwise assembly, through the sequential adsorption of oppositely charged self-assembled monolayers (SAMs). Organization is driven by electrostatic interactions, in this particular case, of anionic POMs and cationic polymers. Caruso et al.[98] have reported an ultrathin multilayer film prepared by stepwise adsorption of a novel giant molybdenum polyoxometalate cluster and poly(allylamine hydrochloride). Well-defined hybrid mono- and multilayer films containing POMs on gold substrates covered with alkanethiol SAMs (cysteamine and 3-mercaptopropionic acid) based on electrostatic interactions have been described.[99] The applications expected for these tunable mono- and multilayers concern electrochromism, photoelectrochemistry, sensors, catalysis, light imaging, and other thin-film molecular devices.

6.2. Class II Hybrid Materials Based on POMs. Organic and organometallic derivatives of polyoxometalates (POMs) bearing functionalized (polymerizable) groups appear to be especially suitable for obtaining valuable hybrid materials. As a consequence of the intrinsic properties of the polyoxometalates, functionalized POMs might lead to composite materials with great potential in catalysis, chemotherapy, and photo- and electrochromism.

To develop a rational method for obtaining covalently linked POM-based hybrid materials, hybrick precursors have to be designed. Several examples of the whole process using different POM-based hybrid systems will be presented below, starting from discrete polyoxotungstates and targeting complex magnetic materials.

Functionalized Polyoxometalates as Starting Derivatives. Polyoxoalkoxometalates constitute a full subclass of polyoxometalate derivatives. Different methods are used to obtain this class of compounds. Surface activation of the polyoxometalate provides localization of the charge density at the oxygen surface, permitting covalent bonding with organometallics. This method is based on the replacement of Mo(VI) or W(VI) centers by one or more lower-valent metals.[100] Another method is the self-assembly of polyoxometalates and polyalcohols. Recently, Hill and co-workers[101] described poly(polyoxometalate) dendrimers synthesized by self-assembly of an organic hydroxylated dendrimer bearing four trialkoxo groups and a heteropolyoxovanadotungstate $[H_4P_2V_3W_{15}O_{62}]^{5-}$.

Another way to functionalize POM blocks is to use organoimido derivatives of polyoxomolybdates containing a direct covalent link between the polyoxomolybdate and the organic moiety. Indeed, the bond between the two parts is ensured by a Mo−N−C bridges. In this way, an original dimer of the general formula $[(Mo_5O_{18})MoN(1,4\text{-}c\text{-}C_6H_{10})NMo(Mo_5O_{18})]^{4-}$ was obtained by Stark et al.[102]

Saturated polyoxometalates such as the Keggin anion $[XW_{12}O_{40}]^{n-}$ (for $X = Si^{IV}$, $n = 4$; for $X = P^V$ or As^V, $n = 3$) exhibit evenly distributed relatively low negative charge densities. The removal of a metal octahedron from a saturated polyoxometalate leads to an increase in and localization of the anionic charge. The resulting lacunary anions are highly nucleophilic and react easily with electrophilic groups such as organostannates,[103] organosilanes,[14] or organophosphonates. Particular attention has been paid to organosilyl and organophosphoryl derivatives of trivacant and divacant Keggin anions. The trivacant polyoxotungstate $[XW_9O_{34}]^{n-}$ (for $X = Si^{IV}$, $n = 10$; for $X = P^V$ or As^V, $n = 9$) has a high surface charge constituted by six nucleophilic oxygen atoms. The divacant polyoxotungstate $[XW_{10}O_{36}]^{n-}$ (for $X = Si^{IV}$, $n = 8$; for $X = P^V$, $n = 7$), presents only four

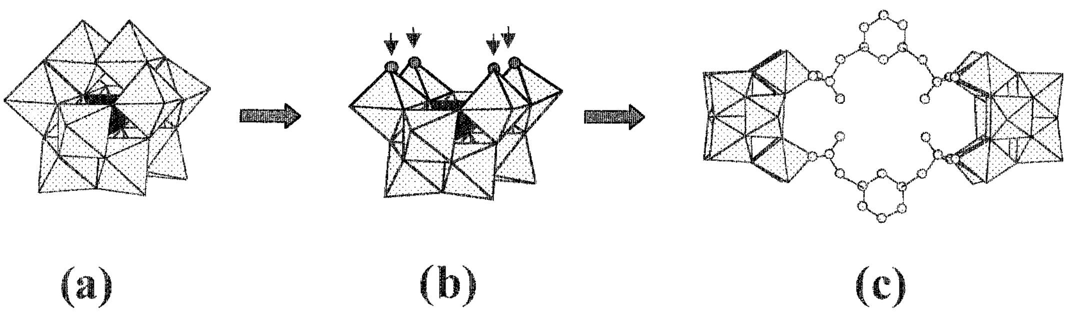

Figure 7. Example of POM functionalization by using a lacunary heteropolyanion. The negative charge increases and is localized on the oxygen atoms of the lacunae. These highly nucleophilic oxygen atoms (arrows) are more reactive toward electrophilic groups such as bissilanes or bis(phosphonates).

nucleophilic oxygen atoms on the lacunar surface. From trivacant polyoxotungstate, different organophosphoryl and organosilyl derivatives have been reported.[14d,g]

Concerning the divacant polyoxotungstate, the RPO^{2+} group reacts to provide one fully saturated hybrid species $[\gamma\text{-}SiW_{10}O_{36}(RPO)_2]^{4-}$.[14h] On the other hand, the high propensity of organosilanes toward polycondensation and reaction with nucleophilic moieties can direct the formation of different types of organic–inorganic hybrids based on the lacunary divacant heteropolyanions $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$. Two series were obtained with the general formula $[SiW_{10}O_{36}(RSi)_2O]^{4-}$ (a) and $[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$ (b), depending on the experimental conditions.[14i] These polyanions correspond to the grafting of an oxo-bridged siloxane unit (cyclic tetrasilyl for b) onto the surface of the lacunary polyoxoanion. When R = 3-methacryloxypropyl, the b species, which presents four hydrophobic chains, behaves as a surfactant with a surface tension of 43.5 mN/m and a critical aggregate concentration of 4.3×10^{-4} M. Finally, by using a double electrophile such as bisphosphonate or bissilane, two series of dimeric cyclic compounds $\{[\gamma\text{-}SiW_{10}O_{36}(SiRSiO)]^{4-}\}_2$ and $\{[\gamma\text{-}SiW_{10}O_{36}(OPRPO)]^{4-}\}_2$ were obtained (Figure 7).[104] Yet, among the large number of organic and organometallic derivatives of POMs, only a few functionalized polyanions have been used as building blocks to obtain polymeric hybrid organic–inorganic systems.

Hybrid Polymers Based on Functionalized POMs. The strategy leading to covalent entrapment of POMs in a polymeric network follows the general examples already described in section 2 (homo- or heteropolymerization). The organic polymerization occurs in the presence of a radical initiator [2,2′-azobis(isobutyronitrile) (AIBN) or $K_2S_2O_8$ in either organic or aqueous solution].

Judeinstein[14a,b] described the first homopolymerization of difunctional POM derivatives of the general formula $[SiW_{11}O_{39}(RSi)_2O]^{4-}$ with unsaturated organic groups (vinyl, allyl, methacrylate, and styryl). More recently, Maatta and co-workers[35b,102] reported well-defined and characterized organoimido-polyoxometalates as polymer pendants, by AIBN-initiated copolymerization of the styrylimido function in the Lindqvist derivative $[NBu_4]_2[(Mo_6O_{18}(NC_6H_4CH{=}CH_2)]$ with a styrene monomer. We will illustrate the application of this strategy for different systems: organic and aqueous gels and magnetic solutions.

(a) Organic Gels. The copolymerization of ethyl methacrylate (EMA) with $[\gamma\text{-}SiW_{10}O_{36}(H_2C{=}C(Me)C(O)OPrSi)_2O]^{4-}$ in acetonitrile using AIBN as the radical initiator is the first example of a hybrid network based on poly(ethyl methacrylate) chains covalently cross-linked by difunctionalized polyanions in organic solvent.[14e] The resulting gel, insoluble in most solvents, accounts for the formation of a covalent network. Multinuclear NMR spectroscopy (^1H, ^{29}Si, and ^{183}W) and FTIR investigations confirm the formation of poly(ethyl methacrylate) chains cross-linked by the difunctionalized POM, which maintains its structural integrity. The gels are able to absorb different amounts of various solvents. The swelling properties of the gels have been discussed and assigned on the basis of the cross-linking densities, which decrease as the POM concentration decreases. Polymerizable functions can be further introduced on the cationic moiety of the hybrid compound by using an ammonium salt bearing a methacrylate group $[(Me)_3N^+C_2H_4OC(O)C(CH_3){=}CH_2]$. The trifunctionalized POM thus obtained presents two polymerization sites, one located on the organosilyl ends and one on the cationic moiety, leading to decreased gel solvation.[14e]

(b) Hydrogels. The previous approach was extended to the synthesis of new hybrid networks based on water-soluble polymer chains (polyacrylamide) cross-linked by water-soluble tetrafunctionalized polyanions ($[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$, where R = $H_2C{=}C(Me)C(O)OPr{-}$).[14f] The modified POMs participate directly in the covalent structure of the networks as molecular cross-linkers. In addition, the inorganic NBB forms aggregates in solution; these aggregates also act as cross-linkers. A new class of hydrogels where the hybrid cross-linker also acts as a nanometric mineral filler and as a polyelectrolyte is thus born. The swelling degrees of some gels are in the bottom range of those of superabsorbent materials. This behavior is due to charged polyanions, which behave as polyelectrolytes regardless of their aggregation state. This property was confirmed using a second type of hydrogel synthesized from acrylamide and *N*,*N*-methylenebis(acrylamide) and $[\gamma\text{-}SiW_{10}O_{36}(PhSiO)_4]^{4-}$, a nonpolymerizable polyanion. However, the degree of swelling at equilibrium is higher when polyanions are covalently anchored to the polymer. These aggregates are able to copolymerize with acrylamide and act further as cross-linking agents with a more significant effect (Figure 8).

(c) Incorporation of Magnetic Nanoparticles into Hybrid Networks Based on Heteropolyanions and Polyacrylamide. The incorporation of an aqueous magnetic colloidal dispersion of negatively charged maghemite ($\gamma\text{-}Fe_2O_3$) nanoparticles into a polymeric network leads to

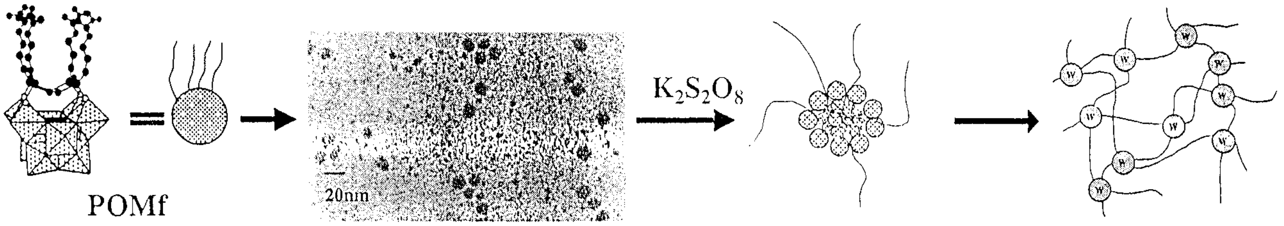

Figure 8. Formation of a hybrid hydrogel based on micellar POM NBBs. The reaction proceeds by copolymerization of POMs tetrafunctionalized with acrylamide.

hybrid hydrogels with magnetic properties.[105,106] The polydisperse magnetic particles, with an average diameter of 6−14 nm,[107] are coated by citrate species. These nano-objects can be dispersed in water as individual particles, owing to electrostatic repulsions, at pH > 4. The copolymerization of acrylamide and the cross-linker polyanions [of general formula $[\gamma\text{-SiW}_{10}O_{36}(RSiO)_4]^{4-}$ (R = $H_2C{=}C(Me)C(O)OPr-$)] is performed at pH 5.4 for different particle volume fractions to maintain particle stability and the negative surface charge. In this way, it is possible to trap large amounts of well-dispersed particles, leading to a ferrogel. The presence of particles does not seem to modify the structure of the gel, which retains the polyelectrolyte effect of the polyanionic aggregates. The obtained hybrid material is based on polyanions covalently linked to a polymeric network that includes magnetic nano-objects. Two properties are of particular interest: the rotational mobility of particles in the network and their release during the swelling process. Furthermore, this hybrid material is potentially promising for size sorting of nanometric objects and might also find applications in biomaterials and optics.

7. Nanoparticule-Based NBBs and the Resulting Hybrid Structures

The transition between clusters and nanoparticles generates much basic research and is still a matter of debate, particularly in regard to structure and properties. The stability problems experienced with small clusters can be avoided by employing larger species, such as nanocolloids. Consequently, the devices that are currently designed are based rarely on clusters but mainly on nanoparticles ranging from 2 to 100 nm in diameter. The development of novel and versatile methodologies that allow for multiscale processing of nanoparticles has an outstanding impact on fundamental research and on chemical and biochemical engineering.

Functionalized nanoparticles already play an important role, for example in pharmaceutical drug delivery systems;[108] paint dispersion; tire reinforcement; catalyst optimization;[109] and in many processes involving adhesives, biocements, varnishes, and lubricants.[110] Several physical methods such as MBE (molecular beam epitaxy), OMVPE (organometallic vapor phase epitaxy), mecano-synthesis, fast quenching of inorganic vapors, nanolithography, and laser or electrical ablation are currently employed to make nanomaterials.[111] Wet chemical routes should provide lower-cost and more versatile access to nanoparticles and nanostructured materials. Moreover, they should allow nano-objects to be produced at larger scales. The control of the size and morphology of inorganic nanoparticles (metals, chalcogenides, metallic oxides) through soft chemistry and related processes is based on several well-known strategies,[112] which consist of tuning of nucleation and growth kinetics;[113] growth inhibition based on a competitive growth/termination mechanisms of the solid phase in the presence of complexing surface capping agents (here, the inhibitor/precursor ratio is a key parameter in the tailoring of the particle size);[81,114,115] confinement of the reaction volume by using micelles, vesicles, or microemulsions;[22d,116] and growth in a pH and ionic strength range for which the interfacial tension is extremely low.[117,118]

For most technological uses and handling purposes, the nanoparticles have to be processed in bulk or as films, yet they still must exhibit their nanoscale-dependent properties (quantum dot, band gap reduction, plasmon resonance, nanomagnetism, superparamagnetism, etc.).[119] Some of these special properties stem from isolated particles and can be lost or modified during processing, possibly through particle−particle interactions or surface modifications, even if the right grain size is conserved. At present, the most advanced systems studied are gold particles, semiconductor nanocrystals, and superparamagnetic particles.[120]

In principle, there are several ways to adapt the NBB approach to create nanoparticle-based hybrid materials. These include introducing already synthesized nanoparticles into polymer or organic hosts, synthesizing the nanoparticles inside such matrixes, connecting particles with adequate organic spacers, and polymerizing functionalized metal−oxo nanoparticles. All of these strategies have been discussed above in the case of clusters. Again, building the hybrid structures requires fine-tuning at the hybrid interface level. The nanoparticles have to be functionalized to be compatible with the organic components of the hybrid. In this case, colloidal interactions must be taken into account, in addition to the chemical nature of the system. The resulting hybrid networks can be amorphous or nanostructured or can even exhibit long-range ordering. In this section, we will focus on some relevant work performed on hybrid nanoparticle-based systems using a NBB approach. An exhaustive review of the synthesis and nature of nanoparticles is beyond of the scope of this work, and the reader is referred to more specific sources.[117,121]

7.1. Synthesis of Functionalized Nanoparticles. An adequate organically functionalized metal oxide nanoparticle allows one to design a large variety of new hybrid materials and devices. However, their organization into structured layers or multilayers deposited onto substrates or as monoliths through tuned “smart” connections remains an important challenge. Chemisorption of organic chains on the particle surface stabilizes the nanoparticles, thus providing functionality. A widespread method of producing colloidal dispersions is by means of coating the inorganic particles using self-assembled monolayers (SAMs). The hybridization of inorganic particles via surface capping with organic functionalities can be performed in one step in situ during particle synthesis or through postfunctionalization of the already-synthesized nanoparticles. A central point is to control the interfacial link between the metal species and the organic molecules.

Organically Prefunctionalized Nanoparticles. Polycondensation of inorganic species can be performed in the presence of organic complexing ligands. A typical method for obtaining dispersions of magnetic ferric oxide nanoparticles, i.e., the so-called magnetic fluids, is to alkalinize aqueous solutions of metallic salts in the presence of citrate[122] or surfactants such as oleic acid.[123] These species allow one to control the particle size and ensure the dispersion of the particles in water or organic solvents, respectively. Dispersions of metallic particles (Au, Ag, Pd, or Pt) are usually obtained by chemical reduction of metallic salts in the presence of surfactants or polymeric ligands.[121a] Surfactant-coated metallic particles (cobalt or iron) are also obtained directly by decomposition of metal carbonyl species in the presence of surfactants or polymer.[124]

Hydrolysis of metal alkoxides with empty d or p orbitals [Zr(IV), Ce (IV), Ti(IV), Sn(IV), Al(III)] in the presence of acetylacetone and a noncomplexing organic acid (*p*-toluene sulfonic acid), followed by aging at 60−80 °C, leads to nonaggregated sols of nanocrystalline particles whose sizes can be tuned between 2 and 4 nm.[81,114] Hybrid sols and xerosols made of nanocrystallites of tetragonal ZrO_2, TiO_2 anatase, or SnO_2 rutile can also be obtained. The surfaces of these nano-objects are protected by complexing ligands, such as acetylacetonates and α- or β-hydroxy acids. These complexing agents establish iono-covalent bonds with the particles, resulting from favorable complexation equilibria with the metallic atoms located at the particle surface. The surface structure and the nature of the protecting belt have been carefully investigated for the titania-based hybrid materials.[81,114d] These hybrid nanomaterials present several interesting properties:

(i) The resulting hybrid sols are precursors of ceramic films and membranes. The coating process is straightforward; no additional organic binders are needed to shape the ceramics. After removal of the protecting organic belt by thermal treatment at 300−450 °C, films made of tunable-size nanocrystallites are obtained. Following this procedure, nanozirconia coatings have been made and processed as nanomembranes, able to work under severe constraints (alkaline medium, $T = 400$ °C); they are currently commercialized by Orelis-Rhodia.[125] TiO_2 nanoanatase coatings exhibiting photocatalytic properties and Sb-doped-SnO_2-based films with antistatic behavior, having square resistance of about 80 kΩ can also be processed.[114e]

(ii) The hybrid xerosols resulting from solvent removal are also soluble in organic or in polar organic solvents.[114d] Therefore, they can be easily redispersed in organic matrixes.

(iii) Moreover, the surface-protecting ligands can be conveniently exchanged with other complexing ligands, which eventually might offer connectable or polymerizable organic functions such as amino, alcohol, methacrylate, pyrrole, or thiophene groups.[126] These new ligands could be used as anchoring points to start polymerization reactions with free monomers. The polymerization should proceed at the surface of the protected nanosized inorganic particles. This strategy, already performed for carbon nanoparticles, silsesquioxanes, and inorganic nanoparticles, could be enormously expanded if developed from cheap inorganic precursors and functional complexing ligands.

Organically Postfunctionalized Nanoparticles. Although several methods are available for obtaining nanoparticles, wet methods using mono- or biphasic media are envisaged as being more suitable for large-scale production. The produced particles can be surface postfunctionalized in a subsequent step. This process, of course, depends strongly on the particle nature.

The surface of silica particles can be easily functionalized by reactions in organic media with alkoxysilane [$R'{-}Si(OR)_3$] or chlorosilane ($R'{-}SiCl_3$) species.[127−129] The links between nanosilicas and the silylated functional organic moieties depend on several parameters, such as surface pretreatment (water and silanol content), solvent, nature of the organic R functions, etc. However, the nature of the links and the mechanisms involved in their formation are still matters of discussion.[130] Some organo-functionalized nanosilicas carrying R groups with alkylamino, alkylacrylate, alkylepoxy, etc., functions have already been commercialized by Degussa[131] and Clariant.[132] The strategy developed for the hybridization of nanosilicas has been used to functionalize alumina, zirconia, and titania nanoparticles with trimethoxysilylpropyl methacrylate precursors to design reactive ceramic fillers for PMMA-based composites.[133] A similar approach has been developed for the functionalization of mesoporous silica, which is, in fact, the inverse problem: high surface are due to ordered pore arrays. This is of utmost importance in the creation of nanoscopic multifunctional materials (selective sorbents, nanoreactors, etc.).[134]

Many other metal-oxide-based particles can be derivatized through the use of a functional complexing ligand. Carboxylate species are widely used to coat ferric oxide particles.[135] Another interesting example is given by TiO_2, which has been modified by different functional groups (F−COOH, F−acetylacetone, etc.). The F group can be, for example, a simple alkyl chain grafted to promote tribological properties of nanotitania,[136] a dye sensitizer anchored to titania to enhance its photochemical response,[137] an alkylamino group to open new functionalities, or any polymerizable organic function. Smart methods for polymerizing MMA at the surface of nanometric titania particles have already been developed in the paint and polymer industries.[138]

Inorganic nanoparticles of titania can also be modified with titanate alkoxo carboxylate coupling agents such as $Ti(OPr^i)_2(O_2C{-}CH_2{-}C_{16}H_{33})(O_2C{-}C(CH_3){=}CH_2)$. The alkoxotitanate reacts with the hydroxyl groups present at the TiO_2 particle surface, leading to modified titanium dioxide particles carrying $Ti{-}O_2C{-}C(CH_3){=}CH_2$ and $Ti{-}O_2C{-}CH_2{-}C_{16}H_{33}$ hydrophobic groups. As a consequence, these modified particles can be dispersed in an aqueous solution of sodium dodecyl sulfate, creating a micelle-like structure with an inorganic particle in the center. In this system, an emulsion polymerization of MMA can be carried out, and the resulting materials present a core−shell morphology with a titania core and a polymer shell made of PMMA. The PMMA is either covalently bound to the titanate surface coupling agents by their methacrylate functions or physically bound by entanglement.

Thiol adsorption is a widely used method for the functional modification of nanosized entities, such as metallic,[139,140] ferric oxide,[141] or chalcogenide nanoparticles.[115,142] The hybridization of gold nanoparticles with modified alkanethiols is widely described and used to build molecular recognition devices and sensors.[143] In a recent example, gold particles were coated by a mixture of octanethiol and diacyldiaminopyridine terminated thiol. The resulting composite can be used for the molecular recognition of flavin.[144] Colloidal redox sensors composed of gold nanoparticles coated by mixtures of redox-active amidoferrocenylalkylthiols ("exo receptors") and aliphatic chain thiols have been described.[145] More rigid surface coverages were achieved by incorporating groups capable of hydrogen bonding (e.g., amide) in the chains constituting the SAMs.[146] Bifunctional chains (like dithiol linkers) are well-suited for the construction of macro-/mesoscopic particle arrays.[147−149] In view of applications in the field of nanoelectronics, aryl dithiol and aryl di-isonitriles, which allow electron transport, have been used.[148] The steric hindrance and functionality of the linkers direct the structure of the final aggregate.

7.2. Hybrid Systems Based on Embedded NBBs. An easy synthetic pathway to the construction of hybrid nanocomposites is based on a simple embedding of the nano-objects within a host matrix. The quality of the dispersion is improved by fine-tuning the interactions between the particle surface and the host. Van der Waals, H-bonding, and solvation interactions ensure cohesion. The host can be a complex lyotropic self-assembly or a polymer-based system inside which inorganic particles can be simply dispersed or generated in situ.

Lyotropic Systems. Magnetic ferric oxide or metallic nanoparticles have been introduced in lyotropic systems. The SAM-coated maghemite (γ-Fe_2O_3) nanoparticles presented in section 6 can be dispersed in lamellar systems of SDS−pentanol−water−cyclohexane.[150] Depending on their surface modification, the nanoparticles can be confined in the cyclohexane lamellae or in the aqueous domains (citrate-coated maghemite).[151] More recently, the same kind of hybrid has been made with silver nanoparticles.[152] These hybrids exhibit a large variety of chemical structures; however, as materials, they present the major disadvantage of being sensitive to temperature or compositional fluctuations.

Ordered superlattices composed of nanosized semiconducting sulfides have been synthesized within surfactant self-assemblies.[2o,2p,153] Diffusion of H_2S in a liquid-crystalline (ethylene oxide)$_{10}$−oleyl−water mesophase containing Cd^{2+} ions allows for controlled nucleation and growth conditions. The resulting hexagonal-packed arrays of nanocrystalline CdS, a "mineral copy" of the lyotropic phase, present periodicities ranging between 7 and 10 nm. The templating effect is apparently driven by specific surfactant−metal interactions. This method has been extended to ZnS, $Cd_{1-x}Zn_xS$, and CdSe nanoparticles.[2p]

Polymer Systems. Tridimensional chemical networks, latex and copolymer self-assemblies have been described as host matrixes or as templates for meso- or macroporous materials. Nanoparticles can be either synthesized within the polymer or postfunctionalized before construction of the hybrid. This section will mostly describe hybrid assemblies of nanoparticles within polymer matrixes: bulk gels, latexes, copolymer self-assembled phases, or dendrimers.

Bulk Gels. Maghemite can be successfully embedded in polymeric [poly(methylmetacrylate), PMMA or poly(vinyl alcohol), PVA][119,154] or hybrid silica-based ($HSiO_{1.5}$)[155] matrixes, allowing for an excellent dispersion of the nanoparticles and retention of their superparamagnetic behavior.[119] Very highly magnetic ferrogels have been obtained by including citrate-coated magnetic nanoparticles within polyacrylamide networks.[106] As no specific interaction is present between the network and the particles in this case, the latter can either be trapped in the gel or be released during the swelling process, depending on the mesh size of the host polymer.

The polymeric material can also be used as a matrix for synthesis of the particles, controlling the particle size and participating in particle dispersion. For example, silver nanoparticles have been obtained in PMMA gels,[156] cobalt particles in polystyrene networks,[157] and magnetic ferric oxide particles in imine polymers.[158] In the latter case, the polymer also acts as a reagent for particle synthesis.

Latex. Commercial magnetic latex have been used for the magnetic separation of biochemical species or cells.[159] The simpler approach consists of dispersing SAM-coated magnetite nanoparticles in styrene, which is subsequently polymerized. A hybrid dispersion of magnetic oxide grains in polystyrene (PS) is thus obtained. Alternative processes have been proposed to increase the latex magnetization, reduce the polydispersity in size, and decrease the diameter of the hybrid particles, i.e., to produce magnetic nanolatex. These include coating the magnetic nanoparticles with polymerizable SAMs[160,161] or triblock copolymers.[162] The same kinds of strategies are described for CdS nanoparticles.[163,164]

Self-Assemblies of Copolymers. Copolymers, as surfactants, also give way to lyotropic structures through cooperative self-assembly.[22d] Magnetic ferric oxide nanoparticles coated with PS chains of various lengths have been confined in the PS domains of smectic phases obtained with symmetric PS−PMMA or PS−poly(butylmetacrylate) (PBMA) copolymers.[165] Using a similar approach, Pd particles coated with homopolymer were incorporated into poly(2-vinyl)pyridine-*block*-polyisoprene (P2VP-*b*-PI) copolymer films.[166] However, a more common approach to such hybrids is to synthesize the particles inside the copolymer structure swollen by a solvent. P2VP-*b*-PI copolymer films incorporating Pd particles were obtained this way by reducing Pd(II) ions in these copolymers swollen in benzyl alcohol.[167] CdS particles have also been obtained in diblock copolymers presenting two hydrophilic blocks.[168] Amphiphilic polymers such as PODS [poly(octadecylsiloxane)] self-organize in superstructures presenting alternate water and organic layers. Metallic particles (Pd, Pt, Au, etc.) were obtained by reduction of metallic salts confined in the water layer.[169] As the structures obtained by self-organization of copolymers depend on the relative length of each block, results obtained for layered systems could, in principle, be extended to other structures (e.g., cubic or hexagonal arrangements).

Dendrimers. High-generation dendrimers are very well-defined polymers, with potential applications as host matrixes for nanoparticles.[170] Metallic nanoparticles are synthesized inside the dendrimer by reduction of metallic salts, provided that specific interactions between some dendrimer functions and the metals are developed. This procedure permits reaction confinement in the intradendrimer volume. Nanoparticles encapsulated in the dendrimers do not agglomerate, becoming interesting candidates indeed for applications in the fields of catalysis, nonlinear optics (NLO), and photonics. An additional possibility consists of the use of dendrons (dendrimer branches) as selective gates to control the access of molecules according to their size. In a recent example, the reaction of thiol-functionalized phosphorus-based dendrimers with $Au_{55}(PPh_3)_{12}Cl_6$ clusters, yields well-defined submicron gold particles formed by bare Au_{55} clusters as building blocks.[171] The dendrimer behaves in this case as a morphology director, playing a dual role: they eliminate all ligands around Au while protecting the surface of the resulting aggregates, based on the high affinity of the thiol extremities for Au.

7.3. Multiscale Ordered Hybrid Materials Made through Self-Assembly Processes. Multiscale ordering of functional colloidal nanoparticles is a powerful technique for the creation of macroscopic devices. This field of research is now coming of age. Multiscale ordering can be performed through self-assembly processes or controlled molecular recognition processes. Recent articles using these specific patterns of interactions[172] describe hybrid materials built from the coupling of biomolecule−NBB,[173] NBB−NBB,[174] polymer−NBB,[175] or dendrimer−NBB[176] systems. Connections between complementary functionalized colloidal systems are addressed following three main strategies: electrostatic coupling and covalent and noncovalent binding. Recent results in this field will be briefly presented; the combination of nanoparticulate assemblies and active molecules has been treated elsewhere[177] and will not be covered.

Networks Formed through Electrostatic Interactions. Although electrostatic interactions are often at the origin of order, only a few colloidal crystals based on them have been described. Mesoscopic structures of TiO_2 anatase nanoparticles have been formed through self-assembly processes involving class I hybrid composites made of multiply charged polytitanate anions and tetramethylammonium cations. These anatase nanocrystals can, in turn, self-assemble into highly ordered superlattices.[178] Another example is given by the assembly of gold particles covered by quaternary ammonium bromide salts ($R_4N^+Br^-$): 2D and 3D organized systems have been observed, the separation between the objects being controlled by the length of R. NBBs functionalized with primary amines [for example, nanosized silica hybridized with (aminopropyl)triethoxysilane] can be subsequently coupled with a “counter NBB” displaying a complementary surface.[172] In the simplest case, the complementary NBB is a gold nanoparticle, capped at its surface by thiol groups that carry alkylcarboxylic functions. By combining these two systems, simple acid−base chemistry induces an immediate charge pairing that results in the spontaneous formation of electrostatically bound mixed colloids.

This strategy is also suitable for preparing nanocomposite supported hybrids in the form of films and membranes. Modified glass (indium tin oxide, ITO, conductive glass) or gold substrates are the most widespread supports. The LBL assembly technique allows for the synthesis of polymer- or particle-based films. However, covalent linking between the species can substantially improve the stability and characteristics of the LBL-assembled nanocomposite films.[179] The first stage involves substrate functionalization; the most often used chemical reagents are thiols and amines. Alkylamines (ODA, octadecylamine)[180,181] and branched polymers such as PEI (polyethylenimine)[182] induce efficient interactions with carboxylate-functionalized metallic particles. Further growth of the layer is ensured by electrostatic interactions or covalent linking with cross-linkers such as *N*,*N*′-bis(2-aminoethyl)-4,4′-bipyridinium.[183] Reduction of $AuCl_4^-$ in the presence of a glass support coated with 3-(mercaptopropyl)trimethoxysilane and dithiols can also lead to LBL assemblies of gold particles.

Covalent Networks. Covalent binding programmed assembly can be simply designed by mixing two sets of NBBs presenting surfaces functionalized with complementary reactive functions. The most common example is provided by the aldehyde−amine couple. In addition, thiol-functionalized nanoparticles are currently employed for assembling nanoparticles in symmetrically and spatially well-defined architectures. Organic dithiol groups acting as molecular bridges ensure a covalent link between adjacent particles. As mentioned above, the flexibility, size, and functionality of the linker can be adjusted according to the application expected for the hybrid materials. In the case of 8-nm gold particles, flexible alkane dithiol spacers yield insoluble precipitates of dithiol cross-linked clusters; according to the experimental procedure, cross-linked networks with 3D-ordered structures can also be obtained.[147] By using rigid thiol-functionalized phenylacetylene species of various symmetries and functionalities as linkers, it is possible to produce gold arrays of several symmetries that exhibit interesting nonlinear optical properties because of the well-defined symmetries and interparticle spacings.[147] Recently, the synthesis of a viologen dithiol as a redox-active linker between gold nanoparticles in three-dimensional structures was reported.[184] A number of strategies for covalently anchoring functionalized metal particles or clusters inside nanoporous structures has been recently reported.[185]

Noncovalent Interactions. Titania- and zirconia-supported gold particles constitute a new type of nanocomposite potentially able to open new perspectives in the field of catalysis. Nanocomposites made of thiol-covered gold nanoparticles and TiO_2 ultrathin films were prepared by a combined use of LBL assembly and surface sol−gel processes. The Au particles stabilized by a monolayer of 11-hydroxyundecylsulfide present a hydroxyl-functionalized surface. This permits the interfacial tuning of the Au building blocks and the supporting titania films. As a result, close-packed monoparticulate layers are obtained as mono- or multilayer composite films.[186] Interesting electronic properties are expected for such hybrid materials based on metallic particles.[187] Novel magnetic properties have also been found with such materials associating magnetite nanoparticles and clays by LBL techniques.[188]

Aside from being a suitable hybrid matrix, latex colloidal nanoparticles can be used to prepare nanoparticle-based hybricks. In fact, the control of core−shell hybrid NBBs of colloidal dimensions is attracting a great deal of interest.[189] Recent work by Rhodes et al.[190] describes the assembly of novel latex core−nanocrystalline silicalite shell composites by a simple stepwise LBL technique. These hybrid combined building blocks can be subsequently assembled to yield hierarchical assemblies, precursors to macro-/microporous materials. This method differs from the usual means of obtaining macroporous materials by infiltration of colloidal templates.[174,191] An interesting point is that, in principle, the wall thickness, structure, and functionalization of the resulting hierarchically designed oxide can be controlled. The latter is yet another very interesting example of the growing biomimetic approach,[192,193] which is gaining considerable interest for the development of synthesis strategies for multiscale and hierarchical materials.[194,195]

A more sophisticated derivation is constituted by the so-called biomolecular route, which makes use of very specific interactions, such as those found in antigen−antibody pairs, to induce assembly of NBBs.[196,197] Streptavidin−biotin complexes are suitable for this purpose because of their large energies of dissociation and high stabilities over wide ranges of pH and temperature.[143,198] This strategy can also open a wide variety of opportunities for making biologically programmed nanobuilding block assemblies with clusters or nanoparticles. A DNA-based method has also been presented, where noncomplementary DNA oligonucleotides capped with thiol groups are attached to gold particles. An oligonucleotide duplex with “sticky ends” that are complementary to the two grafted sequences is subsequently added. The nanoparticles self-assemble into macroscopic materials, with this assembly being reversible by thermal denaturation.[199] Oligonucleotide-functionalized Au nanoparticles, in combination with a complementary thiol−DNA functionalized Au electrode, have been recently applied for dendritic amplification of DNA. The thiol-functionalized oligonucleotide primer is first adsorbed by covalent links onto a gold support. Subsequently, the primary generation of dendrimer is performed by the interaction with the complementary oligonucleotide-functionalized Au nanoparticles; the next generations follow the same procedure of specific recognition between oligonucleotide hybrid nanoparticles, thus performing nonlinear signal amplification.[200] In addition, layered composites have been obtained by in situ synthesis of the inorganic species on polyionic multilayers[201] or on phospholipidic bilayers. In the latter case, lipidic tubules have been described as templates for the synthesis of ferric oxide particles.[202] Bacterial tubules also give way to templated hybrid silica structures.[203] These are actually bioinorganic hybrid materials.

A possible future strategy proposed by S. Mann et al.[196] for the organization of complex architectures in solution would involve dispersions of different nanoparticles, selectively tagged with recognition sites that define their unique positions in the nanoparticle-based superstructure to be assembled. As a consequence, nanoparticles would recognize and selectively bind to each other upon mixing, yielding assemblies having not only a well-defined typical length but also presenting a tailored positional architecture.[196]

8. Conclusion and Outlook

Hybrid organic−inorganic materials conquer more and more of the free spaces left between inorganic chemistry, polymer chemistry, organic chemistry, and biology. 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 with unprecedented performance. An extraordinary amount of research has appeared in the past 20 years in the field of hybrid materials, indicating the growing interest of chemists, physicists, and materials researchers in fully exploiting this technical opportunity for creating materials and devices benefiting from the best of the three realms: inorganic, organic, and biological. This field of research, which initially grew out of the sol−gel community, is presently thriving with the appearance of a new class of mesoscopic hybrid structures engineered at the molecular or nanometer scale to satisfy the requirements for a variety of applications from biological and chemical sensing, catalysis, and selective separation to optical communications. Many new combinations between an inorganic component and an organic or biologic component are bound to appear in the future. “Chimie Douce”-based methods allow for the creation of an awesome variety of highly controlled metal−oxo-based clusters and nanoparticles of well-defined size, structure, and interface composition. Moreover, templated-growth-based processes using organic molecules and macromolecules as structure-directing agents currently permit the construction of complex hybrid hierarchical architectures. All of this is thanks to the basic understanding of the role of molecular and supramolecular interactions between template molecules (surfactants, amphiphilic block copolymers, organogelators, etc.) and hybrid or metal−oxo-based networks and NBBs. These strategies try, in some naive way, to mimic the growth processes occurring in biomineralization. There is indeed much to learn from Nature, which is, in fact, the best chemist for the synthesis of NBB-based hybrids. Biomineralization processes lead to the easy and large-scale production of regularly organized nano-objects with well-defined dimensions, interactions, and hierarchies, a task that still remains a challenge for materials and colloid chemists.

However, the recent mastery of some of these characteristics permits the creation of novel hybrid phases, where the new interest is focused not only on each of the components, but also on their synergy. The key to these new synthesis pathways is the interfacial chemistry between the NBBs and the organic species. Soon, original hierarchically ordered materials will be designed through the synthesis of new hybrid nanosynthons (*hybridons*) having complementary tuned connectivities, allowing for the coding of hybrid assemblies presenting spatial ordering at different length scales. Hybridons carrying chirality or/and dissymmetry (*Janus*-type NBBs) and complementary functionalities will open new pathways for the synthesis of these materials. Indeed, the degree of substitution of NBBs can 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 in directing assembly processes through molecular recognition or/and covalent coupling. The synthesis of functionally dissymmetric nanocolloids is a more difficult task than it is for clusters, for which the reactivity and connectivity can be strongly differentiated depending on the cluster poles. The creation of functional asymmetry in nanocolloids was recently reported. The commonly described techniques work via a kind of masking process that uses the layer deposition of spherical nanoparticles combined with the postfunctionalization of one of the accessible surfaces.[204]

Another promising approach, which has not yet been extensively developed, is based on the kinetic control of the first nucleation steps to build heteronanocolloids or block-conanocolloids NBB1−NBB2 (silica−gold, silica−titania, etc.), which, of course, might be able to bear different functionalities. These controlled differentiations can be enhanced by the differential reactivity toward adsorption and complexation of the nanoparticle surfaces.

The confinement of highly dispersed NBBs in the form of clusters or nanoparticles in mesoporous hybrid matrixes carrying functional organic groups and the organization of NBBs on textured substrates are strategies already described in the literature. They could provide larger concentrations of active dots and better-defined systems and avoid coalescence into larger ill-defined aggregates. Numerous recent reports have already emphasized the specific magnetic, optical, electrochemical, chemical, and catalytic properties of nanostructured hybrid materials built from molecular clusters or colloids.

The outlook for nanosciences in the 21st century is indeed promising. This area will be, as biology, one of the fields that will contribute to a high level of scientific and technological development. Hybrid nanocomposites present paramount advantages to both facilitate integration and miniaturization of the devices (nanomaterials, nanotechnologies) and afford direct connections among the inorganic, organic, and biological worlds. Functional nanobuilding blocks facilitate integrative synthesis pathways, where synergistic assembly and morphosynthesis can be strongly coupled. The chemical strategies offered by the coupling of soft chemistry processes and the NBB approach allow, through an intelligent and tuned coding, for the development of a new *vectorial chemistry* that is able to direct the assembling of a large variety of structurally well-defined clusters or nanoparticles into complex architectures. Multiscale structured hybrids (from nanometer- to millimeter-scale) will open a land of opportunities for designing new materials. Could these new synthesis strategies allow us to dream of building *intelligent advanced materials* that respond to external stimuli, adapt to their environment, self-replicate, self-repair, or self-destroy at the end of their useful life cycle?

Acknowledgment. G.J.A.A.S.-I. gratefully acknowledges a postdoctoral fellowship from CONICET and financial support from Fundación Antorchas.

References

(1) (a) Schmidt, H.; Kaiser, A.; Patzelt H.; Sholze, H. *J. Phys. Colloq.* **1982**, (*C9*), 275. (b) Wilkes, G. L.; Orler, B.; Huang, H. H. *Polym. Prepr.* **1985**, *26*, 300. (c) Sur, G.-S.; Mark, J. E. *Eur. Polym. J.* **1985**, *21*, 1051. (d) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956. (e) Schmidt, H.; Seiferling, B. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 739.

(2) (a) Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. *J. Mater. Chem.* **1992**, *2*, 679. (b) Chujo, Y.; Saegusa, T. *Adv. Polym. Sci.* **1992**, *100*, 11. (c) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422. (d) Sanchez, C., Ribot, F., Eds. *Proceedings of the First European Workshop on Hybrid Organic−Inorganic Materials.* Special issue of *New J. Chem.* **1994**, *18*. (e) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007. (f) Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010. (g) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431. (h) Judeinstein, P.; Sanchez, C. *J. Mater. Chem.* **1996**, *6*, 511. (i) *Matériaux Hybrides*; Masson: Paris, 1996; Série Arago 17. (j) Schubert, U. *J. Chem. Soc., Dalton Trans.* **1996**, 3343. (k) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420. (l) Corriu, R. J. P. *C. R. Acad. Sci. Paris, Ser. II* **1998**, *1*, 83. (m) Ribot, F.; Sanchez, C. *Comments Inorg. Chem.* **1999**, *20*, 327. (n) Sanchez, C.; Ribot, F.; Lebeau, B. *J. Mater. Chem.* **1999**, *9*, 35. (o) Stupp, S. I.; Braun, P. V. *Science* **1999**, *277*, 1242. (p) Braun, P. V.; Osenar, P.; Tohver, V.; Kennedy, S. B.; Stupp, S. I. *J. Am. Chem. Soc.* **1999**, *121*, 7302. (q) Corriu, R. J. P. *Polyhedron* **1998**, *17*, 925.

(3) (a) Cheetham, A., Brinker, C. J., MacCartney, M., Sanchez, C., Eds. *Better Ceramics Through Chemistry VI, Mater. Res. Soc. Symp. Proc.* **1994**, *346*. (b) Coltrain, B. K., Sanchez, C., Schaefer, D. W., Wilkes, G. L., Eds. *Better Ceramics Through Chemistry VII: Organic/Inorganic Hybrid Materials, Mater. Res. Soc. Symp. Proc.* **1996**, *435*. (c) Laine, R., Sanchez, C., Brinker, C. J., Gianellis, E., Eds. *Hybrid Materials, Mater. Res. Soc. Symp. Proc.* **1998**, *519*. (d) Klein, L. C., Francis, L. F., De Guire, M. R., Mark, J. E., Eds. *Organic/Inorganic Hybrid Materials II, Mater. Res. Soc. Symp. Proc.* **1999**, *576*. (e) Laine, R. M., Sanchez, C., Gianellis, E., Brinker, C. J., Eds. *Hybrid Materials, Mater. Res. Soc. Symp. Proc.* **2000**, *628*. (f) Corriu, R. J. P. *Eur. J. Inorg. Chem.* **2001**, 1109.

(4) (a) Mackenzie, J. D., Ulrich, D. R., Eds. *Sol−Gel Optics I, Proc. SPIE* **1990,** *1328*. (b) Mackenzie J. D., Ed. *Sol−Gel Optics II, Proc. SPIE* **1992**, *1758*. (c) Mackenzie J. D., Ed. *Sol−Gel Optics III, Proc. SPIE* **1994,** *2288*. (d) Mackenzie J. D., Ed. *Sol−Gel Optics IV, Proc. SPIE* **1997,** *3136*. (e) Hubert-Pfalzgraf, L. G., Najafi, S. I., Eds. *Organic−Inorganic Hybrids for Photonics, Proc. SPIE* **1998,** *3469*, 192. (f) Dunn, B. S., Pope, E. J. A., Schmidt, H. K., Yamane, M., Eds. *Sol−Gel Optics V, Proc. SPIE* **2000**, *3943*. (g) *Hybrid Organic−Inorganic Composites*; Mark, J. E.; Lee, C. Y. C., Bianconi, P. A., Eds.; American Chemical Society: Washington, D.C., 1995. (i) Dunn, B. S.; Zink, J. I. *J. Mater. Chem.* **1991**, *1*, 903. (j) Lebeau, B.; Sanchez, C. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 11. (k) Boilot, J. P.; Chaput, F; Gacoin, T.; Malier, L.; Canva, M.; Brun, A.; Lévy, Y.; Galaup, J. P. *C. R. Acad. Sci. Paris* **1996**, *322*, 27. (l) Avnir, D.; Braun, S.; Lev, O.; Levy, D.; Ottolenghi, M. In *Sol−Gel Optics, Processing and Applications*; Klein, L., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; p 539. (m) Livage, J. *C. R. Acad. Sci. Paris* **1996**, *322*, 417. (n) Avnir, D. *Acc. Chem. Res.* **1995**, *28*, 328. (o) Moller, K.; Bein, T. *Chem. Mater.* **1998**, *10*, 2950.

(5) Faloss, M.; Canva, M.; Georges, P.; Brun, A.; Chaput, F.; Boilot, J. P. *Appl. Opt.* **1997**, *36*, 6760.

(6) Schaudel, B.; Guermeur, C.; Sanchez, C.; Nakatani, K.; Delaire, J. *J. Mater. Chem.* **1997**, *7*, 61.

(7) Lebeau, B.; Sanchez, C.; Brasselet, S.; Zyss, J. *Chem. Mater.* **1997**, *9*, 1012.

(8) Rottman, C.; Grader, G.; De Hazan, Y.; Melchior, S.; Avnir, D. *J. Am. Chem. Soc.* **1999**, *121*, 8533.

(9) Dantas de Morasi, T.; Chaput, F.; Lahlil, K.; Boilot, J. P. *Adv. Mater.* **1997**, *11*, 107.

(10) (a) Itou, T., Matsuda, H. *Key Eng. Mater.* **1998**, *67*, 150. (b) Schöttner, G.; Kron, J.; Deichmann, K. *J. Sol−Gel Sci. Technol.* **1998**, *13*, 183. (c) Aldrich, Fluka, Sigma and Supelco Chiral Products Catalog, 1997, p 250. (d) Reetz, M.; Zonta, A.; Simpelkamp, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 301.

(11) (a) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978. (b) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: London, 1978. (c) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 663. (d) Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371.

(12) (a) Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F. *J. Non-Cryst. Solids* **1988**, *100*, 650. (b) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.

(13) (a) Diré, S.; Babonneau, F.; Sanchez, C.; Livage, J. *J. Mater. Chem.* **1992**, *2*, 239. (b) Babonneau, F. *Polyhedron* **1994**, *13*, 1123. (c) Alonso, B.; Maquet, J.; Viana, B.; Sanchez, C. *New J. Chem.* **1998**, *22*, 935. (d) Guermeur, C.; Lambard, J.; Gerard, J. F.; Sanchez, C. *J. Mater. Chem.* **1999**, *9*, 769. (e) Alonso, B.; Sanchez, C. *J. Mater. Chem.* **2000**, *10*, 377.

(14) (a) Judeinstein, P. *Chem. Mater.* **1992**, *4*, 4. (b) Judeinstein, P. *J. Sol−Gel Sci. Technol.* **1994**, *2*, 147. (c) Ammari, N.; Hervé, G.; Thouvenot, R. *New J. Chem.* **1991**, *15*, 607. (d) Mazeaud, A.; Ammari, N.; Robert, F.; Thouvenot, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1961. (e) Mayer, C. R.; Thouvenot, R.; Lalot, T. *Chem. Mater.* **2000**, *12*, 257. (f) Mayer, C. R.; Thouvenot, R.; Lalot, T. *Macromolecules* **2000**, *33*, 4433. (g) Mayer, C. R.; Thouvenot, R. *J. Chem. Soc., Dalton. Trans.* **1998**, 7. (h) Mayer, C. R.; Herson, P.; Thouvenot, R. *Inorg. Chem.* **1999**, *38*, 6152. (i) Mayer, C. R.; Fournier, I.; Thouvenot R. *Chem. Eur. J.* **2000**, *6*, 105. (j) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759. (k) Judeinstein, P.; Deprun, C.; Nadjo, L. *J. Chem. Soc., Dalton Trans.* **1991**, 1991.

(15) (a) Nass, R.; Schmidt, H. *Sol−Gel Optics I, Proc. SPIE* **1990,** *1328*, 258. (b) Sanchez, C.; In, M. *J. Non-Cryst. Solids* **1992**, *147−148*, 1. (c) Schubert, U.; Arpac, E.; Glaubitt, W.; Helmerich, A.; Chau, C. *Chem. Mater.* **1992**, *4*, 291. (d) In, M.; Gérardin, C.; Lambart, J.; Sanchez, C. *J. Sol−Gel Sci. Technol.* **1995**, *5*, 101. (e) Barglik-Chory, C.; Schubert, U. *J. Sol−Gel Sci. Technol.* **1995**, *5*, 135.

(16) Laget, V.; Hornick, C.; Rabu, P.; Drillon, M.; Turek, P.; Ziessel, R. *Adv. Mater.* **1998**, *10*, 1024.

(17) Backov, R.; Morgan, N.; Lane, S.; Perez-Cordero, E. E.; Williams, K.; Meisel, M. W.; Sanchez, C.; Talham, D. R. *Mol. Cryt. Liq. Cryst.*, in press.

(18) (a) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700. (b) Jamison, G. M.; Loy, D. A.; Shea, K. J. *Chem. Mater.* **1993**, *5*, 1193. (c) Choi, K. M.; Shea, K. *Chem. Mater.* **1993**, *5*, 1067. (d) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Wong Chi Man, M. *Chem. Mater.* **1996**, *8*, 100. (e) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217. (f) Chevalier, P. M.; Corriu, R. J. P.; Moreau, J. J. E.; Wong Chi Man, M. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 603.

(19) Ribot, F.; Eychenne-Baron, C.; Sanchez, C. *Phosphorus Sulfur Silicon Relat. Elem.* **1999**, *150−151*, 41.

(20) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S.; *Nature*, **1992**, *359*, 710. (b) Beck, J. S.; Vartuli, J. C. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 76 and references therein.

(21) Mann, S.; Burkett, S. L.; Davis, S. A.; Fowler, C. E.; Mendelson, N. H.; Sims, S. D.; Walsh, D.; Whilton, N. T. *Chem. Mater.* **1997**, *9*, 2300.

(22) (a) Ying, J. Y.; Mehnert, C.; Wong, M. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 57. (b) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633. (c) Zhao, D.; Yang, P.; Huo, Q.; Chmelka, B. F.; Stucky, G. D. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 111. (d) Göltner, C. G. Antonietti, M. *Adv. Mater.* **1997**, *9*, 431. (e) Brinker, C. J., Lu, Y., Sellinger, A.; Fan, H. *Adv. Mater.* **1999**, *11*, 579. (f) Ozin, G. A. *Chem. Commun.* **2000**, 419.

(23) Burkett, S.; Sims, S. D.; Mann, S. *Chem. Commun.* **1996**, 1367.

(24) (a) Lim, M. H.; Stein, A. *Chem. Mater*. **1999**, *11*, 3285. (b) Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, 12, 1403.

(25) (a) Soler-Illia, G. J. A. A.; Rozes, L.; Boggiano, M. K.; Sanchez, C.; Turrin, C.-O.; Caminade, A.-M.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4249. (b) Sanchez, C.; Soler-Illia, G. J. A. A.; Rozes, L.; Caminade, A.-M.; Turrin, C.-O. Majoral, J.-P. *Mater. Res. Soc. Symp. Proc.* **2000**, *628*, CC6.2. (c) Soler-Illia, G. J. A. A.; Rozes, L.; Ribot, F.; Turrin, C.-O.; Caminade, A.-M.; Majoral, J.-P.; Sanchez, C. *Surf. Coat. Int.* **2001**, in press.

(26) (a) Hoebbel, D.; Endres, K.; Reinert, T.; Pitsch, I. *J. Non-Cryst. Solids* **1994**, *176*, 179. (b) Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302. (c) Lichtenhan, J. D. *Comments Inorg. Chem.* **1995**, *17*, 115. (d) Lichtenhan, J. D.; Noel, C. J.; Bolf, A. G.; Ruth, P. N. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 3. (e) Sellinger, A.; Laine, R. M. *Chem. Mater.* **1996**, *8*, 1592. (f) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristo, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380. (g) Hoebbel, D.; Pitsch, I.; Heidemann, D.; Jancke, H.; Hiller, W. *Z. Anorg. Allg. Chem.* **1990**, *583*, 133. (h) Hoebbel, D.; Pitsch, I.; Heidemann, D. *Z. Anorg. Allg. Chem.* **1991**, *592*, 207. (i) Agaskar, P. A. *J. Chem. Soc., Chem. Commun.* **1992**, 1024. (j) Agaskar, P. A. *Colloids Surf.* **1992**, *63*, 131. (k) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; Barranco, M.; Losada, J. *Appl. Organomet. Chem.* **1999**, *13*, 245. (l) Hasegawa, I.; Nakane, Y.; Takayama, T. *Appl. Organomet. Chem.* **1999**, *13*, 272. (m) Hasegawa, I. *J. Sol−Gel Sci. Technol.* **1995**, *5*, 93. (n) Mehl, G. H.; Saez, I. M. *Appl. Organomet. Chem.* **1999**, *13*, 261. (o) Gravel, M.-C.; Zhang, C.; Dinderman, M.; Laine, R. M. *Appl. Organomet. Chem.* **1999**, *13*, 336. (p) Shockey, E. G.; Bolf, A. G.; Jones, P. F.; Schwab, J. J.; Chaffee, K. P.; Haddad, T. S.; Lichtenhan, J. D. *Appl. Organomet. Chem.* **1999**, *13*, 311.

(27) (a) Ribot, F.; Eychenne-Baron, C.; Banse, F.; Sanchez, C. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 43. (b) Eychenne-Baron, C.; Ribot, F.; Sanchez, C. *J. Organomet. Chem.*, **1998**, *567*, 137. (c) Ribot, F.; Eychenne-Baron, C.; Sanchez, C. *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 29. (d) Banse, F.; Ribot, F.; Tolédano, P.; Maquet, J.; Sanchez, C. *Inorg. Chem.* **1995**, *34*, 6371. (e) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190. (f) Dakternieks, D.; Zhu, H.; Tiekink, E. R. T.; Colton, R. J. *J. Organomet. Chem.* **1994**, *476*, 33. (g) Jaumier, P.; Jousseaume, B.; Lahcini, M.; Ribot, F.; Sanchez, C. *Chem. Commun.* **1998**, 369. (h) Puff, H.; Reuter, H. *J. Organomet. Chem.* **1989**, *373*, 173. (i) Eychenne-Baron, C.; Ribot, F.; Steunou, N.; Sanchez, C.; Fayon, F.; Biesemans, M.; Martins, J. C., Willem, R. *Organometallics* **2000**, *19*, 1940. (j) Beckmann, J.; Jurkshat, K.; Kaltenbrunner, U.; Rabe, S.; Schürmann, M.; Dakternieks, D.; Duthie, A.; Müller, D. *Organometallics* **2000**, *19*, 4887.

(28) (a) Hubert-Pfalzgraf, L.; Abada, V.; Halut, S.; Rozière, J. *Polyhedron* **1997**, *16*, 581. (b) Kickelbick, G., Schubert, U. *Chem. Ber./Recl.* **1997**, *130*, 473. (c) Kickelbick, G., Schubert, U. *J. Chem. Soc., Dalton Trans.* **1999**, *1301*. (d) Sanchez, C.; In, M.; Tolédano, P.; Griesmar, P. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 669.

(29) Ribot, F.; Banse, F.; Diter, F.; Sanchez, C. *New J. Chem.* **1995**, *19*, 1145.

(30) Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. *Macromolecules* **1993**, *26*, 2141.

(31) Mantz, R. A.; Jones, P. F.; Chaffee, K. P.; Lichtenhan, J. D.; Gilman, J. W.; Ismail, I. M. K.; Burmeister, M. J. *Chem. Mater.* **1995**, *8*, 1250.

(32) Gilman, J. W.; Schlitzer, D. S.; Lichtenhan, J. D. *J. Appl. Polym. Sci.* **1996**, *60*, 591.

(33) Haddad, T. S.; Lichtenhan, J. D. *J. Inorg. Organomet. Polym.* **1995**, *5*, 237.

(34) Saegusa, T.; Chujo, Y. *Polym. Prepr.* **1989**, *1*, 39.

(35) (a) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromolecules* **1995**, *28*, 8435. (b) Moore, A. R.; Kwen, H.; Beatty; A. M.; Maatta, E. A. *Chem. Commun.* **2000**, 1793.

(36) a) Voronkov, M. G.; Lavrent′yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199. (b) Sellinger, A.; Laine, R. *Chem. Mater.* **1996**, *8*, 1592.

(37) Larson, K. *Ark. Kemi* **1960**, *16*, 215.

(38) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741.

(39) (a) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313. (b) Brown, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 4317. (c) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526. (d) Feher, F. J.; Terroba, R.; Ziller, J. W. *Chem. Commun.* **1999**, 2309.

(40) Schwab, J. J., Lichtenhan, J. D. *Appl. Organomet. Chem.* **1998**, *12*, 707.

(41) (a) Feher, F. J.; Lücke, S.; Schwab, J. J.; Lichtenhan, J. D.; Phillips, S.; Lee, A. *Polym. Prepr.* **2000**, *41*, 526. (b) Haddad, T. S.; Lee, A.; Mather, P. T.; Phillips, S. H. *Polym. Prepr.* **2000**, *41*, 584.

(42) (a) Mather, P. T.; Jeon, H. G.; Romo-Uribe, A.; Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1999**, *32*, 1194. (b) Haddad, T. S.; Mather, P. T.; Jeon, H. G.; Chun, S. B.; Phillips, S. H. *Mater. Res. Soc. Symp. Proc.* **2000**, *628*, CC2.6. (c) Mather, P. T.; Jeon, H. G.; Haddad, T. S. *Polym. Prepr.* **2000**, *41*, 528. (d) Bharadwaj, R. K.; Berry, R. J.; Famer, B. L. *Polym.* **2000**, *41*, 7209. (e) Bharadwaj, R. K.; Berry, R. J.; Famer, B. L. *Polym. Prepr.* **2000**, *41*, 530.

(43) Agaskar, P. A. *Inorg. Chem.* **1991**, *30*, 2707.

(44) (a) Brown, J. F.; Vogt, L. H.; Prescott, P. I. *J. Am. Chem. Soc.* **1964**, *86*, 1120. (b) Martynova, T. N.; Chupakhina, T. I. *J. Organomet. Chem.* **1988**, *345*, 11. (c) Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *373*, 153. (d) Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *379*, 33. (e) Hambley, T. W.; Maschmeyer, T.; Masters, A. F. *Appl. Organomet. Chem.* **1992**, *6*, 253. (f) Tacke, T.; Lopez-Mras, A.;

Sheldrick, W. S.; Sebald, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 347. (g) Calzaferri, G.; Marcolli, C.; Imhof, R.; Törnroos, K. W. *J. Chem. Soc., Dalton Trans.* **1996**, 3313.

(45) (a) Vogt, L. H.; Brown, J. F. *Inorg. Chem.* **1963**, *2*, 189. (b) Brown, J. F.; Vogt, L. H.; Prescott, P. I. *J. Am. Chem. Soc.* **1964**, *86*, 1120. (c) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.

(46) (a) Hoebbel, D.; Wieker, W. *Z. Anorg. Allg. Chem.* **1971**, *384*, 43. (b) Hoebbel, D.; Wieker, W.; Franke, P.; Otto, A. *Z. Anorg. Allg. Chem.* **1975**, *418*, 35. (c) Hoebbel, D.; Garzo, G.; Engelhardt, G.; Jancke, H.; Wieker, W. *Z. Anorg. Allg. Chem.* **1976**, *424*, 115. (d) Hoebbel, D.; Garzo, G.; Engelhardt, G.; Ebert, R.; Lippmaa, E.; Alla, M. *Z. Anorg. Allg. Chem.* **1980**, *465*, 15. (e) Smolin, Y. I.; Shepelev, Y. F.; Ershov, A. S.; Hoebbel, D.; Wieker, W. *Sov. Phys. Crystallogr.* **1984**, *29*, 421. (f) Groenen, E. J. J.; Kortbeek, A. G. T. G.; Mackay, M.; Sudmeijer, O. *Zeolites* **1986**, *6*, 403. (g) Hasegawa, I.; Sakka, S.; Sugahara, Y.; Kuroda, K.; Kato, C. *J. Chem. Soc., Chem. Commun.* **1989**, 208.

(47) (a) Hoebbel, D.; Pitsch, I.; Grimmer, A. R.; Jancke, H.; Hiller, W.; Harris, R. K. *Z. Chem.* **1989**, *29*, 260. (b) Hoebbel, D.; Pitsch, I.; Reiher, T.; Hiller, W.; Jancke, H.; Müller, D. *Z. Anorg. Allg. Chem.* **1989**, *576*, 160. (c) Agaskar, P. A. *Inorg. Chem.* **1990**, *29*, 1603. (d) Hasegawa, I.; Motojima, S. *J. Organomet. Chem.* **1992**, *441*, 373. (e) Hasegawa, I.; Ishida, M.; Motojima, S. *Synth. React. Inorg.−Org. Chem.* **1994**, *24*, 1099.

(48) Tsuchida, A.; Bolln, C.; Sernetz, F. G.; Frey, H.; Mülhaupt, R. *Macromolecules* **1997**, *30*, 2818.

(49) Zhang, C.; Laine, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 6979.

(50) Lee, A.; Lichtenhan, J. D. *Macromolecules* **1998**, *31*, 4970.

(51) (a) Pyun, J.; Miller, P. J.; Kickelbick, G.; Matyjaszewski, K.; Scwhab, J. J.; Lichtenhan, J. D. *Polym. Prepr.* **1999**, *40*, 454. (b) Pyun, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 217. (c) Pyun, J.; Miller, P. J.; Matyjaszewski, K. *Polym. Prepr.* **2000**, *41*, 536. (d) Mather P. T.; Chun, S. B.; Pyun, J.; Matyjaszewski, K.; Jeon, H. G. *Polym. Prepr.* **2000**, *41*, 582.

(52) (a) Fu, B. X.; Hsiao, B. S.; Pagola, S.; Stephens, P.; White, H.; Rafailovich, M.; Sokolov, J.; Mather, P. T.; Jeon, H. G.; Phillips, S.; Lichtenhan, J. D.; Schwab, J. *Polymer* **2001**, *42*, 599. (b) Fu, B. X.; Zhang, W.; Hsiao, B. S.; Johanson, G.; Sauer, B. B.; Phillips, S.; Blanski, R.; Rafailovich, M.; Sokolov, J. *Polym. Prepr.* **2000**, *41*, 587. (c) Schwab, J. J.; Lichtenhan, J. D.; Chaffee, K. P.; Mather, P. T.; Romo-Uribe, A. *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 21.

(53) Kabayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1998**, 763.

(54) Auner, N.; Bats, J. W., Katsoulis, D. E.; Suto, M.; Tecklenburg, R. E.; Zank, G. A. *Chem. Mater.* **2000**, *12*, 3418.

(55) Agaskar, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 6858.

(56) Morán, M.; Casado, C. M.; Cuadrado, I.; Losada, J. *Organometallics* **1993**, *12*, 4327.

(57) Laine, R.; Choi, J.; Lee, I. *Adv. Mater.* **2001**, *13*, 800.

(58) (a) Blanski, R. L.; Phillips, S. H.; Chaffee, K.; Lichtenhan, J. D.; Lee, A.; Geng, H. P. *Polym. Prepr.* **2000**, *41*, 585. (b) Blanski, R. L.; Phillips, S. H.; Chaffee, K.; Lichtenhan, J. D.; Lee, A.; Geng, H. P. *Mater. Res. Soc. Symp. Proc.* **2000**, *628*, CC6.27.

(59) Ribot, F.; Minoux, D.; Sanchez, C. *Mater. Res. Soc. Symp. Proc.* **2000**, *628*, CC2.2.

(60) (a) Jousseaume, B.; Lahcini, M.; Rascle, M.-C.; Ribot, F.; Sanchez, C. *Organometallics* **1995**, *14*, 685. (b) Ribot, F.; Banse, F.; Sanchez, C. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 121.

(61) (a) Ribot, F.; Banse, F.; Sanchez, C.; Lahcini, M.; Jousseaume, B. *J. Sol−Gel Sci. Techn.* **1997**, *8*, 529. (b) Angiolini, L.; Caretti, D.; Carlini, C.; De Vito, R.; Niesel, F.; Salatelli, E.; Ribot, F.; Sanchez, C. *J. Inorg. Organomet. Polym.* **1998**, *7*, 151.

(62) Veautier, D.; Ribot, F.; Lalot, T.; Sanchez, C. Unpublished results.

(63) (a) Mosset, A.; Galy, J. *C. R. Acad. Sci. Paris, Sér. II* **1988**, *307*, 1647. (b) Schmid, R.; Mosset, A.; Galy, J. *J. Chem. Soc., Dalton Trans.* **1991**, 1999. (c) Gautier-Luneau, I.; Mosset, A.; Galy, J. *Z. Kristallogr.* **1987**, *180*, 83.

(64) Doeuff, S.; Dromzee, Y.; Taulelle, F.; Sanchez, C. *Inorg. Chem.***1989**, *28*, 4439. (b) Doeuff, S.; Dromzee, Y.; Sanchez, C. *C. R. Acad. Sci. Paris, Sér. II* **1989**, *308*, 1409. (c) Steunou, N.; Robert, F.; Boubekeur, K.; Ribot, F.; Sanchez, C. *Inorg. Chim. Acta* **1998**, *279*, 144.

(65) Kickelbick, G.; Schubert, U. *Eur. J. Inorg. Chem.* **1998**, *159*, 9.

(66) (a) Tolédano, P.; In, M.; Sanchez, C. *C. R. Acad. Sci. Paris, Sér. II* **1990**, *311*, 1161. (b) Tolédano, P.; In, M.; Sanchez, C. *C. R. Acad. Sci. Paris, Sér. II* **1991**, *313*, 1247. (c) Tolédano, P.; Ribot, F.; Sanchez, C. *C. R. Acad. Sci. Paris, Sér. II* **1990**, *311*, 1315.

(67) Morosin, B. *Acta Crystallogr. B* **1997**, *33*, 303.

(68) Watenpaugh, K.; Caughlan, C. N. *Chem. Commun.* **1967**, 76.

(69) Barkley, J. V.; Cannadine, J. C.; Hannaford, I.; Harding, M. M.; Steiner, A.; Tallon, J.; Whyman, R. *Chem. Commun.* **1997**, 1653.

(70) Laaziz, I.; Larbot, A.; Guizard, C.; Durand, J.; Cot, L.; Joffre, J. *Acta Crystallogr. C* **1990**, *46*, 2332.

(71) (a) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W. *J. Am. Chem. Soc.* **1993,** *115*, 8469. (b) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W.; Rosenberg, F. S. *J. Am. Chem. Soc.* **1991**, *113*, 8190. (c) Day, V. W.; Eberspacher, T. A.; Chen, Y.; Hao, J.; Klemperer, W. G. *Inorg. Chim. Acta.* **1995**, *229*, 391. (d) Campana, C. F.; Chen, Y.; Day, V. W.; Klemperer, W. G.; Sparks, R. A. *J. Chem. Soc., Dalton Trans.* **1996**, 691.

(72) (a) Boyle, T. J.; Tyner, R. P.; Alam, T. M.; Scott, B. L.; Ziller, J. W.; Potter, J. B., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 12104. (b) Boyle, T. J.; Alam, T. M.; Tafoya, C. J.; Mechenbier, E. R.; Ziller, J. W. *Inorg. Chem.* **1999**, *38*, 2422.

(73) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969.

(74) Vioux, A.; Leclerq, D. *Heterog. Chem. Rev.* **1996**, *3*, 65.

(75) (a) Steunou, N.; Ribot, F.; Boubekeur, K.; Maquet, J.; Sanchez, C. *New J. Chem.* **1999**, *23*, 1079. (b) Goel, S. C.; Chiang, M. Y.; Gibbons, P. C.; Buhro, W. E. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 3.

(76) Wang, R.; Carducci, M.; Zheng, Z. *Inorg. Chem.* **2000**, *39*, 1836.

(77) Hubert-Pfalzgraf, L. G.; Pajot, N.; Papiernik, R.; Parraud, S. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 137.

(78) (a) Trimmel, G.; Fratzl, P.; Schubert, U. *Chem. Mater.* **2000**, *12*, 602. (b) Schubert, U.; Trimmel, G.; Moraru, B.; Tesch, W.; Fratzl, P.; Gross, S.; Kickelbick, G.; Hüsing, N. *Mater. Res. Soc. Symp. Proc.* **2000**, *628*, CC2.3.

(79) Katz, H. E.; Schilling, M. L.; Stein, S. M.; Hutton, R. S.; Taylor, G. M. *Chem. Mater.* **1995**, *7*, 1534.

(80) Chen, Y. W.; Klemperer, W. G.; Park, C. W. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 57.

(81) Scolan, E.; Magnenet, C; Massiot, D.; Sanchez, C. *J. Mater. Chem.* **1999**, *9*, 2467.

(82) Soler-Illia, G. J. A. A.; Scolan, E.; Louis, A.; Albouy, P. A.; Sanchez, C. *New J. Chem.* **2001**, *25*, 156.

(83) Steunou, N.; Sanchez, C.; Florian, P.; Förster, S.; Göltner C.; Antonietti, M. *Proc. Am. Ceram. Soc.* **2000**, in press.

(84) (a) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 4145. (b) Svensson, M.; Alexandridis, P.; Linse, P. *Macromolecules* **1999**, *32*, 637. (c) Holmqvist, P.; Alexandridis, P.; Lindmann, B. *Langmuir* **1997**, *13*, 2471.

(85) Soler-Illia, G. J. A. A.; Sanchez, C. *New J. Chem.* **2000**, *24*, 493.

(86) Sadakane, M.; Steckhan, E., *Chem. Rev.* **1998**, *98*, 219.

(87) Rhule, J. T.; Hill, C. L., Deborah A. J. *Chem. Rev.* **1998**, *98*, 327.

(88) Yamase, T. *Chem. Rev.* **1998**, *98*, 307.

(89) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 271.

(90) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(91) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359.

(92) (a) Freund, M. S.; Karp, C.; Lewis, N. S. *Inorg. Chim. Acta* **1995**, *240*, 447. (b) Otero, T. F.; Cheng, S. A.; Huerta, F. *J. Phys. Chem. B* **2000**, *104*, 10522. (c) Otero, T. F.; Cheng, S. A.; Alonso, D.; Huerta, F. *J. Phys. Chem. B* **2000**, *104*, 10528.

(93) (a) Clemente-Leon, M.; Coronado, E.; Galan-Mascaros, J. R.; Gimenez-Saiz, C.; Gomez-Garcia, C. J.; Fernandez-Otero, T. *J. Mater. Chem.* **1998**, *8*, 309. (b) Coronado, E.; Clemente-Leon, M.; Galan-Mascaros, J. R.; Gimenez-Saiz, C.; Gomez-Garcia, C. J.; Martinez-Ferrero, E. *J. Chem. Soc., Dalton Trans.* **2000**, 3955.

(94) Closs, F.; Albert, B.; Wienand, H. European Patent EP 619346 A1, 1994.

(95) (a) Orel, B.; Lavrencic-Stangar, U.; Hutchins, M. G.; Kalcher, K. *J. Non-Cryst. Solids* **1994**, *175*, 251. (b) Nakajima, M.; Okanoe, E.; Mogami, T. Japanese Patent JP 62061048 A2, 1987. (c) Guo, Y.; Wang, Y.; Hu, C.; Wang, Y.; Wang, E. *Chem. Mater.* **2000**, *12*, 3501. (d) Polarz, S.; Smarsly, B.; Göltner, C.; Antonietti, M. *Adv. Mater.* **2000**, *12*, 1503. (e) Sang, K. Y.; Maier, J. *Chem. Mater.* **1999**, *11*, 1644.

(96) (a) Stein, A.; Fendorf, M.; Jarvie, T. P.; Mueller, K. T.; Benesi, A. J.; Mallouk, T. E. *Chem. Mater***. 1995**, *7*, 304. (b) Holland, B. T.; Isbester, P. K.; Munson, E. J.; Stein, A. *Mater. Res. Bull.* **1999**, *34*, 471.

(97) (a) Clemente-Leon, M.; Mingotaud, C.; Agricole, B.; Gomez-Garcia, C. J.; Coronado, E.; Delhaès, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1114. (b) Tang, Z.; Liu, S.; Wang, E.; Dong, S.; Wang, E. *Langmuir* **2000**, *16*, 5806.

(98) Caruso, F.; Kurthu, D. G.; Volkmer, D.; Koop, M. J.; Müller, A. *Langmuir* **1998**, *14*, 3462.

(99) Cheng, L.; Niu, L.; Gong, J.; Dong, S. *Chem. Mater.* **1999**, *11*, 1465.

(100) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77.

(101) Zeng, H.; Newkome, G. R.; Hill, C. L. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1771.

(102) Stark, J. L.; Rheingold, A. L.; Maatta, E. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1165.

(103) (a) Xin, F.; Pope, M. T. *Inorg. Chem.* **1996**, *35*, 5693. (b) Sazani, G.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 939.

(104) Mayer, C. R.; Cabuil, V.; Lalot, T.; Thouvenot, R. *Polyoxometalate Chemistry for Nanocomposite Design*; Kluwer Academic Publishers: Dordrecht, The Netherlands, manuscript submitted.

(105) Mayer, C. R.; Cabuil, V.; Lalot, T.; Thouvenot, R. *Angew. Chem.* **1999**, *38*, 3672.

(106) Mayer, C. R.; Cabuil, V.; Lalot, T.; Thouvenot, R. *Adv. Mater.* **2000**, *12*, 417.

(107) Bacri, J. C.; Perzynski, R.; Salin, D.; Cabuil, V.; Massart, R. *J. Magn. Magn. Mater.* **1990**, *85*, 27.

(108) *Scientific and Clinical Applications of Magnetic Carriers*; Häfeli, U., Schütt, W., Teller, J., Zborowski, M., Eds.; Plenum Press: New York, 1997.

(109) (a) Boennemann, H.; Brijoux, W.; Brinkmann, R.; Dingus, E.; Jonssen, T.; Korall, B. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1312. (b) Reetz, M. T.; Waldvogel, S. R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 865.

(110) Matting, A.; Brockmann, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 598.

(111) (a) *Chemistry of Advanced Materials: An Overview*; Interrante, L. V., Hampden-Smith, M., Eds.; Wiley-VCH: New York, 1998. (b) *Nanomaterials, Synthesis, Properties and Applications*; Edelstein, A. S., Cammarata, R. C., Eds.; Institute of Physics Publishing: Philadelphia, PA, 1996.

(112) (a) Bradley, J. S., Chaudret, B., Eds. *Nanoparticles, Part I.* Special Issue of *New J. Chem*. **1998**, *22* (7). (b) Bradley, J. S., Chaudret, B., Eds. *Nanoparticles, Part II.* Special Issue of *New J. Chem*. **1998**, *22* (11). (c) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.

(113) La Mer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4847.

(114) (a) Sanchez, C.; In, M.; Henry, M.; Chatry, M. Brevet Français no. 11633, Sep 20, 1991. (b) Chatry, M.; Henry, M.; Sanchez, C.; In, M. WO 9305875. (c) Chatry, M.; In, M.; Henry, M.; Sanchez, C.; Livage, J. *J. Sol−Gel Sci. Technol.* **1994**, *2*, 233. (d) Scolan, E.; Sanchez, C. *Chem. Mater.* **1998**, *10*, 3217. (e) Cellot, A.; de Monredon, S.; Delattre, L.; Guéneau, L.; Ribot, F.; Sanchez, C. Presented at Nanostructured Materials Made from Self-Assembled Molecules and Particles, Hindås, Sweden, Jan 7−10, 2001.

(115) Herron, N.; Wang, Y.; Eckert, H. *J. Am. Chem. Soc.* **1990**, *112*, 1322.

(116) (a) Pileni, M. P. *Supramol. Sci.* **1998**, *5*, 321. (b) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.

(117) Jolivet, J.-P. *Metal Oxide Chemistry and Synthesis: From Solution to Solid State*; Wiley-VCH Publishers: New York, 2000.

(118) Vayssières, L.; Chanéac, C.; Tronc, E.; Jolivet, J.-P. *J. Colloid Interface Sci.* **1998**, *205*, 205.

(119) Szabó D. V.; Vollath D. *Adv. Mater.* **1999**, *11*, 1313.

(120) Wang, Z. L. *Adv. Mater.* **1998**, *10*, 13.

(121) See, for example: (a) Rao, C. N. R.; Kulkarni, G. U.; Thomas, P. J.; Edwards, P. P. *Chem. Soc. Rev.* **2000**, *29*, 17 and references therein. (b) Matijevic, E. In *Fine Particle Science and Technology*; Pellizzetti, E., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996; p 1. (c) Goia, D. V.; Matijevic, E. *New J. Chem.* **1998**, *22*, 1203. (d) For a comprehensive review of synthesis methods and properties, see also: *Nanophase Materials: Synthesis—Properties—Applications*; Hadjipanayis, G. C., Siegel, R. W., Eds.; Nato ASI Series E, Applied Sciences; NATO Advanced Studies Institute: Alphen aan den Rijn, The Netherlands, 1994; Vol. 260.

(122) Bee, A.; Massart, R.; Neveu, S. *J. Magn. Magn. Mater.* **1995**, *149*, 6.

(123) Reimers, G. W.; Khalafalla, S. E. U.S. Bureau of Mines, Technology Progress Report; U.S. Bureau of Mines, Department of the Interior, U.S. Government Printing Office: Washington, D.C., 1972; p 59.

(124) Wagener, M.; Günther, B.; Blums, E. *J. Magn. Magn. Mater.* **1999**, *201*, 18.

(125) Kerasep nanofiltering membranes produced by Orelis-Rhodia, Boulogne, France.

(126) (a) Roux, S.; Audebert, P.; Pagetti, J.; Roche, M. *New J. Chem.* **2000**, *24*, 877. (b) Roux, S.; Audebert, P.; Pagetti, J.; Roche, M. *New J. Chem.* **2000**, *24*, 885.

(127) Yu, D.; Belyakpva, L. A. *React. Kinet. Catal. Lett.* **1993**, *50*, 333.

(128) Zaitseva, G. N.; Strelko, V. V. In *Fundamental and Applied Aspects of Chemically Modified Surfaces*; Blitz, J., Little, C. B., Eds.; Springer-Verlag: New York, 1999.

(129) Beck, C.; Härtl, W.; Hempelmann, R. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1297.

(130) Brunel, D. *Microporous Mesoporous Mater.* **1998**, *27*, 329.

(131) Such Degussa products include Aerosil fumed silica, which can be custom-functionalized, and Ultrasil reinforced silica.

(132) See the Clariant Web page http://www.clariant.com.

(133) Abboud, M.; Turener, M.; Duguet, E.; Fontanille, M. *J. Mater. Chem.* **1997**, *7*, 1527.

(134) Stein, A.; Melde, B. J.; Schroden, R. *Adv. Mater.* **2000**, *12*, 1403.

(135) Bacri, J.-C.; Perzynski, R.; Salin, D.; Cabuil, V.; Massart, R. *J. Magn. Magn. Mater***.** **1990**, *85*, 27.

(136) Gao, Y.; Sun, R.; Zhang, Z.; Xue, Q. *Mater. Sci. Eng. A* **2000**,*149*, 286

(137) (a) O′Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (c) Nazeeruddin, M. D. K.; Humphry-Baker, R.; Grätzel, M.; Murrer, B. A. *Chem. Commun.* **1998**, 719. (d) Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 4490. (e) Wang, Z.-S.; Huang, C.-H.; Zhang, B.-W.; Hou, Y.-J.; Xie, P. H.; Qian, H.-J.; Ibrahim, K. *New J. Chem.* **2000**, *24*, 567.

(138) (a) Caris, C. H. M.; van Elven, L. P. M.; van Herk, A. M.; German, A. L. *British Polymer Journal* **1989**, *21*, 133. (b) For a review, see: Hoffman-Caris, C. H. M. *New J. Chem.* **1994**, *18*, 1087.

(139) Brust M.; Walker M.; Bethell D.; Schiffrin D. J.; Whyman R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

(140) Dassenoy, F.; Philippot, K.; Ould Ely, T.; Amiens, C.; Lecante, P.; Snoeck, E.; Mosset, A.; Casanove, M.-J.; Chaudret, B. *New J. Chem.* **1998**, *22*, 703.

(141) Roger, J.; Pons, J.-N.; Massart, R.; Halbreicht, A.; Bacri, J.-C. *Eur. Phys. J.* **1999**, *AP 5*, 321.

(142) Chan, W.; Nie, S. *Science* **1998**, 281, 2016.

(143) Zanchet, D.; Micheel, C.; Parak, W.; Gerion, D.; Avistos, A. P. *Nano Lett.* **2001**, *1*, 32.

(144) (a) Boal, A.; Rotello, V. *J. Am. Chem. Soc.* **1999**, *121*, 4914. (b) Boal, A.; Rotello, V. *J. Am. Chem. Soc.* **2000**, *122*, 734.

(145) Labande, A.; Astruc, D. *Chem. Commun.* **2000**, 1007.

(146) Boal, A.; Rotello, V. *Langmuir* **2000**, *16*, 9527.

(147) Brust, M.; Bethell, D.; Schiffrin, D.; Kiely, C. *Adv. Mater.* **1995**, *7*, 795.

(148) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science*, **1996**, *273*, 1690.

(149) Novak, J. P.; Brousseau, L. C., III; Vance, F. W.; Johnson, R. C.; Lemon, B. I.; Hupp, J. T.; Feldheim, D. L. *J. Am. Chem. Soc.* **2000**, *122*, 12029.

(150) Fabre, P.; Casagrande, C.; Veyssié, M.; Cabuil, V.; Massart, R. *Phys. Rev. Lett.* **1990**, *64*, 539.

(151) Dubois, E.; Fabre, P.; Ramos, L. *J. Chem. Phys.* **1996**, *100*, 4533.

(152) Wang, W.; Efrima, S.; Regev, O. *J. Phys. Chem. B* **1999**, *103*, 5613.

(153) (a) Braun, P. V.; Osenar, P.; Stupp, S. I.; *Nature* **1996**, *380*, 325. (b) Braun, P. V.; Stupp, S. I. *Mater. Res. Bull.* **1997**, *34*, 463. (c) Tohver, V.; Braun, P. V.; Pralle, M. U.; Stupp, S. I. *Chem. Mater.* **1997**, *9*, 1495.

(154) Tronc, E.; Prené, P.; Jolivet, J.-P.; d'Orazio, F.; Lucari, F.; Fiorani, D.; Godinho, M.; Cherkaoui, R.; Nogues, M.; Dormann, J. L. *Hyperfine Interact.* **1995**, *95*, 129.

(155) Chanéac, C.; Tronc, E.; Jolivet, J.-P. *J. Mater. Chem.* **1996**, *6*, 1905.

(156) Yanagihara, N.; Uchida, K.; Wakabayashi, M.; Uetake, Y.; Hara, T. *Langmuir* **1999**, *15*, 3038.

(157) Sidorov, S. N.; Bronstein, L. M.; Davankov, V. A.; Tsyurupa, M. P.; Solodovnikov, S. P.; Valetsky, P. M. *Chem. Mater.* **1999**, *11*, 3210.

(158) Castro, C.; Ramos, J.; Millan, A.; Gonzalez-Calbet, J.; Palacio, F. *Chem. Mater.* **2000**, *12*, 3681.

(159) Yanase, N.; Noguchi, H.; Asakura, T.; Suzuta, T. *J. Appl. Polym. Sci.* **1993**, *50*, 765.

(160) Dresco, P.; Zaitsev, V.; Gambino, R.; Chu, B. *Langmuir* **1999**, *15*, 1945.

(161) Shen, L.; Stachowiak, A.; Hatton, T.; Laibinis, P. *Langmuir* **2000**, *16*, 9907.

(162) Underhill, R.; Liu, G. *Chem. Mater.* **2000**, *12*, 2082.

(163) Hirai, T.; Watanabe, T.; Komasawa, I. *J. Phys. Chem. B* **2000**, *104*, 8962.

(164) Pavel, F.; Mackay, R. *Langmuir* **2000**, *16*, 8568.

(165) Lefébure, S.; Cabuil, V.; Ausséré, D.; Paris, F.; Gallot, Y.; Lauter-Pasyuk, V. *Prog. Colloid Polym. Sci.* **1998**, *110*, 94.

(166) Tsutsumi K.; Funaki, Y.; Hirokawa, Y.; Hashimoto, T. *Langmuir* **1999**, *15*, 5200.

(167) Hashimoto, T.; Harada, M.; Sakamoto, N. *Macromolecules* **1999**, *32*, 6867.

(168) Qi, L.; Cölfen, H.; Antonietti, M. *Nano Lett.* **2001**, *1*, 61.

(169) Bronstein, L.; Chernyshov, D.; Valetsky, P.; Wilder, E.; Spontak, R. *Langmuir* **2000**, *16*, 8221.

(170) For reviews concerning dendrimers, see, for example: (a) Crooks, R.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. *Acc. Chem. Res.* **2001**, *34*, 181 and references therein. (b) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A, III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (c) Chow, H. F.; Mong, T. K. K.; Nongrum, M. F.; Wan, C. W. *Tetrahedron* **1998**, *54*, 8543. (d) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 884. (e) Bosman, A. W.; Janssen, H. M.; Meijer, *E. W. Chem. Rev.* **1999**, *99*, 1665. (f) Majoral, J. P.; Caminade, A. M. *Chem. Rev.* **1999**, *99*, 845.

(171) Schmid, G.; Meyer-Zaika, W.; Pugin, R.; Sawitowski, T.; Majoral, J.-P.; Caminade, A.-M.; Turrin, C.-O. *Chem. Eur. J.* **2000**, *9*, 1693.

(172) Galow, T. H.; Boal, A. K.; Rotello, V. M. *Adv. Mater.* **2000**, *12*, 576.

(173) (a) Loweth, C. J.; Caldwell, W. B.; Peng, X. G.; Alivisatos, A. P.; Schultz, P. G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1808. (b) Alivisatos, A. P.; Johnsson, K. P.; Peng, X. G.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P.; Schultz, P. G. *Nature* **1996**, *382*, 607.

(174) (a) Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957. (b) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132.

(175) (a) Schmitt, J.; Decher, G.; Dressick, W. J.; Brandow, S. L.; Geer, R. E.; Shashidar, R.; Calvert, J. M. *Adv. Mater.* **1997**, *9*, 61. (b) Feldheim, D. L.; Grabar, K. C.; Natan, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118*, 7640. (c) Marinakos, S. M.; Novak, J. P.; Brosseau, L. C., III; House, A. B.; Edeki, M.; Feldhouse, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 8518. (d) Deki, S.; Sayo, K.; Fujita, T.; Yamada, A. *J. Mater. Chem.* **1999**, *9*, 943.

(176) (a) Crooks, R. M.; Chechik, V. *Langmuir* **1999**, *15*, 6364. (b) Zhao, L.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877.

(177) (a) Marguerettaz, X.; Merrins, A.; Fitmaurice, D. *J. Mater. Chem.* **1998**, *8*, 2157. (b) Connolly, S.; Nagaraja Rao, S.; Rizza, R.; Zaccheroni, N.; Fitzmaurice, D. *Coord. Chem. Rev.* **1999**, *185*−*86*, 277.

(178) Chemseddine, A.; Moritz, T. *Eur. J. Inorg. Chem.* **1999**, 235.

(179) Gole, A.; Sainkar, S. R.; Sasrey, M. *Chem. Mater.* **2000**, *12*, 1234.

(180) Blonder, R.; Sheeney, L.; Willner, I. *Chem. Commun.* **1998**, 1393.

(181) Patil, V.; Sastry, M. *Langmuir* **2000**, *16*, 2207.

(182) Hao, E.; Lian, T. *Chem. Mater.* **2000**, *12*, 3392.

(183) Brust, M.; Bethell, D.; Kiely, C.; Schiffrin, D. *Langmuir* **1998**, *14*, 5425

(184) Gittins, D.; Bethell, D.; Nichols, R.; Schiffrin, D. *Adv. Mater.* **1999**, *11*, 737.

(185) Braunstein, P.; Kormann, H.-P.; Meyer-Zaika, W.; Pugin, R.; Schmid, G. *Chem. Eur. J.* **2000**, *6*, 4637.

(186) Yonezawa, T.; Matsune, H.; Kunitake, T. *Chem. Mater.* **1999**, *11*, 33.

(187) Claus, P.; Brückner, A.; Mohr, C.; Hofmeister, H. *J. Am. Chem. Soc.* **2000**, *122*, 11430.

(188) Mamedov, A.; Ostrander, J.; Aliev, F.; Kotov, N. *Langmuir* **2000**, *16*, 3941.

(189) See, e.g.: Caruso, F. *Adv. Mater.* **2001**, *13*, 11.

(190) Rhodes, K. H.; Davis, S. A.; Caruso, F.; Zhang, B.; Mann, S. *Chem. Mater.* **2000**, *12*, 2832.

(191) (a) Imhof, A.; Pine, D. J. *Nature* **1997**, *389*, 948. (b) Wijnhoven, J. E. G.; Vos, W. L. *Science* **1998**, *281*, 802. (c) Holland, B. T.; Blanford, C. F.; Do, T.; Stein, A. *Chem. Mater.* **1999**, *11*, 795.

(192) *Biomimetic Materials Chemistry*; Mann, S., Ed.; VCH Publishers: New York, 1996.

(193) *Biomimétisme et Matériaux*; Sanchez, C., Ed.; Masson: Paris, 2001; Série Arago 25.

(194) Mann, S.; Ozin, G. A. *Nature* **1996**, *382*, 313.

(195) (a) Fendler, J. H. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 365. (b) Fendler, J. H. *Chem. Mater.* **1996**, *8*, 1616.

(196) Shenton, W.; Davis, S. A.; Mann S. *Adv. Mater.* **1999**, *11*, 449.

(197) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.

(198) Sapp, S. A.; Mitchell, D. T.; Martin, C. R. *Chem. Mater.* **1999**, *11*, 1183.

(199) Mann, S.; Shenton, W.; Li, M.; Conolly, S.; Fitzmaurice, D. *Adv. Mater.* **2000**, *12*, 147.

(200) Patolsky, F.; Ranjit, K.; Lichtenstein, A.; Wollner, I. *Chem. Commun.* **2000**, 1025.

(201) Dante, S.; Hou, Z.; Risbud, S.; Stroeve, P. *Langmuir* **1999**, *15*, 2176.

(202) Schnurr, J. M.; Price, R.; Schoen, P.; Yager, P.; Calvert, J. M.; Georger, J.; Singh, A. *Thin Solid Films* **1987**, *152*, 191.

(203) Davies, S. A.; Burkett, S. L.; Mendelson, N. H.; Mann, S. *Nature* **1997**, *385*, 420.

(204) Petit, L.; Sellier, E.; Duguet, E.; Ravaine, S.; Mingotaud, C. *J. Mater. Chem.* **2000**, *10*, 253.

CM011061E