Nanoporous materials: a good opportunity for nanosciences

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Abstract

This paper emphasizes the wide possibilities open to organometallic chemistry by the bottom-up approach for nanosciences. In this new field of research, organometallic chemistry and coordination chemistry are in position to play a very important role in the development of nanomaterials. At first, organometallic and coordination chemistries will be the mothers of plenty of nanotools, which are the elemental bricks of nanosciences. The nanomaterials are obtained from them either by inclusion in a matrix (Nanocomposites) or by grafting methods (grafted nanomaterials). However, the most exciting field of investigation are the nanostructured hybrid materials which permit to open new fields of investigation such as self-organization of organic moieties or the coordination chemistry in the solid. Some examples are given. Moreover, the organometallic chemistry performed on both the framework and the pores of the nanoporous solids obtained by sol-gel chemistry in the presence of structure directing agents is opening the way to smart materials. These materials will have the ability to couple interactively two different properties.
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1. Nanosciences – some generalities as a short introduction

Nanosciences represent certainly one of the most promising developments for chemistry [1–3]. In this field, the major challenge will be the control of physical or chemical properties from the nanometric scale (atomic or molecular). This paper will emphasize the contribution of Organometallic Chemistry [4–7] in this very promising scientific domain by using some of the possibilities open by nanoporous materials.

1.1. Which ways to nanosciences?

Two very different routes correspond to the field covered by nanosciences: the top-down and the bottom-up.

The TOP-DOWN concerns mainly the electronic domain. It is focused on the technologies which permit to reach the miniaturization of the microprocessors used in the electronic devices and particularly in the computers memories. The industry is now producing, in large scale, devices in which the memory unit is in the range of micrometer. Reaching 0.1 μ will be made in the near future certainly by extension of the technologies used today. Chemistry is not really involved in this part of nanosciences.

The bottom-up way concerns the possibility to build up devices (NANOMATERIALS) starting from NANOTOOLS, which correspond to nanometric size units. This approach is more convenient for chemistry since all the nanotools (nanometric size units) are corresponding to species well defined in chemistry: molecules, complexes, particles, clusters, aggregates, etc.

The synthesis of nanotools enhanced with well defined properties as well as the discovery of assembly methods
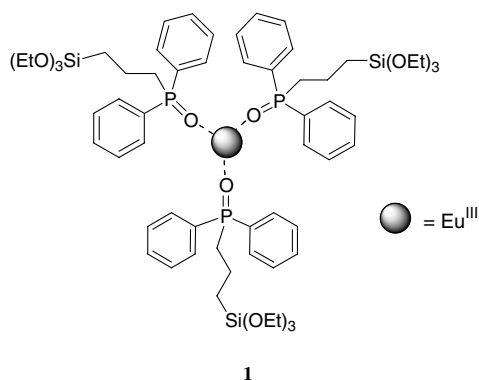
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permitting the transformation of nanotools into nanomaterials are just chemistry. Thus, chemistry will be a very important partner in the bottom-up way, since it has now a very good control of the synthesis in every field concerned (organic, inorganic, coordination, etc.) and it has succeeded to find many routes for assembling molecules, particles, like for instance, organic and inorganic polymerization or supramolecular self-assembling.

1.2. Nanotools

These make up the elementary bricks of the future materials. They can be a molecule, an assembly of molecules such as a cluster, a metallic nanoparticle or the elementary stage of an inorganic combination (oxide, sulphide, etc.). However, many of them will correspond to a specifically designed molecule for obtaining a desired property. This one can be physical (optical, magnetic, electric, etc.) or chemical (reactivity, catalysis, selective separation, etc.) but sometimes also mechanical applications can be designed. In the near future, bio applications will also certainly be developed. In all cases, the property must be precise, able to be measured, and controlled. *Nowadays, the synthesis of the nanotools cannot be just a single chemical target. It must be mainly designed for reaching a potential property.*

The degree and the precision reached by chemical synthesis permits one now to prepare any chemical unit conceived around a property, whatever is the field of chemistry. Wide perspectives are thus open to the chemist. It is important to point out that some very simple molecules are potentially available to make up nanotools. It is worth noting as examples the europium (III) complex **1**, which presents specific photoluminescent properties in the red [8]

Fig. 1. ORTEP view of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$.

The selective complexation of ions by using well designed ligands permits to obtain nanotools which are opening interesting perspectives for selective separation. Thus, the tetrakispropionamide-1,4,8,11-tetraazacyclotetradecane depicted below is a sequestrant for lead **2** [12] and the N-tetrapropionate-substituted tetraazacycloalkanes are sequestrant for uranides [13]

2

In the field of pure organic chemistry, a number of molecules exhibit very high non linear optic properties [14–18]. Some are very simple **3**. Some others are more sophisticated **4**

3 [14]

4 [15]

Finally, coordination chemistry was recently used for the preparation of metal nanoparticles, the synthesis of which is of fundamental importance for the develop-

1

In the field of magnetism, clusters, which exhibit unusual magnetic properties, have been synthesized [9]. As example, $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ [10,11] (Fig. 1) presents the properties of a single-molecule magnet with a $S = 10$ ground state.
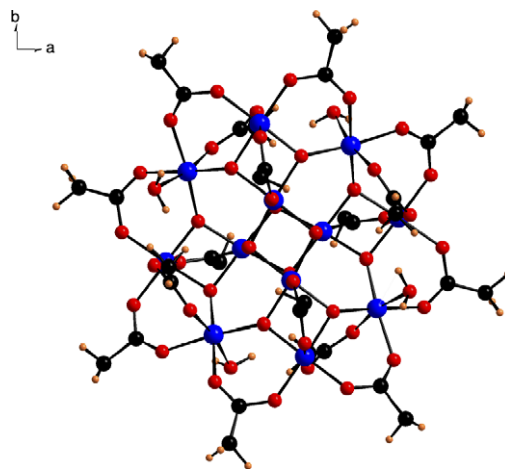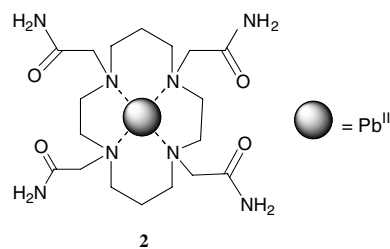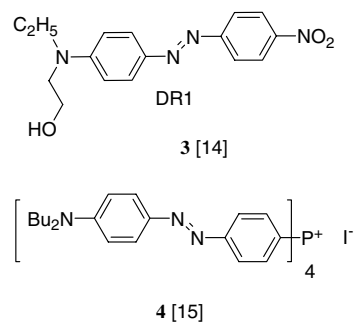
ment of novel technologies based on nanomaterials [19]. The procedure consists in performing the decomposition of a organometallic complex in the presence of groups which permit the controlled growing of the nanoparticules. Thus, the formation of unprecedented 2D and 3D superlatices of monodisperse cobalt nanorods was reported through the decomposition of $[Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})]$ in the presence of a mixture of hexadecylamine (HDA) and stearic acid [20]. Evidence for the self-organization of spherical particles prior to coalescence into nanorods was provided. The decomposition of $Fe[N(SiMe_3)_2]_2$ under a dihydrogen atmosphere in the presence of HDA and a long chain acid in various proportion produced monodisperse zerovalent iron nanoparticles [21].

These examples illustrate some possibilities offered by organometallic chemistry. It is important to point out that the perspectives are extremely wide, since most of the complexes of transition metal and lanthanides are connected with physical properties. The field open by the preparation of nanoparticles is also very wide and emerges on physical properties.

1.3. Nanomaterials by assembling nanotools

The synthesis and the study of nanotools enhanced with properties (physical or chemical) constitute the base to any research related to nanosciences. The study of the properties of nanotools [22] is a very important step for the knowledge of the possibilities that are open, taking into account the fact that the physical properties are highly dependent on the scale of observation, nanometric or micrometric. This part of research is closer to physics than to chemistry and many interesting studies have been developed for studying the physical properties of isolated nanotools using force field microscopy. These studies are very important as unexpected properties will be found, which may open new perspectives of scientific development.

It must however be pointed out that it is only a part of the target to reach nanomaterials and, in the long term, Smart materials. *The isolated Nanotool is not a material: in the absence of an assembly and structure, it will remain a laboratory curiosity: nanotools are only a step on the way to nanomaterials.*

Chemists have already discovered a large number of assembly methods and found effective organization schemes for independent molecules. In the scope of nanoscience, this chemistry must be adapted and extended. It will be also important to explore new chemical ways for assembling nanotools in order to obtain nanomaterials corresponding to devices such as coatings, fibers, matrixes or also solids with a controlled porosity.

2. General methods for access to nanomaterials: nanocomposites versus nanostructured materials

At the moment, the most used matrices are the inorganic ones, particularly silica obtained by sol–gel methodology.
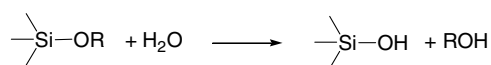
2.1. Inorganic polycondensation (a sol–gel type process)

Inorganic-polycondensation is known since Ebelman observed in the mid-1800s that the hydrolysis of tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) under acidic conditions yielded SiO_2 [23]. It is important to point out that this purely mineral synthesis is the sister of the organic polymerization. This hydrolytic polycondensation reaction [24] of a Si–OR bond corresponds to a nucleophilic substitution of the oxygen atom either of H_2O or a Si–OH bond on the metallic centre of another molecule (Scheme 1). These reactions lead to the formation of Si–O–Si bonds, the propagation of which results in oxide [25] formation by a kinetically controlled process [26]. Fig. 2 represents the details of the different stages leading to silica [27] starting from the hydrolysis of $Si(OR)_4$.
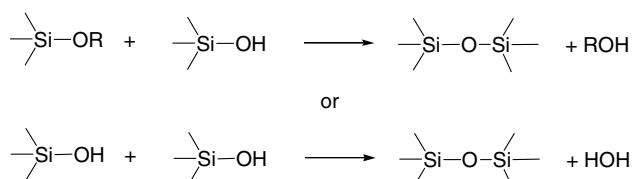
This way is a very convenient one for the preparation of nanomaterials since in one step it is possible to obtain a solid by passing through the tuneable colloidal sol (step 3), which opens the possibility to perform coatings and to obtain a fibber or a matrix.

This research field will be more developed in the following section since it represents a very efficient and very powerful tool for the chemist, making the material science compatible with many different aspects of chemistry that initially were separated: solid state chemistry, organic and inorganic chemistry, organometallic and coordination chemistry, macromolecular chemistry and also biochemical aspects. The terminology "chimie douce" [28] was introduced to emphasize the contrast with the usual method of solid-state chemistry requiring high temperature processes [29,30]. The

Hydrolysis of alkoxysilane function

$$\text{—Si—OR} + H_2O \longrightarrow \text{—Si—OH} + ROH$$

Polycondensation of silanols groups

$$\text{—Si—OR} + \text{—Si—OH} \longrightarrow \text{—Si—O—Si—} + ROH$$

or

$$\text{—Si—OH} + \text{—Si—OH} \longrightarrow \text{—Si—O—Si—} + HOH$$

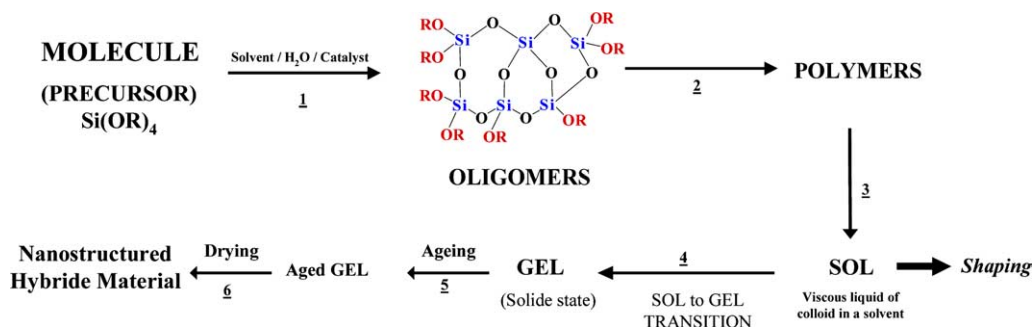Scheme 1. Hydrolysis and polycondensation of alkoxysilane.

Fig. 2. Chimie Douce [28]: inorganic polymerization of silica precursors.

materials prepared by the classical high temperature method are *thermodynamically controlled materials*. In contrast, the inorganic polymerization (sol–gel type process) leads to *kinetically controlled* solids [28]. These two ways do not give the same results. Thus, the route illustrated in Fig. 2, and readily extended to other solids than SiO_2 is not in competition with the classical thermal routes used in solid state chemistry: it corresponds to a molecular way for material science, leading to different kind of materials. Moreover, the kinetic control is a very powerful mean of design the solid since all the parameters which control the kinetic of the reaction (temperature, concentration of reagents, nature and concentration of catalyst, solvent drying methodologies, etc.) can be used for changing and optimising the texture of the solids (specific surface, pore diameters). This approach is similar to that adopted in molecular chemistry for optimising a reaction pathway.

2.2. Nanocomposites

Nanocomposites [31,32] are obtained by inclusion of nanotools in a matrix. They are biphasic materials as, it is possible to separate the nanotool from the matrix (organic or inorganic) by simple extraction procedures.

Many organic dyes such as rhodamines, pyranines or coumarines and NLO dyes have been embedded in sol–gel matrices. Interestingly, several studies have pointed the important role played by the dye–matrix interactions on the optical properties of these hybrid compounds. Thus, many studies show that the sol–gel matrix prevents the formation of rhodamine dimers, which is an obvious advantage as dimers are known to quench fluorescence [33,34]. Levy and Avnir also demonstrated the important role played by the dye–matrix interactions on the photochromic response of spiropyrans [35]. They studied the photochromism of spiropyrans trapped in sol–gel matrices synthesized by hydrolytic polymerization of $Si(OCH_3)_4$ (TMOS) or a mixture TMOS/polydimethylsiloxanes.
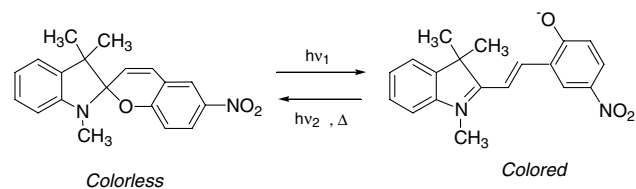

Scheme 2. Molecular structures of spiropyrans, as example of photochromic dye.

Upon irradiation, the colorless spiropyrans undergoes a heterolytic C–O ring cleavage, producing colored zwitterionic forms (Scheme 2). Under certain conditions, the stable forms in the dark are the colored ones. These can be bleached by UV irradiation, this process being termed "reverse photochromism". When spiropyrans are embedded in the silica-gel matrix a gradual change is observed from direct to "reverse photochromism" [36,37] along the gel–xerogel transformations. On the other hand, spiropyrans embedded in a hybrid network always exhibits direct photochromism. Interactions between the dye and the matrix are obviously responsible for such differences. Several authors introduced the hydrophobic/hydrophilic balance (HHB) of the hybrid matrix as an important factor.

2.3. Grafted materials

Grafted materials are obtained by anchoring of the nanotool on a solid. Therefore, they are monophasic as the nanotool is bound to the matrix by a covalent Si–C bond. The general route is illustrated in Scheme 3. It consists in anchorage a molecular precursor of type $R'Si(OR)_3$ to the silica matrix thanks to the SiOH bonds. As for nanocomposites, the choice of the matrix is depending on the application purposes. The matrixes can be an organic polymer or an inorganic solid, the most popular in the latter case being silica.

For lead separation, silica matrix is used in order to permit the regeneration of the material to use it again
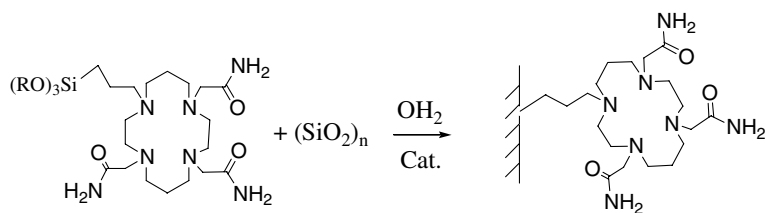
Scheme 3. Grafting of a lead-selective macrocyclic sequestering agent onto the surface of silica gel.

[12]. In contrast, in the treatment of nuclear wastages, grafting is performed on an organic polymer, which permits to concentrate the wastage in a minimal volume of storage after calcinations [38].

It is important to note that both kinds of nanocomposites materials or grafted nanomaterials are very convenient to obtain materials with a well defined property. This is, and it will be, a more and more popular approach to nanomaterials.
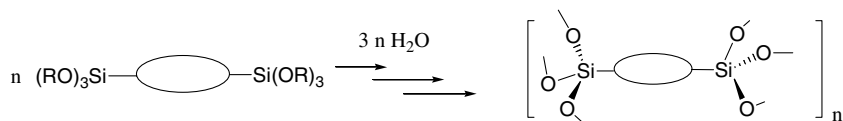
2.4. Nanostuctured hybrid materials: the first step to sophisticated nanomaterials

2.4.1. Nanostructured materials [38–40]

The general way to prepare the nanostructured materials consists in the hydrolysis and polycondensation of the nanotools bearing at least two $Si(OR)_3$ groups covalently attached to the organic group (Scheme 4). In such a case, the solids obtained are monophasic as the nanotool is chemically bound to the silica matrix.

A number of organic groups have been incorporated by this way in a silica matrix. The organic units are maintained in the solid without any change so that the materials exhibit the properties of the organic units. Among the numerous organic groups which have been silylated, some of them are given as examples in Scheme 5: **5** for electrochemical properties [41], **6** for non linear optical properties [42], **7** for chelating properties towards transition metal centres [43], **8** for photoluminescence [44], **9** for electroluminescent properties [45] and **10** as ruthenium complexes [46].

Scheme 4. Building up a silica matrix around a nanotool.
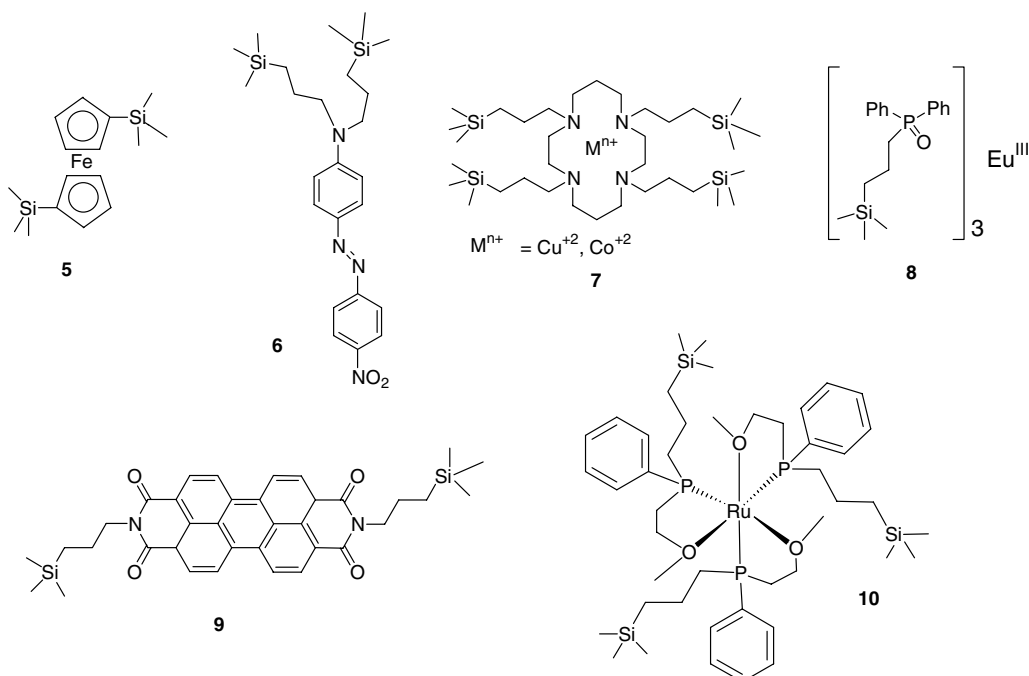
Scheme 5. Some examples of organic units included in silicon-based nanostructured hybrid materials.

This route illustrates the very rich potentialities opened up by organosilicon chemistry in the perspective of assembling Nanotools. Moreover, the formation of solid, which is kinetically controlled permits its tuneability by changing experimental conditions.

Besides the inclusion of the property of the nanotool, the nanostructured hybrid materials exhibit interesting characteristics, which could not be predicted. Two of them deserve to be mentioned: the self-organization of organic units on one side and on the other side, the coordination chemistry in the solid, which is connected with the organization of the solid.

2.4.2. Self-organization

Self-organization of bridged organosilica precursors $(MeO)_3Si–R–Si(OMe)_3$ has been evidenced during their hydrolysis and polycondensation by X-ray diffraction analysis [47]. The X-ray diffraction patterns of nanostructured materials $R[SiO_{1.5}]_n$ ($n \geqslant 2$) exhibit broad signals, the positions and intensities of which denote a short range nanometric scale organization. An organization at the meso and micrometric scale was revealed by their birefringence when observed in cross-polarized light. It was found that the rigidity of the organic groups leads to birefringent materials (rigid rod-like, planar rigid, twisted linear molecules (Scheme 6)). In some cases, the organization has been extended to the millimetric scale. In contrast, a flexible organic group such as alkyl chains $(CH_2)_n$ leads to nonbirefringent systems [48–51].

We will not discuss more in details this property here because some reviews have been previously written [47]. However, it was of importance to mention it as many properties may depend on the organization inside the solid. The coordination chemistry in the solid is an example.

2.4.3. Coordination chemistry in the solid

The organization of organic units in a short range order within nanostructured materials can involve a coordination chemistry in the solid completely different from this in solution. The reactivity of aromatic groups bound to silica matrix towards $Cr(CO)_6$ will be given as an example [52–54].

Indeed, aromatic groups can react readily with $Cr(CO)_6$ to form aryl/$Cr(CO)_3$ complexes. We showed that the reactivity of aromatic groups of an organic moiety covalently linked to the silica matrix depends on the geometry of the precursor, which controls the organization of the solid: the hydrolysis and polycondensation of bis-silylated phenylene compounds **11** and **12** was achieved under the same experimental conditions giving rise to materials **X11** and **X12** (Scheme 7).

Interestingly, these materials presented very different physico-chemical characteristics. **X11** is a hydrophilic solid with a high specific surface area (550 $m^2 g^{-1}$). It exhibited no fragment arising from C_6H_5 in TOF-SIMS analysis, which detected only SiOH fragment. Furthermore, **X11** reacts with $Cr(CO)_6$, with a poor yield (<10%), which is consistent with aromatic groups embedded in the core of the solid and organized in such a way the reaction with the bulky $Cr(CO)_6$ reagent is very difficult.

In contrast, **X12** is a hydrophobic material, displaying in TOF-SIMS analysis phenyl ($m/z = 77$) and tropylium fragments ($m/z = 91$) but no SiOH groups. These data suggest strongly that in this last case, the organic groups are located at the surface of the solid, which is in agreement with the high yield of complexation with $Cr(CO)_6$ (80%).

Thus, these two examples illustrate very well the role of the nature of organic groups in the control of the arrangement of solids prepared under the same experimental conditions. The rigid precursor **11** led to the material **X11**, which exhibits no reactivity towards $Cr(CO)_6$ because the organic moieties are in the bulk of the solid, while the material prepared from the more flexible precursor **12** gave rise to the material **X12**, which exhibits a reactivity close to that observed in solution (high yield in complexation reaction). This difference
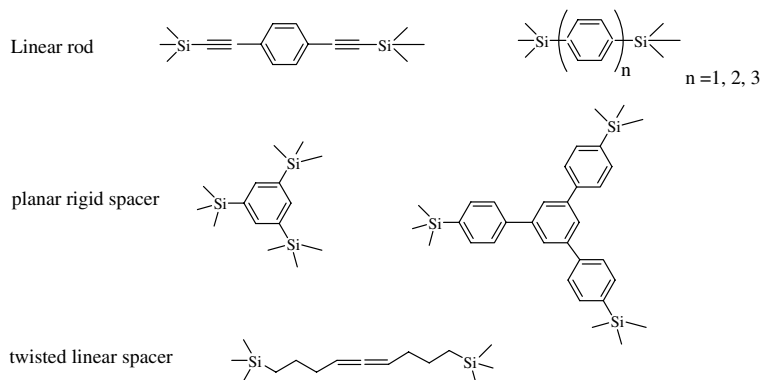
Scheme 6. Some examples of organic units giving rise to auto-organization.
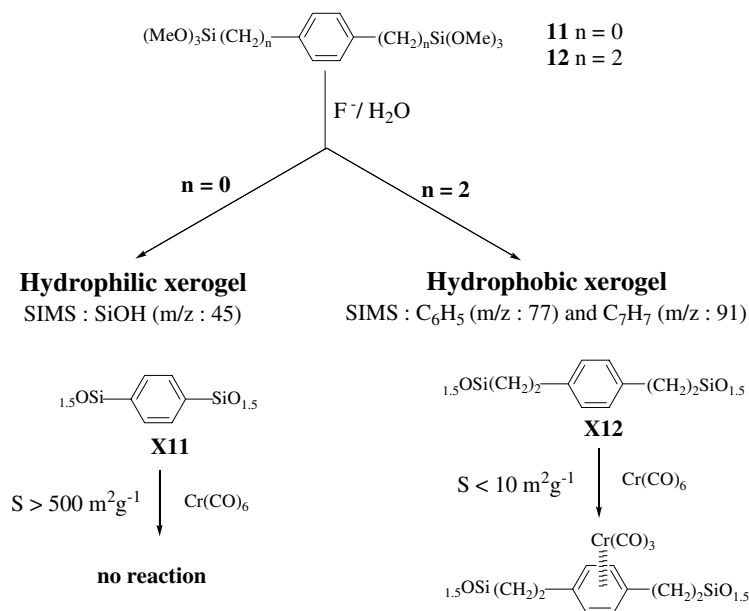
Scheme 7. Influence of the geometry of the molecular precursor on the reactivity of aromatic groups incorporated into a silica matrix.

of behaviour between **X11** and **X12** was confirmed by a difference of organization between both materials evidenced by X-Ray diffraction and birefringence measurements [47].

Another example illustrating the relation coordination chemistry-structure of the material concerns the chelating properties of tetraazamacrocycles (cyclam units). Two routes have been investigated to incorporate chelated transition metal salts within hybrid materials [55]. They are describe in Scheme 8.

The route **A** corresponds to the hydrolysis and polycondensation of silylated Cu^{II}/cyclam complexes. In that case, ESR spectroscopy exhibits the signal characteristic for Cu^{II} centres. The route **B** corresponds to the hydrolysis and polycondensation of the tetrasilylated cyclam precursor **13** followed by the direct and quantitative incorporation of CuCl$_2$ within the solid. Surprisingly, beside the weak ESR signal expected for Cu^{II},

antiferromagnetic Cu–Cu interactions have been observed in the ESR spectrum. The same ESR spectrum indicating Cu–Cu interactions has been observed in solution with cyclam-basket type molecules where two cyclam units are chemically linked to each other with a geometry which permits to well define the position of two Cu centres [56]. This observation suggests that during the sol–gel process (route **B**) the cyclam moieties arrange in such a way that two chelated copper ions are in an analogous situation to that in the cyclam-basket type molecules. In contrast, the arrangement of solids prepared by route **A** does not give rise to such Cu–Cu interactions. The difference in the arrangement of cyclam units in both materials was also evidenced by their ability for dioxygen uptake. The materials prepared according the route **A** have no affinity for dioxygen. In contrast, those prepared according to the route **B** display a great affinity for O$_2$ (about
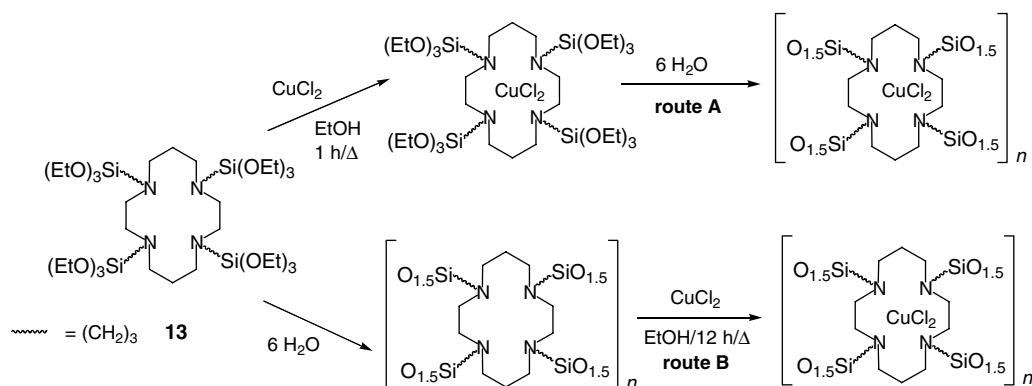
Scheme 8. Two routes leading to nanostructured materials containing Cu^{II}/cyclam derivatives complexes.
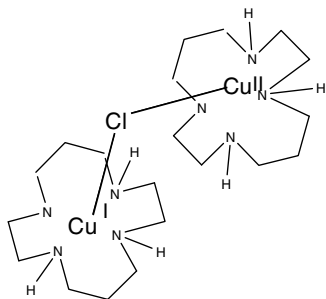
Scheme 9. Mixed valence complex Cu(I)–Cu(II) bridged by a chloride ion, the active species for dioxygen binding.

12–15 cm^3 g^{-1}). EXAFS, XANES, ESR, UV–Vis spectroscopies showed that the active species from which there is oxygen uptake, is a mixed valence complex Cu(I)–Cu(II) bridged by a chloride ion, with a Cu–Cu distance of 3.99 Å (Scheme 9) [57].

Thus, these results illustrate very well that the property of the material (dioxygen uptake in this case) is controlled by the short range organization of the organic moieties: in the materials prepared by route **B**, the cyclam units are in such a close proximity, that the formation of dimeric species is possible, which is not he case for the materials prepared from the Cu^{II}/cyclam complexes (route **A**).

A further evidence for the proximity of cyclam units in the materials prepared according to route **B** was given by the ability of these materials to complex Eu^{III} [58]. Treatment of materials prepared according to the route **B** by an ethanolic solution of EuCl$_3$ led to the incorporation of 1 Eu^{III} *per* two cyclam units. That suggests the formation in the solid of Eu^{III}/cyclam complexes of 4N + 4N coordination, which is unusual (Scheme 10).

Indeed, to the best of our knowledge, there is no lanthanides complexes of 4N + 4N coordination whereas a number of examples of lanthanides complexes resulting from coordination 4N + 4O have been reported [59–61]. The incorporation of 1 Eu^{III} between two cyclam units is in good agreement with the Cu–Cu interactions due to the proximity of cyclam moieties in the bulk. In that case, the route **A** cannot be explored as this cyclam
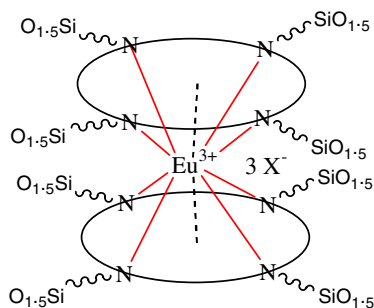
Scheme 10. Representation of Eu^{III}/cyclam complexes of 4N + 4N coordination.

derivative as well as the cyclam itself do not complex Eu^{III} in solution. The formation of complexes in the solid, which do not exist in solution could appear surprising. But in solution, because of the Brownian molecular movement, there is a competition between different structures and only the more stable may survive. In contrast, in the bulk, the movement being highly restricted, the possible diffusion of reagents involves the formation of complexes, which adopt a geometry imposed by the organization of the solid. This example illustrates the versatility of the coordination chemistry in the solid which deserves to be further explored and which is in relation with a short range organization in the solid.

3. Nanoporous hybrid materials prepared in the presence of structure-directing agent: on the way to smart materials [1]

Smart materials are one of the main challenges for nanosciences. They correspond to nanomaterials in which at least two physical properties will be interactively coupled together. Until now the chemistry has never be thought in terms of possible interactive coupling of properties. This research field is widely open. The nanoporous hybrid materials prepared in the presence of structure-directing agent are certainly, at the moment, the best supports for exploring some ways to polyfunctional materials.

The use of surfactant as structure-directing agent for the synthesis of mesostructured silica has constituted a major discovery in the material science in the past decade [62–67]. These materials are characterized by high surface areas, uniform and controlled pores sizes and long-range order which render them potential candidates for a variety of applications in chemistry (catalysis [68] and selective separations) for instance [69,70] but also for physical properties (optic, magnetism, electric conductivity, etc.). They are obtained by a sol–gel type polycondensation performed in the presence of surfactant working as a template (Scheme 11). After elimination of the surfactant, the materials exhibit a very regular distribution of pores, the size of which is controlled by this of the surfactant.

The inclusion of functionalities precisely located in the channel pores can be performed groups of ordered silica (Scheme 12) was very often used [71–75] after removal of the surfactant. This method is very interesting in that it is general and allows the grafting of even bulky organic groups by choosing a mesoporous ordered silica with a convenient pore size. However, grafting allows

[1] The terminology "mesoporous material" does not describe precisely these materials in which the mean pore size is in between 2 and 50 nm. The terminology "nanoporous Materials" is rather precise and now more and more used.
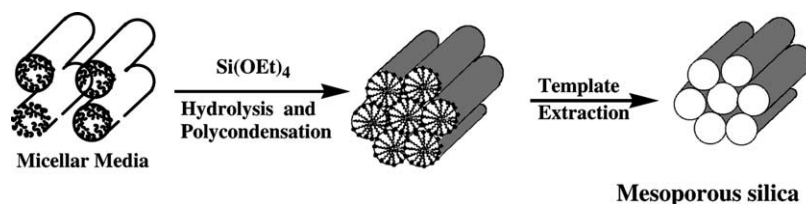
Scheme 11. Schematic pathway proposed by Beck et al. [63] for silica MCM-41 type formation.
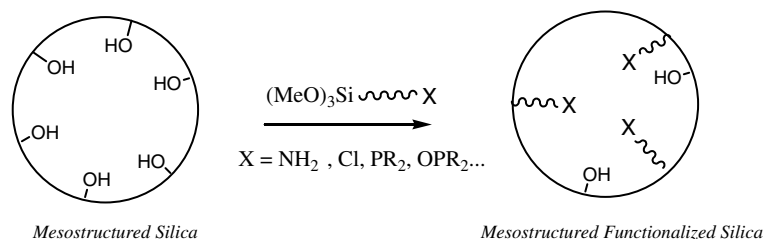
Scheme 12. Functionalization of mesostuctured silica by grafting.

neither the control of the concentration of organic groups nor this of their distribution, which depends on several parameters, the number of the surface silanol groups, the diffusion of reagents through the pores channels and steric factors.

An alternative approach in one step, overcoming the main restrictions of the post-synthesis method, has been developed for the preparation of ordered hybrid materials with functionalization within the channel pores. It consists in the co-hydrolysis and polycondensation of tetraethylorthosilicate (TEOS) and a organotrialkoxysilane $RSi(OR')_3$ in the presence of a structure directing agent (Scheme 13) [76–91]. This route provides a more regular distribution of organic groups inside the channel pores than by grafting and allows the control of the organic content. However, it supposes that the R group exhibits lipophilic properties compatible with the core of the micelle. This method was first explored in the presence of cationic surfactant [76–79]. Shortly after, the non-ionic assembly route was investigated by using primary alkylamine as structure directing agent [80–88] and finally the triblock copolymer $EO_{20}PO_{70}EO_{20}$ [poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide)] called P123 was used [89–91]. This last surfactant was proved to be very convenient under acidic conditions for the preparation of functionalized silica with hexagonal mes-

oscopic order. The resulting materials have large uniform pore sizes, high surface areas, and high thermal and hydrothermal stabilities.

These hybrid materials prepared in the presence of structure directing agent are of great interest for nanosciences. For the first time, chemists are faced with a single material, which exhibits all together aspects of chemistry: chemistry in the solid (bulk of the nanoporous material) chemistry in confined space (channel pores) and chemistry at the internal surface of the channel pores (functionalization of channels). This last possibility is very interesting as the surface of the nanoporous material is very high (sometimes higher than 1000 $m^2 g^{-1}$). That enables the linkage at the surface of an amount of functionalities sufficient for an easy characterization using directly classical methods (solid state NMR, IR, etc). This represents a very interesting enhancement of the available possibilities with regard to characterization of a simple planar surface by indirect methods.

In order to illustrate the easy characterization of organic groups anchored at the surface of channel pores, we will present some published results, showing how very precise indications concerning the distribution of phosphino groups located in the channels pores were obtained by using ^{31}P NMR spectroscopy.
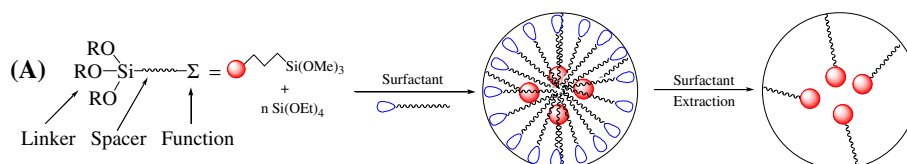
Scheme 13. Direct synthesis of a hybrid material in the presence of surfactant.
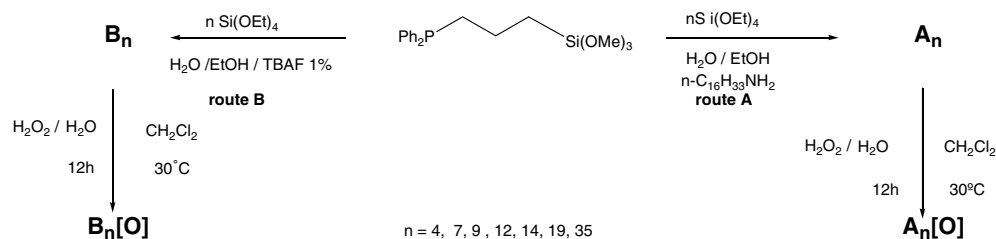
Scheme 14. Direct synthesis of hybrid materials containing phosphino groups in the presence (A_n) and in the absence (B_n) of a surfactant, followed by the oxidation of phosphino groups in phosphine oxide groups.
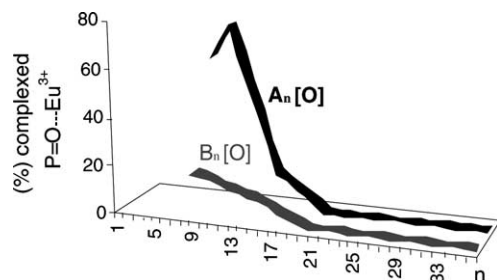
Scheme 15. Percentage of complexed P=O–Eu^{III} groups (calculated from solid-state ^{31}P NMR spectroscopy) as a function of the equivalent n of TEOS within the materials prepared in the presence of surfactant $A_n[O]$ and in the absence of surfactant $B_n[O]$.

Hybrid materials containing phosphino groups were prepared by the direct synthesis methodology in the presence and in the absence of surfactant (Scheme 14).

The oxidation of phosphino groups into phosphine oxides was subsequently achieved quantitatively within the materials in order to incorporate europium salts, which are photoluminescent. Indeed, the binding ability of phosphine oxides towards the lanthanide ions was well known. The results of incorporation of Eu^{III} in both materials are given in the Scheme 15 as a function of the concentration of organic groups in silica. Interestingly, the anchorage of Eu^{III}, which requires the proximity of 3 P=O groups is obviously highly dependent on the concentration of organic groups in the materials but above all of the preparation of materials. As it is shown in Scheme 15, the Europium uptake is very weak in the materials prepared in the absence of surfactant ($B_n[O]$) while it can reach 80% in the materials prepared in the presence of surfactant ($A_n[O]$).

These results demonstrate very well the regular distribution of the functionalities located within the channel pores of ordered hybrid materials prepared in the presence of surfactant and suggest a random distribution of organic groups in the materials prepared without surfactant.

Another example showing the regular distribution of organic groups was given by ordered SBA-15 mesoporous silica containing N-propylcyclam moieties. These materials were obtained by post-modification of ordered SBA-15 mesoporous silica functionalized with chloropropyl groups and prepared by direct synthesis (Scheme 16) [92a].

Successful complexation of europium (III) salt by N-propylcyclam moieties located inside the channel pores of these materials was further achieved giving rise to 1:1 Eu^{III}/cyclam complexes (Scheme 16). EXAFS experiments [92b] revealed an unexpected six coordination number whatever the concentration of cyclam moieties into the channels pores. That is a good indication of the regular distribution of chelating groups within the channel pores. Furthermore, it is worth noting that the coordination number is different from both this observed in solution (no formation of complex between Eu^{III} and N-triethoxysilylpropylcyclam) and this in the bulk (see Scheme 10). That illustrates the versatility of the coordination chemistry in the solid. Scheme 17 represents two possible coordination modes of Eu^{III} by cyclam moieties: coordination of Eu^{III} by the four N atoms from the cyclam moiety and two oxygen atoms in the axial direction forming an octahedron. The oxygen donors can originate from water molecules contained in the material and/or SiOH groups remaining at the surface of the pores.
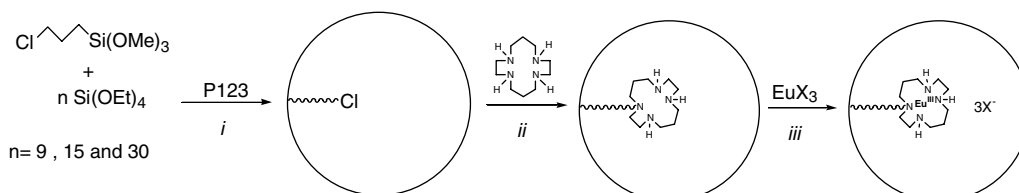
Scheme 16. Preparation of mesoporous silica with chloropropyl groups (i), modification by cyclam groups (ii) and complexation of europium salt (iii).
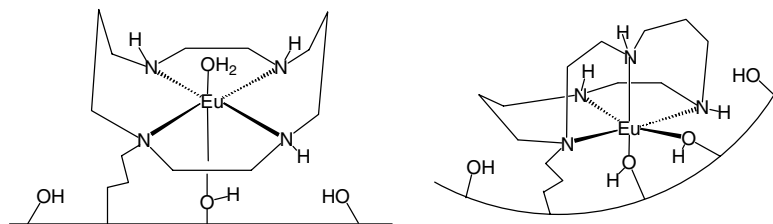
Scheme 17. Representation of europium/cyclam complex within the channel pores.

The potentialities open by the functionalization of the channel pores are very wide. That permits the introduction of much more than one simple chemical function. We have described the introduction of photoluminescent ions (Eu[III]) thanks to the oxidation within the material of phosphino groups into phosphine oxide groups and by substitution of chloro groups in the channel pores by chelating moieties. As other examples, we can mention the introduction of metallic nanoparticles stabilized by the functionalities located into the channel pores of ordered mesoporous silica: gold nanoparticles stabilized by SH groups [93], indium and indium oxide nanoparticules stabilized by diethylphosphonate groups [94].

Finally, it must be mentioned the recent developments concerning hybrid materials prepared in the presence of surfactant. Indeed, several groups [95–98] succeeded independently in 1999 to prepare ordered nanoporous materials from bis(trialkoxysilyl)organic precursors in the presence of surfactant. These materials were novel in that the organic fragments are located within the framework leaving the channel pores unoccupied. That renders this class of materials called Periodic Mesoporous Organosilica (PMOs) of great interest, the functionalization of channel pores leading to bifunctional materials [99–101].

By extending this methodology to the case of chelating units, we obtained materials including tetraazamacrocyles in both the framework and the channels pores [102]. The coordination chemistry of these solids was investigated [103] (Scheme 18). Thus, it was possible to include Cu[II] and Co[II] in both the framework and the channels pores with an absolute control of all the possibilities: only in the framework, one kind of transition metal ion in both channels and bulk, and also one kind of transition metal ion in the pores and another one in the framework and vice versa without any ion exchange.

These examples show very well that chemistry can allow to obtain the control of the location of organic groups at the same time in the bulk and in the channel pores. The introduction of ions corresponds to the potential inclusion of a physical property. The extension of this work permits the incorporation of Eu[III] (photoluminescence) and Gd[III] (luminescence and magnetism) in the framework, while other ions like Cu[II], Co[II], Fe[III] and Ni[II] are included in the channel pores [103a].
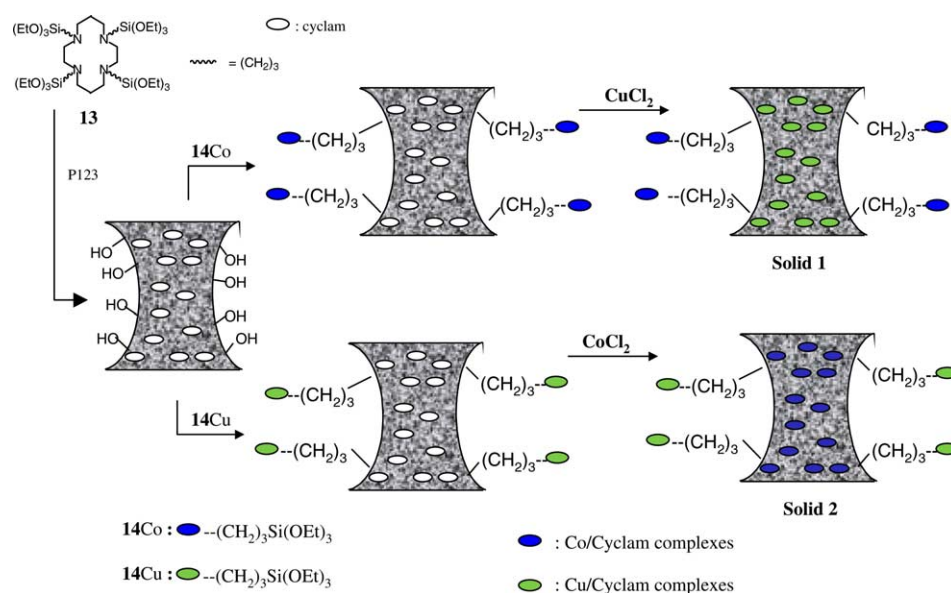
Scheme 18. Mesoporous hybrid materials containing two different chelated transition metal ions, one in the channel pores and the other in the framework. *Solid 1*, Co^{2+} in the channel pores and Cu^{2+} in the framework, *Solid 2*, Cu^{2+} in the channel pores and Co^{2+} in the framework.

4. Conclusion

Advances in organic, inorganic synthesis as well as in coordination chemistry in addition to those for the control of solid chemistry allow to chemists to extend their scope and to declare their ambition to find the routes to organize the matter in terms of properties (physical, chemical, mechanical). Biology is not mentioned in this list. However, it will be of great importance to adjust some materials for biological purposes. For instance, highly selective biosensors are a research field, which fits perfectly with the bottom-up approach of nanosciences. This approach will open to chemists interesting prospects of an exceptional variety. Let us indicate a few possible challenges.

Concerning the physic properties, the possibilities offered are very large as all transition metal or lanthanide ions have optical, magnetic or electrical properties. Their coordination chemistry is well known. Some routes for the organization of materials have been opened. They should be worked in cooperation with physicists to reach targets such as optical or magnetic storage of information or the control of optical transmission. To get these materials, the chemists could operate with a large range of parameters: functionalization of pores and framework of nanoporous materials, nature and properties of spacers, nature of matrix and at last the use of mutilayers materials.

In the field of chemistry, methods for selective separations, catalysis and synthesis in solid phase could probably be improved. We have previously given as an example the separation of lead. The depollution of nuclear effluents as well as the separation of isotopes [104] by routes as efficient but more convenient as the methods used at the moment could also be mentioned as examples. It is worth noting that there were already some interesting advances in catalysis (catalysts for depolymerization of C–C bonds and catalysts allowing methanocracking to supply hydrocracking by substitution of H_2 by CH_4) [105].

Syntheses in solid state thanks to the functionalization of silica have already allowed to obtain remarkable results, which could give rise to new industrial process. Thus, opposing reagents entrapped in silica sol–gel can be used successfully in one-pot reaction without interfering with each other [106].

Finally, in mechanical field, it is worth recalling that Yajima work [107] preceded the concept of nanomaterials from some decades.

The future prospects in this field can even be expanded to the use of non-siliceous matrices [108,109]. It is important to emphasize some possibilities offered by oxides which can be obtained by inorganic polymerization. Among numerous possible examples, we will mention tin dioxide, which is an n-type wide band gap semiconductor. Therefore, tin dioxide-based materials could find widespread applications in various fields including catalysis, photocatalysis, electrochromic devices [110,111].

Titanium dioxide (titania) [112,113], which is also attractive because of its performance in photocatalytic reactions and photovoltaïc properties. As it is known that the basic requirement for photoactive materials are high crystallinity and large surface area, high-surface area mesoporous titania with controlled crystalline framework is an important material.

Iron oxide (Fe_3O_4) [114] and nickel oxide [115] can also be mentioned as they are magnetic materials. Furthermore, nickel oxide is a material extensively used in catalysis, gas sensors and electrochromic films. Ordered hexagonal mesoporous nickel oxide has been recently shown to be an excellent electrode material for energy storage applications.

These few examples give a survey of extraordinary possibilities open to chemists within the framework of the route bottom-up of nanosciences. A number of new materials offering various properties coupled together will be synthesized in the next future thanks to the creative force of the chemical synthesis.

References

[1] (a) J.-P. Sauvage, Molecular Machines and Motors, Springer, Berlin, 2001;
(b) J.-P. Sauvage, Acc. Chem. Res. 34 (2001) 477.
[2] Nanosciences, Special Issue of Scientific American 290, 2001.
[3] R.J.P. Corriu, Chimie Moléculaire et Nanosciences, Actualité Chimique (in press).
[4] C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960.
[5] D. Avnir, L.C. Klein, D. Levy, U. Schubert, A.B. Wojcik, in: Z. Pappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compound, vol. 2, Wiley, New York, 1998, p. 2317.
[6] B. Arkles, Chemtech 12 (1999) 7.
[7] (a) B. Boury, R.J.P. Corriu, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 10, Wiley, New York, 2001, p. 565;
(b) M.A. Brook, Silicon in Organic, Organometallic, and Polymer Chemistry, Wiley, New York, 2000.
[8] F. Embert, A. Mehdi, C. Reyé, R.J.P. Corriu, Chem. Mater. 13 (2001) 4542.
[9] D. Gatteschi, R. Sessoli, Angew. Chem. Int. Ed. 42 (2003) 268.
[10] T. Lis, Acta Crystallogr., Sect. B 36 (1980) 2042.
[11] A. Caneschi, D. Gatteschi, R. Sessoli, J. Am. Chem. Soc. 113 (1991) 5873.
[12] F. Cuenot, M. Meyer, A. Bucaille, R. Guilard, J. Mol. Liquids (in press).
[13] F. Barbette, F. Rascalou, H. Chollet, J.L. Bahouhot, F. Denat, R. Guilard, Anal. Chim. Acta 502 (2004) 179.
[14] D. Riehl, F. Chaput, A. Roustamian, Y. Levy, J.-P. Boilot, Nonlinear Opt. 8 (1994) 141.
[15] C. Lambert, E. Schmälzlin, K. Meerholz, C. Bräuchle, Chem. Eur. J. 4 (1998) 512.
[16] J. Luo, J. Hua, J. Qin, J. Cheng, Y. Shen, Z. Lu, P. Wang, C. Ye, Chem. Commun. (2001) 171.
[17] T. Le Bouder, O. Maury, H. Le Bozec, I. Ledoux, J. Zyss, Chem. Commun. (2001) 2430.

[18] T. Le Bouder, O. Maury, A. Bondon, K. Costuas, E. Amouyal, I. Ledoux, J. Zyss, H. Le Bozec, J. Am. Chem. Soc. 125 (2003) 12284.
[19] K. Pelzer, O. Vidoni, K. Philippot, B. Chaudret, V. Collière, Adv. Funct. Mater. 13 (2003) 118.
[20] F. Dumestre, B. Chaudret, C. Amiens, M. Respaud, P. Renaud, P. Zurcher, Angew. Chem. Int. Ed. 42 (2003) 5213.
[21] F. Dumestre, B. Chaudret, C. Amiens, P. Renaud, P. Fejes, Science 303 (2004) 821.
[22] (a) C. Joachim, J.K. Gimzewski, A. Aviram, Nature 408 (2000) 541;
(b) C. Joachim, J.-P. Launay, R. Companó, La Recherche 347 (2001) 27.
[23] (a) M. Ebelmen, Ann. Chim. Phys. 16 (1846) 129;
(b) M. Ebelmen, C. R. Acad. Sci. 25 (1847) 854.
[24] L.L. Hench, J.K. West, Chem. Rev. 90 (1990) 33.
[25] J.-P. Jolivet, De la solution à l'oxyde, InterEd., Paris, 1994.
[26] G. Cerveau, R.J.P. Corriu, E. Framery, Chem. Mater. 13 (2001) 3373.
[27] C.J. Brinker, G.W. Scherer, Sol–Gel Science, Academic Press, Boston, 1990.
[28] (a) J. Livage, Chem. Scr. 28 (1988) 9–13;
(b) C. Sanchez, J. Livage, New J. Chem. 14 (1990) 513;
(c) J. Livage, Mater. Sci. Forum (1994) 152–153 (Soft Chemistry Routes to new materials) 43–54;
(d) J. Livage, Bull. Mater. Sci. 22 (1999) 201.
[29] J. Livage, C. Sanchez, J. Non-Cryst. Solids 145 (1992) 11.
[30] M. Henry, J.P. Jolivet, J. Livage, Ultrastruct. Process. Adv. Mater., [Proc. Int. Conf. Ultrastruct. Process. Ceram., Glasses Compos.], 4th (1992) 23.
[31] C. Sanchez, F. Ribot, New J. Chem. 18 (1994) 1007, and refs there in.
[32] J.P. Boilot, F. Chaput, T. Gacoin, L. Malier, M. Cauva, A. Brun, Y. Levy, J.P. Galaup, C. R. Acad. Sci. Paris 322 (Série IIb) (1996) 27, and refs there in.
[33] D. Avnir, V.R. Kaufman, R. Reisfeld, J. Non-Cryst. Solids 74 (1985) 395.
[34] S. Diré, F. Babonneau, C. Sanchez, J. Livage, J. Mater. Chem. 2 (1992) 239.
[35] (a) D. Levy, J. Phys. Chem. 9 (1988) 4734;
(b) D. Levy, S. Einhorn, D. Avnir, J. Non-Cryst. Solids 113 (1989) 137.
[36] B. Schaudel, C. Guermeur, C. Sanchez, K. Nakatani, J. Delaire, J. Mater. Chem. 7 (1997) 61.
[37] J. Biteau, F. Chaput, J.-P. Boilot, J. Phys. Chem. 100 (1996) 9024.
[38] (a) D.A. Loy, K.J. Shea, Chem. Rev. 95 (1995) 1431, and refs there in;
(b) K.J. Shea, D.A. Loy, Chem. Mater. 13 (2001) 3306, and refs there in.
[39] P. Judeinstein, C. Sanchez, J. Mater. Chem. 6 (1996) 511.
[40] (a) G. Cerveau, R.J.P. Corriu, Coord. Chem. Rev. 178–180 (1998) 1051;
(b) R. Corriu, Polyhedron 17 (1998) 925.
[41] G. Cerveau, R. Corriu, N. Costa, J. Non-Cryst. Solids 163 (1993) 226.
[42] (a) B. Lebeau, J. Marquet, C. Sanchez, E. Toussaere, R. Hierle, J. Zyss, J. Mater. Chem. 4 (1994) 1855;
(b) B. Lebeau, C. Sanchez, S. Brasselet, J. Zyss, G. Froc, M. Dumont, New J. Chem. 20 (1996) 13;
(c) B. Lebeau, S. Brasselet, J. Zyss, C. Sanchez, Chem. Mater. 9 (1997) 1012.
[43] G. Dubois, R.J.P. Corriu, C. Reyé, S. Brandès, F. Denat, R. Guilard, Chem. Commun. (1999) 2283.
[44] F. Embert, A. Mehdi, C. Reyé, R.J.P. Corriu, Chem. Mater. 13 (2001) 4542.
[45] S. Hobson, K.J. Shea, Chem. Mater. 9 (1997) 616.

[46] E. Lindner, T. Schneller, F. Auer, H.A. Mayer, Angew. Chem. Int. Ed. 38 (1999) 2154.
[47] (a) B. Boury, R.J.P. Corriu, Chem. Commun. (2002) 795;
(b) B. Boury, R. Corriu, Chem. Record 3 (2003) 120.
[48] F. Ben, B. Boury, R.J.P. Corriu, Chem. Mater. 12 (2000) 3249.
[49] B. Boury, R.J.P. Corriu, P. Delord, V. Le Strat, J. Non-Cryst. Solids 265 (2000) 41.
[50] F. Ben, B. Boury, P. Delord, M. Nobili, Chem. Mater. 14 (2002) 730.
[51] (a) G. Cerveau, R.J.P. Corriu, E. Framery, F. Lerouge, J. Mater. Chem. in press;
(b) G. Cerveau, R.J.P. Corriu, E. Framery, F. Lerouge, Chem. Mater. (submitted).
[52] G. Cerveau, R.J.P. Corriu, C. Lepeytre, Chem. Mater. 5 (1995) 793.
[53] G. Cerveau, R.J.P. Corriu, C. Lepeytre, Chem. Mater. 9 (1997) 2561.
[54] G. Cerveau, R.J.P. Corriu, J. Dabosi, J.L. Aubagnac, R. Combarieu, Y. de Puydt, J. Mater. Chem. 8 (1998) 1761.
[55] G. Dubois, C. Reyé, R.J.P. Corriu, S. Brandès, F. Denat, R. Guilard, Angew. Chem. Int. Ed. 40 (2001) 1087.
[56] M. Lachkar, R. Guilard, A. Atmani, A. De Cian, J. Fisher, R. Weiss, Inorg. Chem. 37 (1998) 1575.
[57] Gabriel David, Thèse Université de Bourgogne, Dijon, 2004.
[58] R.J.P. Corriu, F. Embert, Y. Guari, C. Reyé, R. Guilard, Chem. Eur. J. 8 (2002) 5732.
[59] J.R. Morrow, S. Amin, C.H. Lake, M.R. Churchill, Inorg. Chem. 32 (1993) 4566.
[60] S. Amin, J.R. Morrow, C.H. Lake, M.R. Churchill, Angew. Chem., Int. Ed. Engl. 33 (1994) 773.
[61] R.S. Dickins, J.A.K. Howard, C.W. Lehmann, J. Moloney, D. Parker, R.D. Peacock, Angew. Chem. 109 (1997) 541;
Angew. Chem., Int. Ed. Engl. 36 (1997) 521.
[62] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[63] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[64] P.T. Tanev, T.J. Pinnavaia, Science 267 (1995) 865.
[65] P.T. Tanev, T.J. Pinnavaia, Chem. Mater 8 (1996) 2068.
[66] E. Prouzet, T.J. Pinnavaia, Angew. Chem., Int. Ed. Engl. 36 (1997) 516;
S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia, Science 267 (1995) 1242.
[67] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.
[68] T. Maschmeyer, F. Rey, G. Sankar, J.M. Thomas, Nature 378 (1995) 159.
[69] L. Mercier, T.J. Pinnavaia, Adv. Mater. 9 (1997) 500.
[70] X. Feng, G.E. Fryxxell, L.-Q. Wang, A.Y. Kim, J. Liu, K.M. Kemner, Science 276 (1997) 923.
[71] W. Zhang, M. Froba, J. Wang, P.T. Tanev, J. Wong, T.J. Pinnavaia, J. Amer. Chem. Soc. 118 (1996) 9164.
[72] L. Mercier, T.J. Pinnavaia, Adv. Mater. 9 (1997) 500.
[73] A. Cauvel, G. Renard, D. Brunel, J. Org. Chem. 62 (1997) 749.
[74] P.M. Price, J.H. Clark, D.J. Macquarrie, J. Chem. Dalton Trans. (2000) 101.
[75] A.M. Liu, K. Hidajat, S. Kawi, D.Y. Zhao, Chem. Commun. (2000) 1145.
[76] C.E. Fowler, S.L. Burkett, S. Mann, Chem. Commun. (1997) 1769.
[77] M.H. Lim, C.F. Blanford, A. Stein, J. Am. Chem. Soc. 119 (1997) 4090.
[78] M.H. Lim, C.F. Blanford, A. Stein, Chem. Mater. 10 (1998) 467.

[79] S.R. Hall, C.E. Fowler, B. Lebeau, S. Mann, Chem. Commun. (1999) 201.

[80] D.J. Macquarrie, D.B. Jackson, J.E.G. Mdoe, J.H. Clark, New J. Chem. 23 (1999) 539.

[81] J.A. Elings, R. Ait-Meddour, J.H. Clark, D.J. Macquarrie, Chem. Commun. (1998) 2707.

[82] D.J. Macquarrie, D.B. Jackson, S. Tailland, K.A. Utting, J. Mater. Chem. 11 (2001) 1843.

[83] Y. Mori, T.J. Pinnavaia, Chem. Mater. 13 (2001) 2173.

[84] R.J.P. Corriu, A. Mehdi, C. Reyé, C. R. Acad. Sci. Paris 2 (Série IIc) (1999) 35.

[85] L. Mercier, T.J. Pinnavaia, Chem. Mater. 12 (2000) 188.

[86] R.J.P. Corriu, C. Hoarau, A. Mehdi, C. Reye, Chem. Commun. (2000) 71.

[87] R.J.P. Corriu, F. Embert, Y. Guari, A. Mehdi, C. Reye, Chem. Commun. (2001) 1116.

[88] R. Richer, L. Mercier, Chem. Commun. (1998) 1775.

[89] D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, Chem. Mater. 12 (2000) 2448.

[90] R.J.P. Corriu, L. Datas, Y. Guari, A. Mehdi, C. Reye, C. Thieuleux, Chem. Commun. (2001) 763.

[91] J.A. Melero, G.D. Stucky, R. van Grieken, G. Morales, J. Mater. Chem. 12 (2002) 1664.

[92] (a) R.J.P. Corriu, A. Mehdi, C. Reye, C. Thieuleux, Chem. Mater. 16 (2004) 159;
(b) R.J.P. Corriu, A. Mehdi, C. Reye, C. Thieuleux, New J. Chem. 28 (2004) 156.

[93] (a) Y. Guari, C. Thieuleux, A. Mehdi, C. Reye, R.J.P. Corriu, S. Gomez-Gallardo, K. Phillipot, B. Chaudret, R. Dutartre, Chem. Commun. 1374 (2001);
(b) Y. Guari, C. Thieuleux, A. Mehdi, C. Reye, R.J.P. Corriu, S. Gomez-Gallardo, K. Phillipot, B. Chaudret, Chem. Mater. 15 (2003) 2017.

[94] Y. Guari, K. Soulantica, K. Phillipot, C. Thieuleux, A. Mehdi, C. Reye, B. Chaudret, R.J.P. Corriu, New J. Chem. 7 (2003) 1029.

[95] S. Inagaki, Y. Fukushima, S. Guan, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 121 (1999) 9611.

[96] B.J. Melde, B.T. Holland, C.F. Blanford, A. Stein, Chem. Mater. 11 (1999) 3302.

[97] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, Nature 402 (1999) 867.

[98] C. Yoshina-Ishii, T. Asefa, N. Coombs, M.J. MacLachlan, G.A. Ozin, Chem. Commun. (1999) 2539.

[99] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, J. Phys. Chem.B 105 (2001) 9935.

[100] T. Asefa, M. Kruk, M.J. MacLachlan, N. Coombs, H. Grondey, M. Jaroniec, G.A. Ozin, J. Am. Chem. Soc. 123 (2001) 8520.

[101] Q. Yang, M.P. Kapoor, S. Inagaki, J. Am. Chem. Soc. 124 (2002) 9694.

[102] R.J.P. Corriu, A. Mehdi, C. Reye, C. Thieuleux, Chem. Commun. (2002) 1382.

[103] (a) R.J.P. Corriu, A. Mehdi, C. Reye, C. Thieuleux, New.J. Chem. 27 (2003) 905;
(b) R.J.P. Corriu, A. Mehdi, C. Reye, C. Thieuleux, Chem. Commun. (2003) 1564.

[104] F. Chitry, S. Pellet-Rostaing, O. Vigneau, M. Lemaire, Chem. Lett. 8 (2001) 770.

[105] C. Coperet, M. Chabanas, R. Petroff Saint-Arroman, J.-M. Basset, Angew. Chem. Int. Ed. 42 (2003) 156.

[106] (a) F. Gelman, J. Blum, D. Avnir, J. Am. Chem. Soc. 122 (2000) 11999;
(b) F. Gelman, J. Blum, D. Avnir, Angew. Chem. Int. Ed. 40 (2001) 3647;
(c) F. Gelman, J. Blum, D. Avnir, New. J. Chem. 27 (2003) 205.

[107] S. Yajima, K. Okamura, J. Hayashi, Chem. Lett. (1975) 931;
S. Yajima, K. Okamura, Chem. Lett. (1975) 1209.

[108] F. Schüth, Chem. Mater. 13 (2001) 3184.

[109] X. He, D. Antonelli, Angew. Chem. Int. Ed. 41 (2002) 214.

[110] K.G. Severin, T.M. Abdel-Fattah, T.J. Pinnavaia, Chem. Commun. (1998) 1471.

[111] T. Toupance, O. Babot, B. Jousseaume, G. Vilaça, Chem. Mater. 15 (2003) 4691.

[112] G.J.A. Soler-Illia, A. Louis, C. Sanchez, Chem. Mater. 14 (2002) 750.

[113] H. Luo, C. Wang, Y. Yan, Chem. Mater. 15 (2003) 3841.

[114] L.J. Michot, C. Mathieu, E. Bouquet, C. R. Serie IIC 1 (1998) 167.

[115] S. Banerjee, A. Santhanam, A. Dhathathreyan, P.M. Rao, Langmuir 19 (2003) 5522.