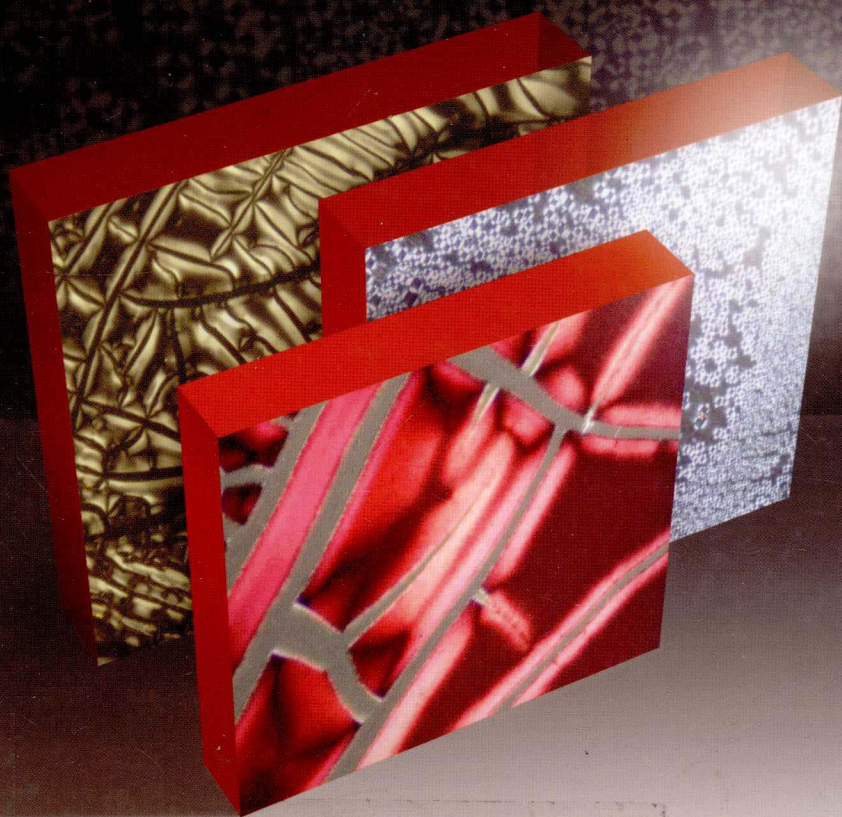


ROBERT CORRIU · NGUYỄN TRONG ANH

MOLECULAR CHEMISTRY OF  
**Sol-Gel Derived  
Nanomaterials**



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# Molecular Chemistry of Sol-Gel Derived Nanomaterials

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# **Molecular Chemistry of Sol-Gel Derived Nanomaterials**

# Preface

The writing of this book was motivated by the ever increasing interest in the rapid development of nanosciences and nanotechnologies. As scientists in the field, we are perturbed that nanosciences are *de facto* perceived as physics. Admittedly, the “nanoworld” is studied with physical instruments (e. g. scanning, tunneling and atomic force microscopes) and these studies are important, as it is already known that physical properties vary at different scales. Also, nanotechnologies have precipitated a miniaturization race, especially in electronics, following the famous aphorism ‘There is plenty of room at the bottom’ (R. P. Feynman). This miniaturization is essentially carried out by physical methods. This has led to nanosciences and nanotechnologies being identified by a large part of the general and the scientific community as a new physical domain, and therefore as no concern to chemistry.

*It seemed necessary to us to amend this point of view by outlining the possibilities opened up by chemistry in this very promising field.* Let us remember that nanosciences study *nano-objects* (entities of nanometric sizes) and their assembling into *nanomaterials*. Chemists have always thought in terms of nanometric objects (atoms, ions, molecules, etc.). Chemical syntheses are a planned assembling of these elementary units. Thus the ‘bottom-up’ approach in nanosciences is simply an application of familiar chemical ways of thinking and doing in a new domain.

Chemistry has also become in the recent past a creative science. To assert that chemists, with the tools already available, can prepare any conceivable structure is neither false nor extravagant. Therefore, the ‘know how’ of molecular chemists in synthetics can play a significant



role in nanosciences. This is presented in Chapters 1 and 2 with particular emphasis on the potential development of new materials exhibiting specific physical or chemical properties.

The focus of this book is on the new possibilities in material science opened up by the recent advances in inorganic polymerizations, better known as sol-gel processes. These ancient methods<sup>1</sup> sank into oblivion and were not rediscovered until the 1950s when chemists in the glass industry took advantage of the passage through a viscous state in order to shape the glasses and/or to transform them into coatings (see Chapter 3). Even then, for many years the primary concern was with industrial problems; only in the last twenty years have fundamental studies been undertaken in order to exploit the potential of these methods more widely.

Sol-gel processes are inorganic polymerizations which obey similar although more complex rules to organic polymerizations. The solid state chemistry approach produces two major new routes to original materials. On the one hand, there are the 'chimie douce' (or 'mild chemistry') methods<sup>2</sup> which allow complete compatibility between organic or biological and inorganic components. On the other hand, there are these sol-gel processes which lead to new materials through kinetically controlled syntheses, a usable complementary alternative to the customary thermodynamically controlled syntheses. If we recall, traditional preparations of glasses and ceramics take place at high temperatures (>400 °C and very often in the 1000–2000 °C range) which usually destroy organic and biological molecules. Thus, what started as a simple improvement to industrial processes has become a *bona fide* revolution which drastically changes inorganic synthesis.

We can now prepare materials which were previously unfeasible; it is already possible to obtain solids in which organic, organometallic or even biological entities can be incorporated or chemically bonded to inorganic matrices. This could open up a whole new field of chemistry to be explored, as the majority of materials obtained up to now are silicon hybrids, due to the ability of silicon to bind to carbon and to sustain controlled polymerization. We have not yet mastered the polymerization of other oxides (SnO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, NiO, etc.), in order to take advantage of their semiconducting (SnO<sub>2</sub>), photovoltaic (TiO<sub>2</sub>) or magnetic (Fe<sub>3</sub>O<sub>4</sub>) properties (properties that do not exist in SnO<sub>2</sub>), nor do we know how to combine them with organic molecules. Likewise, nitride and phosphide matrices have not been studied yet. In time, these hybrid organic-inorganic materials could become an inexhaustible

source of new materials. In Chapters 3–6 we show some initial results which describe the present state of the art.

Although many types of hybrids are described in this book, the emphasis is on nanostructured materials (Chapter 5). These materials correspond to the polymerization of organic entities having at least two carbon atoms substituted by  $-\text{Si}(\text{OR})_3$  groups. The hydrolytic (sol-gel) polycondensation of these precursors provides materials in which the organic components are inseparable from the inorganic parts. The organic entities are evenly ordered in these solids, which for this reason are called nanostructured hybrids. In fact, two independent organizations are observed: a nanometric structure revealed by X-ray diffraction and a micrometric structure confirmed by white light birefringence. The nanometric organization is generated in the colloidal sol phase and the micrometric organization during the ageing of the solid gel phase. This type of non-crystalline organization, never observed before, shows another interesting feature of inorganic polymerization. It has been detected with precursors having linear, planar, twisted or tetrahedral geometries.

Chapter 6 describes some developments of the mesoporous materials discovered by Kresge *et al.*<sup>3</sup> For the first time in the history of molecular and macromolecular chemistry, it has become possible to precisely locate the relative positions of different chemical entities. When these entities have distinct properties, materials can be obtained in which interacting properties occur at the nanoscale (until now such interactivity has only been observed between supramicrometric layers). Indeed, molecules, organometallic or coordination complexes, and metallic or inorganic (oxides, nitrides, phosphides) nanoparticles can add different physical (magnetic, optical, electrical, etc.) or chemical (catalysis, sequestration, separation, etc.) properties.

Some potential developments of the chemistry of hybrids will be presented in Chapter 7, along with some present and future applications. The molecular approach can fully exploit the synthetic capacities of chemistry and in contrast to the traditional one-step thermodynamically controlled preparations; sol-gel processes involve several kinetically controlled stages and allow the marriage of molecular chemistry and material science.

Nanosciences are defined purely by the size of the objects studied. This is best served by the cooperation of various parties employing different and complementary competencies in order to produce a multidisciplinary approach. Exploiting the materials' properties requires teamwork of

various expertises, ranging from molecular synthesis through physical chemistry to technologies. New materials will result from this interdisciplinary synergy and their preparation necessitates a diverse knowledge base. Nanomaterials with interacting properties are no longer an ideal (see Chapter 6).

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## Nguyễn Trong Anh

Nguyễn Trong Anh was formerly Director of Research at the Centre National de la Recherche Scientifique, Professor of Chemistry at the Ecole Polytechnique (Palaiseau, France) and Editor in Chief of *New Journal of Chemistry*. Trained as an experimental organic chemist, he became interested in applied theoretical chemistry and has worked on problems of organic stereochemistry and reaction mechanisms. He is the author of several books including “*Frontier Orbitals*” and “*Les Règles de Woodward-Hoffmann*” first published in 1971 which has since been translated into German, Italian, Spanish and Japanese.

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# 1

## Molecular Chemistry and Nanosciences

### 1.1 INTRODUCTION

Nanosciences study *nano-objects*, *i.e.* nanometric-size objects ( $1\text{ nm} = 1 \times 10^{-9}\text{ m}$ ) and their transformation into *nanomaterials*.<sup>\*†</sup> Unquestionably, they represent a most promising field of material sciences for the next few years. The main challenge will be the control of physical and chemical properties by methods operating at atomic or molecular level.

However, in the mind of many scientists, physics is the major factor in nanosciences, chemistry playing but a minor role. This opinion is largely the consequence of the historical development of nanosciences, as explained in the next section.

The purpose of this book is to amend this view by pointing out the potential of chemistry in this area. We shall present in Section 1.2 the two principal approaches in nanosciences (the ‘top-down’ approach which relies mostly on physics and the ‘bottom-up’ approach which is essentially a matter of chemistry), and relate in Section 1.3 how chemistry has evolved from an exploratory to a creative science. Chemistry can now tackle successfully a great variety of problems, from the creation of new

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<sup>\*</sup>Thus nanosciences are defined by the size of the objects, rather than by the nature of the phenomenon studied as in optics, electricity, etc. It follows that they are by definition multidisciplinary.

<sup>†</sup>Nanomaterials differ from ‘ordinary’ materials in that their properties can be traced back to those of their nano-object component: in other words, these properties are already incorporated at the nanoscale.



materials to the synthesis of auto-organized systems which can almost mimic living matter. With the synthetic methods already perfected and/or to be discovered in the near future, chemistry can convert nano-objects into a vast number of operational materials, exemplified by carbon and ceramic fibers, the forerunners of nanomaterials (Section 1.4).

Nanosciences are multidisciplinary, with physics and chemistry as natural partners. Chemistry can create new molecules, particles, nano-objects, etc., which can lead to innovative designs for new materials, *e.g.* materials in which several physical or chemical properties interact. If their preparation is the chemist's responsibility, the study and utilization of these materials' original properties come under the remit of the physicist. Other disciplines may be involved as well. For instance, mechanics will be implicated because no materials exist without mechanical properties. Mechanical attributes can also be fine-tuned at the nanometric scale. Biology is less directly involved because most biological entities exceed a micrometer in size; however, it will benefit from the development of nano-objects capable of working in a biological environment. The most illustrative example is that of biosensors capable of detecting and measuring certain substances *in situ* (*e.g.* in blood). Furthermore, modeling biological properties may suggest new designs for nanomaterials. Thus the membrane phospholipids have served as a model for the development of vesicle-forming surfactant compounds.

Modern science is demanding, requiring expert knowledge from each contributing discipline. Only close cooperation between experienced and competent specialists, who are able to communicate with each other, understand each other and conceive a joint project, can lead to new and significant achievements.

## 1.2 SCOPE AND ORIGIN OF NANOSCIENCES: THE 'TOP-DOWN' AND 'BOTTOM-UP' APPROACHES

Although chemists handle objects of nanometric sizes daily, physicists must be credited with formalizing the concept of nanosciences. This is due to two reasons.

The first one is purely scientific. It comes from the quasi-certitude that exploration of the 'nanoworld',<sup>1</sup> that is to say matter at the nanometer scale, will lead to the discovery of new, unexpected physical properties. Indeed, it is known that physical properties are dependent on the observation scale: studies at the micrometric scale will not reveal the same

properties as studies at the nanometric scale. Investigation of the behavior of isolated units (metal atoms, particles, molecules) becomes possible with the invention of the atomic force microscope and the scanning tunneling microscope. Some results obtained are spectacular and open up exciting vistas to scientists. For example, physicists have been able to study the transition of a single electron from the fundamental to the excited state in semiconductors as well as in suitably chosen organic molecules. IBM scientists have written their company's acronym on an appropriate surface by displacing atoms one by one. To recap, physics has the instruments for exploring the nanoworld and the capacity to study and exploit the (optical, electrical, magnetic, etc. . .) properties of nano-objects.

The second reason, more technological, has economic motivations. The mass diffusion of electronic products and their involvement in almost everyday activity have generated a mounting need for smaller and yet more powerful microprocessors. This demand is quantified by the famous Moore law which predicts that the performance of electronic components increase by one order of magnitude every two years. Microprocessors are, therefore, miniaturized and tend towards 'nanoprocessors'. This approach has been termed 'top-down' and corresponds to the first manifestation of the nanoscience concept. From an economic point of view, the top-down methodology is unquestionably the most important approach at present and has created a lively international competition.

There is also a symmetrical approach called 'bottom-up' in which the nanomaterial is chemically assembled from elementary chemical components, just like a wall is constructed from bricks and mortar. While the top-down approach is essentially a miniaturization technology from which chemistry is absent, the bottom-up approach, based on synthesis, fits perfectly with chemical methodology. The building blocks – molecules, molecular complexes, atoms or aggregates, all entities whose sizes vary from tenths of a nanometer to tens of nanometers – are familiar to chemists. The assembling methods (the mason's mortar) use inclusion and polymerizations of organic or inorganic entities. As shall be explained in the next chapter, chemistry possesses all the necessary requirements for developing nanosciences by the bottom-up approach.

One of the most illuminating examples concerns the *selective elimination* of lead from drinking water.<sup>2-4</sup> After passage through a filtering cartridge, the  $\text{Pb}^{2+}$  concentration is  $<5 \mu\text{g l}^{-1}$ . The concentration of other ions ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc.) is unchanged. This achievement, unbelievable just 10 years ago, is now possible because coordination chemists can prepare compounds capable of chelating selectively different metal ions. These compounds are incorporated into solids by polymerizations. In this

case, a  $\text{Pb}^{2+}$ -selective chelating molecule was bonded to silica, resulting in a material, which can be shaped into cartridges. This example is proof that chemistry can synthesize operational and selective nanomaterials.

However, physics is not absent from the bottom-up approach. Some nano-objects, for example fullerenes and carbon nanotubes, can only be obtained by physical methods. There exist also physical assembling methods: vapor phase deposition, molecular beam, etc. All these approaches can lead to new materials.

### 1.3 CHEMICAL MUTATION: FROM AN EXPLORATORY TO A CREATIVE SCIENCE

During the last fifty years, science has progressively metamorphosed.<sup>‡</sup> Let us illustrate these changes with some examples, with particular emphasis on synthesis, which is the foundation of chemical creativity.

A revolution in structural determination launched this chemical mutation. In the late 1950s, recording spectrographs gradually allowed chemists to complete chemical analyses with physical methods (IR, UV, NMR, EPR, MS, X-ray diffraction, etc.) An exhaustive list would take too long and be too difficult to provide, with the number of these identification methods being very large and increasing by the day. Note, however, that chemical quantitative analysis remains *a necessary safeguard* in material sciences (we shall return to this point in Chapter 6).

These analytical tools have permitted a better comprehension of reactivity. Mastering the concepts governing the formation of chemical entities, the organization of solids and molecular structure has enabled chemists to synthesize incredibly complex molecules. Thus, Professor Y. Kishi's group has prepared palytoxin, a natural product isolated from soft coral. This compound<sup>5,6</sup> possesses 62 chiral carbons and has  $2^{62}$  ( $\sim 4 \times 10^{18}$ ) stereoisomers (Figure 1.1). On account of the precision of existing synthetic methods, it has been possible to produce the natural isomer.

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<sup>‡</sup>At the end of the nineteenth century, classical physics was a coherent corpus of doctrines, able to rationalize practically all known phenomena, thanks to mechanics, thermodynamics and electromagnetism. As for chemistry, which was largely empirical during the nineteenth century, it had sufficiently progressed by the middle of the twentieth century to be considered as 'having come of age'. Indeed, fundamental concepts like covalent bond or aromaticity, initially introduced empirically, can be explained by quantum mechanics. Students no longer need to learn by rote hundreds of reactions; they have only to understand a dozen mechanisms (additions, eliminations, substitutions, rearrangements, etc.) Also, the number of complex multistage syntheses already realized show that organic chemists could synthesize practically any existing molecule.