

Functional Hybrid Materials

edited by

Pedro Gómez-Romero, Clément Sanchez



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Preface

The book you have in your hands is the result of a thrilling struggle. A struggle to depict, in a bit more than a handful of chapters, the blooming and multifaceted world of hybrid materials with functional properties and applications.

Hybrid organic-inorganic materials constitute indeed a remarkable and growing category within the world of Materials Science. A realm where engineering the combination of dissimilar components at the nanometric and molecular level leads both to new challenges and opportunities for the development of novel and improved materials. This is a field where the boundaries between molecular and extended materials blur out, a field where ceramics and polymers meet at the chemical dimension to yield new materials that go well beyond conventional composites, a domain in which nanocomposites push forward the frontier of discovery. In this exciting field, remarkable structural materials, halfway between glass and polymers have been developed. Yet, the hybrid approach also offers great opportunities for the development of functional materials, a fertile ground to harness the chemical, physical, electrochemical or biological activity of a myriad organic and inorganic components and put them to work in the materials of tomorrow.

Collecting a thorough taxonomic list of contents that could fairly represent this fascinating family of materials would be impossible. Instead, we have strived to select a few topics that would criss-cross the field revealing in some detail both a variety of materials and a variety of functional properties and applications. Thus, beginning with some historical perspective – if that is possible at all in a field that has developed in the last two or three decades-the book goes from mineral intercalates, sol-gel hybrids and polysiloxanes, to other radically different types of hybrids and approaches, such as hybrids based on conducting polymers. Also very varied are the functional properties and multifunctional combinations and applications you will find in these chapters, ranging from optical or magnetic properties, to energy storage and conversion or from the wealth of electroactive materials used in sensors, batteries or solar cells, to the fascinating bioactive materials discussed in the final chapter.

We hope this impressionistic portrait of a very dynamic field will contribute to give the reader a feeling of the great potential, the multiple possibilities and the many promising trends behind the development of functional hybrid materials.

August 2003

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1

Hybrid Materials, Functional Applications. An Introduction

Pedro Gómez-Romero and Clément Sanchez

1.1

From Ancient Tradition to 21st Century Materials

In 1946, at a site in eastern Chiapas (Mexico) known as Bonampak (painted walls) a startling archaeological discovery was made. This ancient Maya site contained an impressive collection of fresco paintings characterized by bright blue and ochre colors that had been miraculously preserved (Figure 1.1). A specially striking feature of these wall paintings was precisely their vivid blue hues, characteristic of what turned out to be an hitherto unknown pigment which came to be known as Maya blue [1].

In addition to its beautiful tones, that seemed to span all the shades of the Caribbean Sea, the most remarkable feature of Maya blue was its durability. Despite the unavoidable deterioration of the Bonampak painted scenes, that particular blue pigment had withstood more than twelve centuries of a harsh jungle environment looking almost as fresh as when it was used in the 8th century. Maya blue is indeed a robust pigment, not only resisting biodegradation, but showing also unprecedented stability when exposed to acids, alkalis and organic solvents.

Only after half a century from its archaeological discovery and not without scientific controversy [1] could sophisticated analytical techniques uncover the secret of Maya blue. The pigment is not a copper mineral, nor is it related to natural ultramarine, ground Lapis Lazuli or Lazurite as originally thought. Maya blue is a hybrid organic-inorganic material with molecules of the natural blue dye known as indigo encapsulated within the channels of a clay mineral known as palygorskite [1]. It is a man-made material that combines the color of the organic pigment and the resistance of the inorganic host, a synergic material, with properties and performance well beyond those of a simple mixture of its components.

Maya blue is a beautiful example of a remarkable hybrid material and a very old one to be sure, but its conception was most likely the fruit of a fortunate accident, an ancient serendipitous discovery.

More than twelve centuries later, when a deep knowledge of atomic and molecular structure is replacing trial and error tradition in the design of novel useful

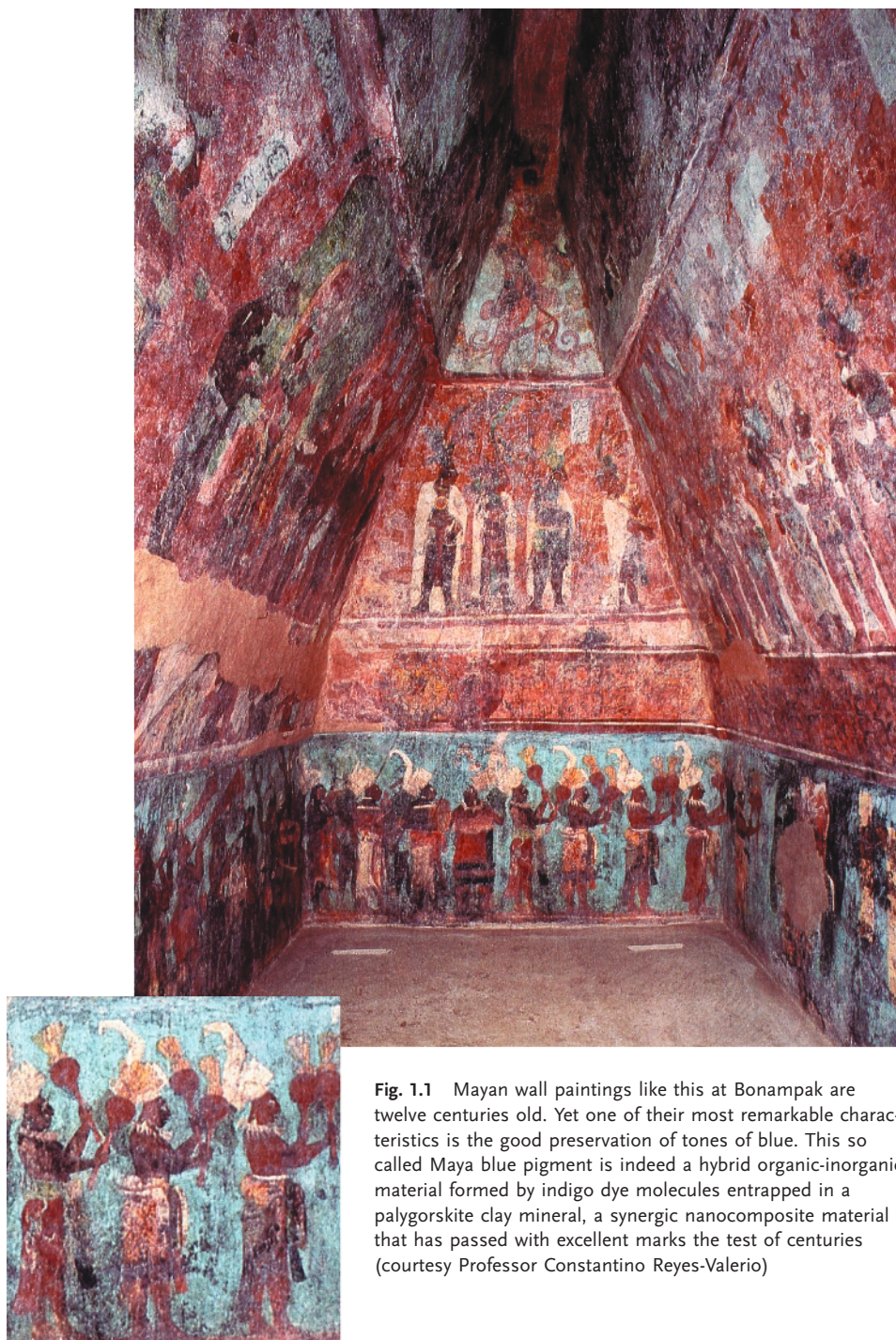


Fig. 1.1 Mayan wall paintings like this at Bonampak are twelve centuries old. Yet one of their most remarkable characteristics is the good preservation of tones of blue. This so called Maya blue pigment is indeed a hybrid organic-inorganic material formed by indigo dye molecules entrapped in a palygorskite clay mineral, a synergic nanocomposite material that has passed with excellent marks the test of centuries (courtesy Professor Constantino Reyes-Valerio)

materials, when our refined analytical techniques have allowed us to understand the true nature and structure of this pigment, Maya blue stands as an inspiration and a challenge for the designers of novel hybrid materials, for the explorers of a technological territory with quickly expanding frontiers of which this book wants to provide an account.

Aside from serendipity – the fruits of which should never be undervalued – the deliberate effort to combine properties of organic and inorganic components in a single composite material is an old challenge starting with the beginning of the industrial era. Some of the earliest and best known organic-inorganic admixtures 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 has more to do with chemistry than with physical mixtures. Thus, as the size of interacting particles gets reduced in going from mixtures to composite materials, the importance of the interface in determining final properties grows, and as we move towards nanocomposite materials, where components interact at a molecular level, the concept of organic-inorganic composites gets a new dimension, a chemical dimension.

The development of hybrid organic-inorganic materials stemmed from several different areas of chemistry, including intercalation chemistry (see Chapter 2), but exploded only very recently with the birth of soft inorganic chemistry processes (“Chimie Douce”), where mild synthetic conditions open a versatile access to chemically designed hybrid organic-inorganic materials [2, 3]. Later on, research shifted towards more sophisticated nanocomposites with higher added values [4, 5]. Nowadays the field of organic-inorganic materials has grown to include a large variety of types, extending to other fields as diverse as molecular and supramolecular materials or polymer chemistry [6]. Furthermore, a very significant trend has been the growing interest in functional hybrids, which broadens the field even further. Thus, in addition to structural hybrid materials bringing the best of glass and plastics together, there is a quickly expanding area of research on functional materials in which mechanical properties are secondary – though certainly not unimportant – and the emphasis is on chemical, electrochemical, or biochemical activity, as well as on magnetic, electronic, optical or other physical properties, or a combination of them [6a].

Numerous new applications in the field of advanced materials science are related to functional hybrids. Thus, the combination at the nanosize level of active 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 multi-functional materials [2–6]. The chemical nature of this emerging class of hybrids varies wildly, from molecular and supramolecular adducts [7] to extended solids, mineral or biomineral phases [8]. These functional hybrids are considered as innovative advanced materials, and promising applications are expected in many fields: optics, electronics, ionics, energy storage and conversion, mechanics, membranes, protective coatings, catalysis, sensors, biology, etc. [2–6]. Many interesting new materials have already been prepared with

mechanical properties tunable between those of glasses and those of polymers, with improved optical properties, or with improved catalytic or membrane based properties [4, 5]. For example, hybrid materials having excellent laser efficiencies and good photostability [9a], very fast photochromic response [9b], very high and stable second order non-linear optical response [9c], or being original pH sensors [9d] and electroluminescent diodes [9e] have been reported in the past five years. And some hybrid products have already entered the applied field and the market. Examples include organically doped sol-gel glassware sold by Spiegelau [10a], sol-gel entrapped enzymes sold by Fluka [10b], or 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 [10c]; interestingly, a 21st century material which brings us echoes of ancient Maya Blue.

1.2

Hybrid Materials. Types and Classifications

When it comes to formal classifications hybrid materials tend to resist rigid categorizing. Their variety is too large – and growing – to allow for a systematic grouping criterion. Figure 1.2 tries to convey this variety by showing examples of general types of hybrids spreading on a field of organic and inorganic dimensions. In this scheme material types are arranged according to the approximate dimensions of their organic and inorganic components. The limited space prevents an exhaustive list of materials and only several representative types are shown. Yet, this visual arrangement provides a first general overview of the area, spanning from molecular to extended organic-inorganic combinations. In this respect the graph also shows the greater richness of the field in the twilight region of supramolecular and nanostructured materials, forming a broad continuum between molecular and solid state chemistry.

The bidimensionality of this graph could suggest some type of classification according to the nature of the predominant phase in the hybrid, i.e. organic-inorganic vs. inorganic-organic materials depending on whether the extended, host or matrix phase were organic or inorganic respectively. Such classification has been conveniently used to categorize a particular type of polymer-based hybrid (see Chapter 7) although it could be difficult to generalize due to the abundance of intermediate cases and to the indistinct use of both terms in the literature, where the label organic-inorganic is most commonly used in a generic way.

On the other hand, a classification most widely used for all sorts of hybrid materials relies on the nature of interaction between organic and inorganic components.

The particular nanostructure, the degree of organization and the properties that can be obtained for hybrid materials certainly depend on the chemical nature of their components, but they are also heavily influenced by the interaction between these components. Thus, a key point for the design of new hybrids is the tuning of the nature, the extent and the accessibility of the inner interfaces. As a consequence, the nature of the interface or the nature of the links and interactions

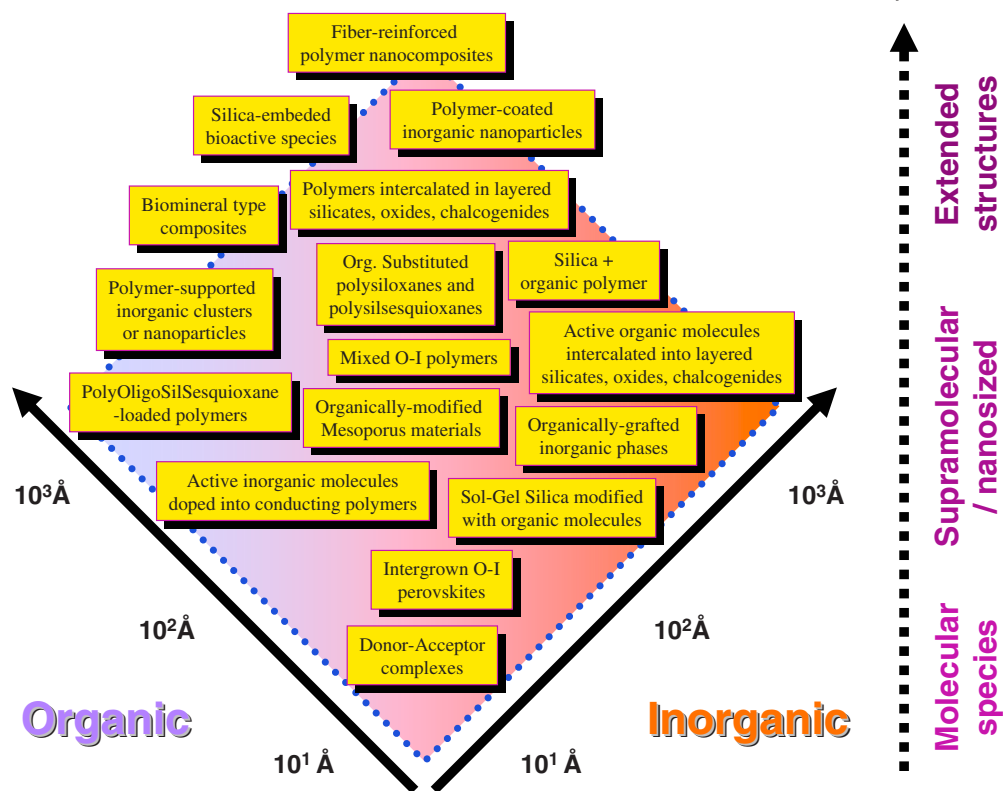


Fig. 1.2 The field of hybrid organic-inorganic materials has bloomed at the interface of many conventional disciplines, and is producing an amazing variety of materials and applications, ranging from molecular and supramolecular structures, to cluster-polymer adducts, sol-gel hybrids, or to nanocomposite materials based on extended phases

exchanged by the organic and inorganic components has been used to categorize these hybrids into two main different classes [3e, h, i]. Class I corresponds to all the systems where no covalent or iono-covalent bonds are present between the organic and inorganic components. In such materials, the various components only exchange weak interactions (at least in terms of orbital overlap) such as hydrogen bonding, van der Waals contacts, π - π interactions or electrostatic forces. On the contrary, in class II materials, at least a fraction of the organic and inorganic components are linked through strong chemical bonds (covalent, iono-covalent or Lewis acid-base bonds).

The chemical strategy followed for the construction of class II hybrid networks depends of course on the relative stability of the chemical links that associate the different components. Thus, under hydrolytic conditions $\text{Sn-C}_{\text{sp}^3}$ and $\text{Si-C}_{\text{sp}^3}$ are usually stable bonds that can be used for organic functionalization whereas for transition metal cations complexing organic ligands (such as carboxylic acids, phos-

phonates, hydroxyacids, polyols or betadiketones etc ...) could be used to anchor organic components [3e, 2e, 19].

Finally, the obvious classification of materials according to their properties and applications and, in particular, into the broad groups of structural and functional materials will help to put in perspective the scope of this book, which, notwithstanding the importance of mechanical properties, will put the emphasis on functionality and on functional hybrid materials.

The book includes a solid series of chapters dealing both with the chemistry and design of hybrids as well as with properties and applications. The emphasis goes from the former to the latter as we go from the first to the last chapters of the book but the reader will find a systematic attempt to bridge chemical design with physical properties and final applications in each single chapter, spanning overall a wide range of different types of hybrids and their applications. Thus, the book includes chapters devoted to the description of the synthesis, structure and chemical nature of several major kinds of hybrids, including intercalation compounds, sol-gel nanocomposite hybrids, polymer-based hybrids, or donor acceptor molecular materials as well as chapters dealing with the design of mesoporous hybrid materials and derivatives. Sol-gel chemistry of hybrids [3, 11] and organized matter sol-gel chemistry [12–16] have been reviewed extensively very recently [3s, 16] and consequently will not be reported with special detail in the present book. On the other hand, properties and applications are well covered by several chapters dealing with mechanical, optical, electrochemical, magnetic and multifunctional properties, as well as specific applications such as energy storage and solar energy conversion, electroanalytical, magnetic or microelectronics applications, to finish with a chapter on the novel and fascinating bioactive hybrid materials.

1.3

General Strategies for the Design of Functional Hybrids

Independently of the types or applications, and in addition to the nature of the interface between organic and inorganic components, a second important feature in the tailoring of hybrid networks concerns the chemical pathways that are used to design a given hybrid material. But, as has been hinted in the previous section, the design and synthesis of hybrid materials depend markedly on the type of hybrid sought. Class I and II hybrids differ radically in the type of synthetic approaches adequate to their successful preparation. In the same way, the widely varied types of hybrids shown in Figure 1.2 will require equally varied strategies for their synthesis.

Yet, general strategies can be considered within each subfield. For instance, we could point out several general approaches for the synthesis of sol-gel derived hybrid materials. These main chemical routes are schematically represented in Figure 1.3.

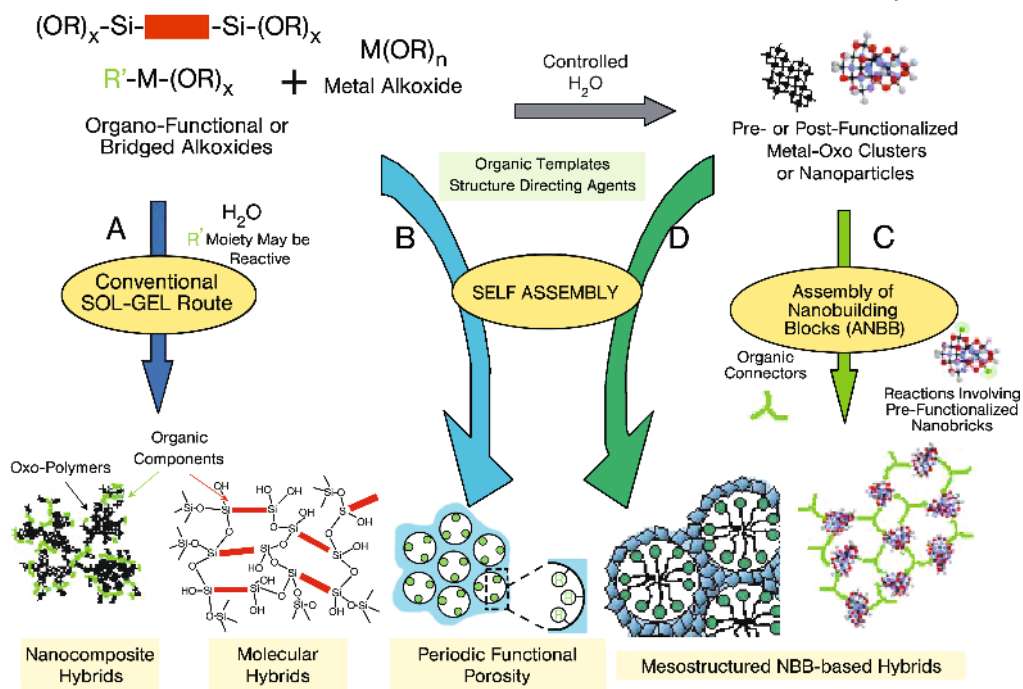


Fig. 1.3 a) One key factor in the development of hybrid materials is the understanding and control of synthetic mechanisms and approaches, which allows the design of tailor-made materials with predictable properties for specific applications. This figure summarizes several general approaches for the design of sol-gel derived hybrid materials (see text)

Path A corresponds to conventional sol-gel chemistry. Hybrid networks are obtained through hydrolysis of organically modified metal alkoxides or metal halides condensed with or without simple metallic alkoxides. Examples of such compounds are $R'_nSi(OR)_{4-n}$ ($n = 1, 2$), $OR_3Si-R'-SiOR_3$, or $R'_nSn(OR)_{4-n}$, with R' being a simple non-hydrolyzable group. R' will have a network modifying effect if it contains for example a phenyl, an alkyl group or an organic dye. R' will act as a network former if it bears any reactive group which can, for example, polymerize or copolymerize, (e. g. pyrrol, methacryl, epoxy or styryl groups) or $M(OR)_{m-n}(LZ)_n$, (where LZ is a functional complexing organic ligand with L an anchoring function and Z a general organic group)[19].

The solvent may or may not contain a specific organic molecule, a biocomponent or polyfunctional polymers that can be crosslinkable or that can interact or be trapped within the inorganic components through a large set of fuzzy interactions (H-bonds, π - π interactions, Van der Waals). These strategies are simple, low cost and yield amorphous nanocomposite 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.

Better understanding and control of the local and semi-local structure of these materials and their degree of organization are important issues, especially if tailored properties are sought for.

Five main approaches may be conceived to achieve such a control of the materials structure; they are schematized in Figure 1.3:

1. The use of **bridged precursors of silsesquioxanes** $X_3Si-R'-SiX_3$ (R' is an organic spacer, $X=Cl, Br, -OR$), following the route A, allows the making of homogeneous molecular hybrid organic-inorganic materials [17].
2. **Self assembling procedures** (route B) [12–16]:

In the last ten years, a new field has been explored, which corresponds to the organization or the texturation of growing inorganic or hybrid networks, templated by organic structure-directing agents (Figure 1.3, routes B, D). 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, due to the versatility they demonstrate in the building of a whole continuous range of nanocomposites, from ordered disper-

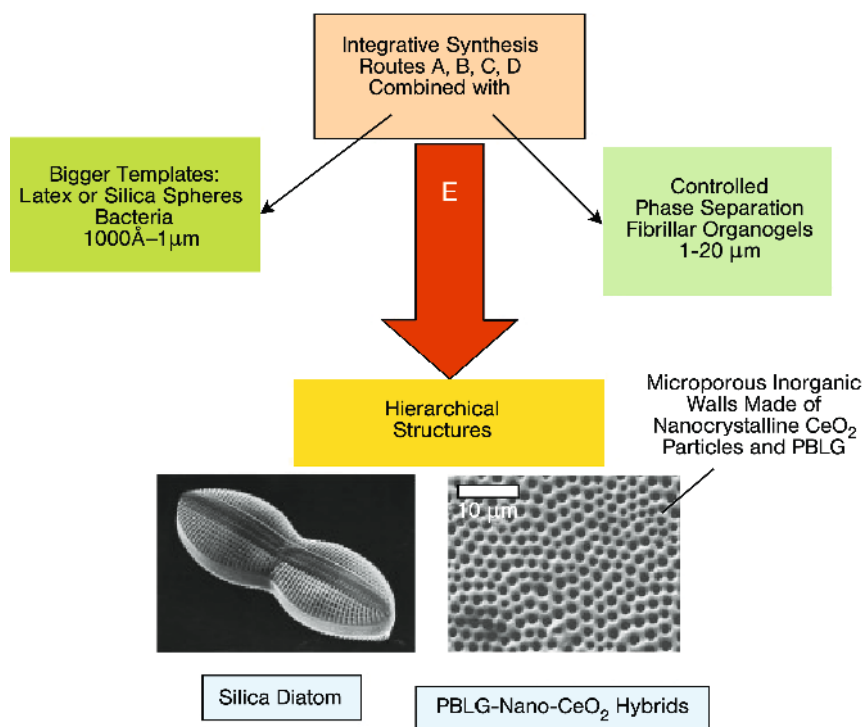


Fig. 1.3 b)

sions of inorganic bricks in a hybrid matrix to highly controlled nanosegregation of organic polymers within inorganic matrices. In the latter case, one of the most striking examples is the synthesis of mesostructured hybrid networks (routes B and D).

3. The assembling of well-defined nanobuilding blocks (NBB, route C) [3s]:

A suitable method to reach a better definition of the inorganic component consists in the use of perfectly calibrated preformed objects that keep their integrity in the final material. These NBB can be clusters, organically pre- or post-functionalized nanoparticles (metallic oxides, metals, chalcogenides, etc ...), nanocore-shells [3s, 11] or layered compounds able to intercalate organic components [18]. NBB can be capped with polymerizable ligands or connected through organic spacers, like telechelic molecules or polymers, or functional dendrimers (Figure 1.3, route C) [2 m]. The use of highly pre-condensed species presents several advantages:

They exhibit a lower reactivity towards hydrolysis or attack of nucleophilic moieties than metal alkoxides.

The nanobuilding components are nanometric and monodispersed, and with perfectly defined structures, which facilitate 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 the materials usually allows for a high degree of control over their semi-local structure.

4. The combination of self-assembly and NBB approaches (route D)[3s]:

Strategies combining the nanobuilding blocks approach with the use of organic templates that self-assemble and allow one to control the assembling step are also appearing (Figure 1.3, route D). This combination between the “nanobuilding block approach” and “templated assembling” will have a paramount importance in exploring the theme of “synthesis with construction”. Indeed, such materials exhibit a large variety of interfaces between the organic and the inorganic components (covalent bonding, complexation, electrostatic interactions, etc.). These NBB with tunable functionalities can, through molecular recognition processes, permit the development of a new vectorial chemistry.

5. Integrative synthesis (route E) [13–16]:

The strategies reported above mainly allow control of the design and the assembly of hybrid materials in the 1 Å to 500 Å range. Recently, micro-molding methods have been developed, in which the use of controlled phase separation phenomena, emulsion droplets, latex beads, bacterial threads, colloidal templates or organogelators leads to controlling the shapes of complex objects on the micron scale [16]. The combination between these strategies and those described along routes A, B, C and D allows the construction of hierarchically organized materials, in terms of structure and functions [16, 8c]. Such synthesis procedures are inspired by those observed to take place in natural systems for some hundreds of million years. Learning the “*savoir faire*” of hybrid living systems

and organisms from understanding their rules and transcription modes could enable us to design and build ever more challenging and sophisticated novel hybrid materials.

1.4

The Road Ahead

Looking forward to the 21st century, nano-sciences will be, as well as biology, one of the fields that will contribute to a high level of scientific and technological development. Hybrid (organic-bio-inorganic) materials must play a major role in the development of advanced functional materials.

Nowadays the molecular approaches of solid state chemistry and nanochemistry have reached a high level of sophistication. Today the synthesis of many or any organic ligands or molecules, coordination metal complexes, functional organo or functional metalo-organic precursors, functional nanobuilding units carrying magnetic, electrical, optical or catalytic properties, is very close to being mastered.

On the other hand, a large amount of research has been carried out to obtain organic templates (surfactants, dendrimers, organogelators, polymers, block copolymers, multifunctional organic connectors, biopolymers etc ...) and to understand and rationalize their physicochemical properties. Indeed, many research programs or research actions have been devoted to OMS (Organized Molecular Systems) or OPS (Organized Polymeric Systems).

As a consequence, nowadays, chemists can practically tailor-make any molecular species from molecules to clusters or even to nanosized particles, nanolamellar compounds, nanotubes etc. Clusters are mainly used as model compounds while nanoobjects can directly enter into more applied research fields.

In the near future, original materials will be designed through the synthesis of new hybrid nanosynthons (hybridons), selectively tagged with complementary connectivities, allowing for the coding of hybrid assemblies presenting a spatial ordering at different length scales. Hybridons carrying chirality or/and dissymmetry, and multiple or complementary functionalities will open new pathways for the synthesis of these materials.

Numerous scientific breakthroughs can be expected in this field through a closer involvement of skilled chemists in original pathways of materials processing. The synergy between chemistry and chemical engineering will permit access to materials having complex structures allowing a high degree of integration.

In particular, the synthesis and construction of materials through the simultaneous use of self-assembly processes and morphosynthesis (exploiting chemical transformation in spatially restricted reaction fields) together with external factors like gravity, electrical or magnetic fields, mechanical stress, or even through the use of strong compositional flux variations of the reagents during the synthesis (open systems) are particularly interesting to explore. The chemical strategies offered by such coupled processes allow, through an intelligent and tuned coding, to develop a new vectorial chemistry, able to direct the assembling of a large variety of struc-