Functionalized hybrid materials-from concept, through laboratory to business

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Introduction

The turn of XX and XXI centuries can be characterized in chemistry as the time of the elaboration of very efficient synthesis methods in chemical laboratories, sometimes based on selective reagents that enable the producing of freely planned molecules. It is estimated that at the beginning of a new century, there were over thirteen millions of known and described in a literature chemical compounds. From the enormous number of known molecules only insignificant part of them was precisely investigated and characterized. Following the professional chemical literature, every day we are informed about new compounds obtained but generally the information about the purpose of the synthesis is missing. The authors often point out only the area of possible practical application without any studies. The synthesis itself of new chemicals seems to be the area of research that is systematically replaced by a different approach to the chemistry, strictly speaking the synthesis of new compounds of specified properties for a specified purpose. Previous procedure, which amounts to the searching of some application for a compound that is already synthesized, is replaced by the planning of such a system that guarantees desired application. This process is supported by a strong instrument that is computer modeling. The present chemist is now included in the global marketing system that realizes the philosophy of the modern approach to the surrounding world, in which the idea "from concept to business" is now one of the most important direction that guarantees the success.

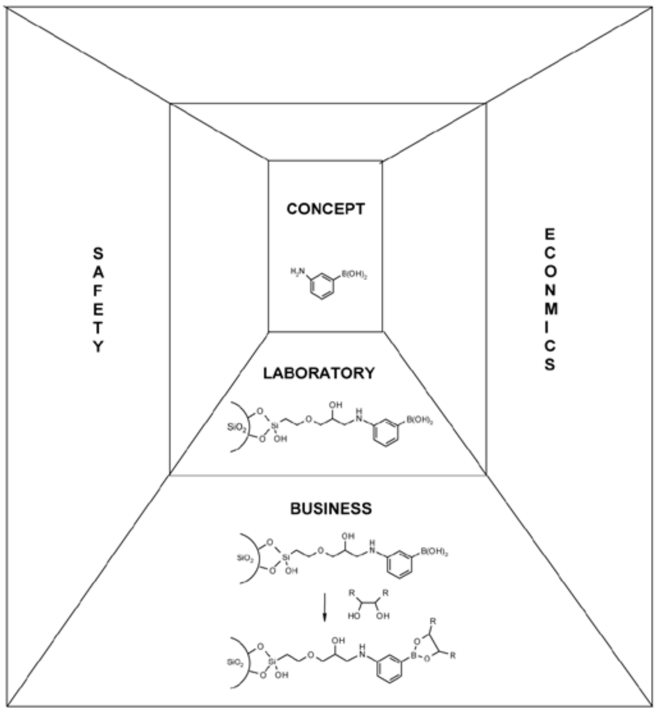


Fig. 1. The way from concept to business

The demand of innovative, socially useful chemistry starts a new page of a chemistry development. Nowadays, it is accepted without the astonishment that material chemistry articles are entitled: "From Laboratory to Market", "Chemists in Patent Law", "Business Idea in Chemistry?" or "Business of Chemistry". At the moment, the basic studies in chemistry are more specialized to practical application compared with the ones carried out a few years ago.

The laboratories are searching for a real application for new or known molecules. Due to the knowledge about the interaction between molecules, described mostly by supramolecular chemistry, as well as the ability of their application for the production of new materials, there are favorable circumstances in this area of research studies for the realization of the project: form concept to a new material of strictly characterized properties (Fig. 1).

The application of inorganic-organic hybrid materials, having molecular receptors in their structure, is an excellent example of the modification of the basic studies area by the demand for new materials.

Inorganic-organic or bio-inorganic hybrid materials are nowadays not only new area of research studies but also or even above all, the materials of specified properties and wide range of practical application in different spheres of life.

Hybrid materials

The idea of mixing of organic and inorganic components is applied in material technology since forties of the last century. However, the sudden development of this field of chemistry took place in the last period of time, when on the basis of supramolecular chemistry the production of new functionalized materials with specified properties was obtained on a large scale. The functionalized materials obtain such properties after the deposition on inorganic fragment: mostly metal oxides (like Fe2O3, Fe3O4, SiO2, TiO2), carbon nanomaterials (carbon nanotubes, fullerenes, grapheme) or metal surface(Pt, Au, Au-nano Ag, Ag-nano, Fe, Co, Ni, Si), organic molecules.

Molecular receptors form very special group of organic compounds. Such molecules, often described as host ones, are characterized by specific spatial structure, which guarantees the ability of selective binding of different molecules (substrates). Those substrates are selected from the library of different chemicals through selective intermolecular interaction during a host-guest complex formation (Fig. 2).

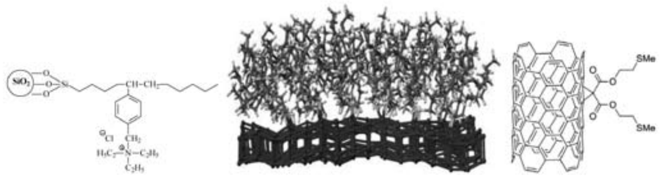


Fig. 2. Functionalized silica, metal surface and carbon nanotube

In the role of host molecules appear cations, anions or neutral molecules. From the practical point of view, the type of chemical bounding between organic (molecular receptor) and inorganic fragments is very important.

Hybrid materials are categorized into two classes depending on the type of bonding between inorganic and organic part. The first class of materials is characterized by weak chemical bonds between inorganic and organic fragments (hydrogen bonding, van der Waals forces or ionic bonding), while the second one-by strong and stable covalent bonding (Fig. 3).

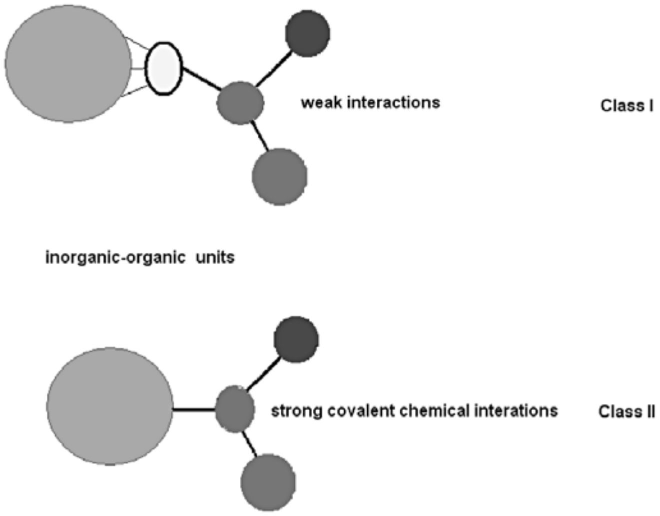


Fig. 3. Two classes of hybrid materials

If only organic part is represented by molecular receptor that is able to bond other molecule, then the receptor discussed can be bonded with inorganic fragment directly or indirectly through bifunctional linker (Fig. 4).

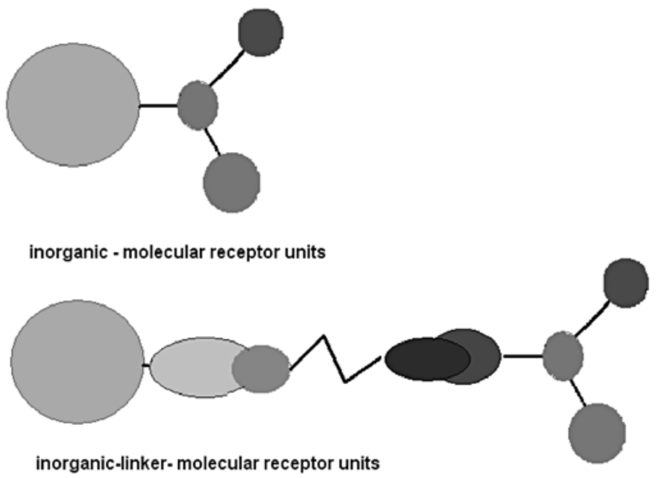


Fig. 4. Methods of molecular receptors bonding in hybrid materials

Nanomolecules that make up nowadays the foundation for molecular receptor deposition, open up new direction of the formation of materials characterized by high chemical activity and the size under 100 nm.

The impressive interest in hybrid nanomaterials comes from the variety of potential application in medical science, electronics and optics or energy storage. The important areas, in which new solutions are intensively searched for nanomolecules, are biological systems (like nucleic acids adsorption, in vivo extraction, water purification, viruses' elimination, drugs activation, drugs delivery and imaging). In case of these systems apart from their activity, the safety of their long-term application is fundamental.

Among many synthesized magnetic, hybrids nanoparticles, there are three groups, i.e. nanoparticles of Fe, Co and Ni; nanoparticles of Fe and Co alloys (like FePt, FePd, CoPt); nanoparticles of ferrites (like $CoFe_2O_4$). There are many methods of their synthesis, starting from metal halides reduction in the presence of alkali metals, through molecular self-assembly, sonochemistry, mechanical alloying, carbon arc, to recrystallization of amorphous materials. In order to apply those systems in practice, their surface is often modified, for example by hydrophilic or reactive functional groups incorporation, the organic or inorganic protective shell incorporation carrying reactive functional groups. This type of materials is susceptible to magnetic field. The motion of magnetic nanomolecules is controlled by magnetic field of magnet or electromagnet (Fig. 5).

Fig. 5. The influence of magnetic field on magnetic nanomolecules

The diverse structure of both inorganic and organic parts of hybrid materials, suggests the wide range of potential application of such systems. Hybrid materials are nowadays not only reacting substances, catalysts, selective reagents in chemical analysis, systems for water purification, but also elements of measurement instruments carrying through analyte detection at very low concentration in the solution [6÷10]. Table 1 presents exemplary applications of hybrid materials according to the idea concept-realization-application.

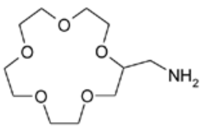
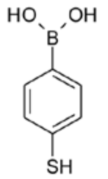
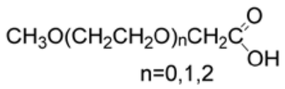
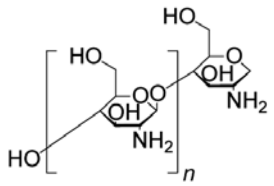
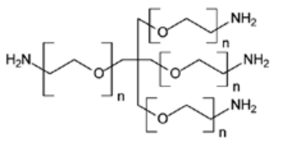
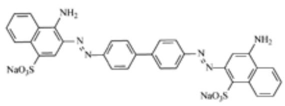
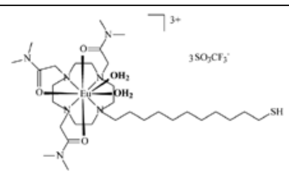
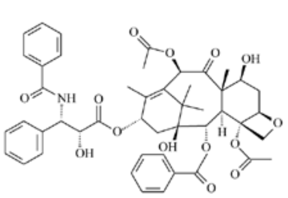
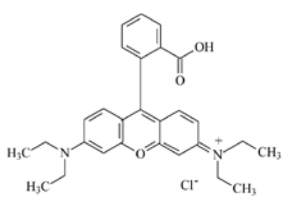
The way from the idea to the results commercialization and their practical application, is usually realized on the basis of nanotechnology. This process, which finally results in new nanomaterials formation, has to take into consideration all procedures related to safety-not only during the formation process, but also during bringing it into commerce.

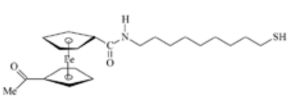
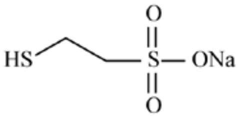
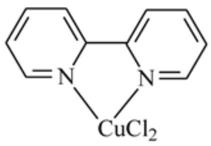
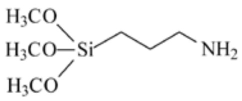
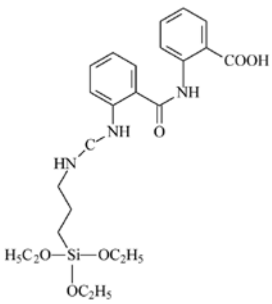
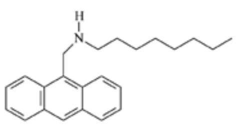
Conclusion

Functionalized hybrid materials underline not only the newest mini labs (Lab on the chip) [29, 30], fast diagnostic systems like ELISA [31], but also they form a new direction in the formation of catalysts [32] or polymers [33]. The enormous demand for new hybrid materials is connected with the facility of their synthesis, well-known properties of molecular receptors (fundamental research) and relatively low production costs. The economical aspects play fundamental role in the production of hybrid materials.

Table 1

Application of hybrid materials

Concept	Molecular receptor	Inorganic support	Linker	Hybrid materials	Application	References
Sodium and potassium ions removal from solution	 Crown ether	Silica gel	3-Aminopropyl trimetoxysilane	Functionalized silica	Water solution desalination	[11]
Quantitative analysis of 1,2-diols and sugars for very low concentrations	 Arylboronic acid	Microbeam surface (Au)		Functionalized microbeam	Quantitative analysis of sugars in solution (nano level)	[12]
Sodium ions removal from solution	 Polioxaethylene acetic acid derivatives	Magnetic iron oxide (γ-Fe_2O_3)-silica	3-Aminopropyl trimetoxysilane	Magnetic iron oxide-functionalized silica	Water solution desalination in the presence of magnetic field	[13]
Heavy metal removal from solution	 Chitosan	Magnetic (Fe, Co, Ni) carbon nanomaterial-silica	3-Aminopropyl trimetoxysilane	Magnetic (Fe, Co, Ni) carbon nanomaterial-functionalized silica	Purification of water solution (Pb, Cu ions) in the presence of magnetic field	[14]
Heavy metal removal from solution	 Polymer with terminal amine groups	Silica gel	3-Aminopropyl Trimetoxysilane; Suberic acid derivative	Functionalized silica	Purification of water solution (Cu ions)	[15]
Metal removal from solution; pH indicator	 Congo red	Silica gel	3-Aminopropyl Trimetoxysilane; Suberic acid derivative	Functionalized silica	Purification of water solution (Ag, Cu ions); Solid indicator of pH value	[16]
Use for the sensing of biologically relevant phosphates	 Heptadendate macrocyclic Eu(III) cyclen	Gold nanoparticles (AuNPs)		Functionalized gold nanoparticles	The sensing of biologically relevant phosphates	[17]
Chemotherapeutic drug	 Paclitaxel	Gold nanoparticles (Au NPs)	Hexaethylene glycol	Functionalized gold nanoparticles	As chemotherapeutic drug	[18]
Use for the sensing of cyanide in aqueous solution	 Rhodamine B	Gold nanoparticles (Au NPs)		Functional gold nanoparticles	Free cyanide in aqueous solution with high sensitivity (detection limit of 8.0x 10^{-8} M)	[19,20]

Use for the sensing of oxoanions	 mixed dodecanethiol/ (amidoferrocenyl) alkanethiol (AFAT)	Gold colloids		Functionalized gold colloids	To selecte different oxoanions	[21]
Use for the sensing of cyanide in aqueous solution	 2-mercaptoethane sulfonate	Low-dimensional semiconductor nanoparticles (CdSe QDs quantum dots)		Surface modified CdSe QDs	The sensing of free cyanide in aqueous solution with high sensitivity (detection limit of 1.1×10^{-6} M),	[22]
Use for the sensing of cyanide ions	 2,2-bipyridine-bound copper(II) ions	Low-dimensional semiconductor nanoparticles (CdSe QDs quantum dots)		Surface modified CdSe QDs	As the selective turn-on fluorescence cyanide sensor	[23]
Use the mesoporous hybrid materials containing nanoscopic "binding pockets" to produce new anion sensing devices that function in water via a displacement assay approach	 3-Aminopropyltriethoxysilane and its derivatives obtained by reaction with 2- methylthio-2-imidazoline hydroiodide and butyl isocyanate; N-methyl-N0-propyltrimethoxysilyl imidazolium chloride; 3-(trimethoxysilyl)propyl-N,N,N,-trimethylammonium chloride	UVM-7 (a mesoporous MCM41-type material)		Functionalized mesoporous solids with anion-binding groups	The sensing of carboxylates acetate, citrate, lactate, succinate, oxalate, tartrate, malate, mandelate, and glutamate in pure water	[24]
Use for sensing of fluoride anions	 The terbium complex of ligand	Mesoporous silica MCM-41		Mesoporous silica MCM-41 through a sol-gel approach	The detection limit for fluoride anions could reach 1 μM	[25]
Use for sensing of small and bigger anions		Mesoporous MCM-41		Functionalized MCM-41 grafted with amino group	For sensing chloride, bromide, phosphate, ADP (adenosine 5'-di-phosphate), AMP (adenosine 5'-monophosphate)	[26]
Polyanion-selective fluorescence sensing system	Aminoethyl-modified MCM41-type mesoporous silica particles	MCM-41 mesoporous silica particles modified with aminoethyl groups, enzymes and a supramolecular hydrogel		Hybrid material of supramolecular hydrogel, enzymes, and aminoethyl-modified MCM41-type mesoporous silica particles (NH_2-MCM41)	The sensing for polyanions such as heparin, chondroitin sulfate, sucrose octasulfate	[27]
Use for sensing ATP and pyrophosphate ions	Metal complexes: mono- and dinuclear zinc(II)–cyclen and iminodiacetato copper [CuII–IDA]	polydiacetylene (PDA) particles, embedded in amphiphilic diacet-Gylene monomers		Polydiacetylene molecules functionalised with metal complexes	ATP and pyrophosphate in buffered aqueous solution	[28]

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