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Organic and hybrid molecular systems

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The design of functional organic and hybrid molecular systems has shown outstanding recent growth and is a high priority in the development of new technologies and novel functional materials. Recent advancements in the chemical sciences have provided fascinating opportunities to access the most complex molecular architectures ever possible so far. Herein, we discuss the principles of the structural organization of recently studied molecular systems, basic approaches for their assembly, and challenging directions for their practical applications.

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Introduction

A global trend in modern chemical science is the design and investigation of molecular systems with various degrees of complexity to maximize the incorporation of useful properties while optimizing cost and efficiency. Individual molecular systems cover a wide range of complexity, from relatively simple small organic molecules to large and complex bioorganic systems and hierarchical nanomaterials. Synthetic organic and organometallic chemistry has contributed substantially to these areas, such that the preparation of even highly complex molecules with 'atomic precision' is not uncommon.[1,2]

The successful assembly of individual molecules into the next level of complexity has facilitated the development of hybrid molecular systems. Several fascinating systems based on organic/bioorganic and organometallic/inorganic components have been developed and have demonstrated outstanding potential in demanding real-life applications. Some systems have already been implemented in research and industry, covering such areas as pharmaceutical and medical applications, materials science, energy conversion, environment protection, catalytic technologies and several other key sectors of the economy that provide the necessary basis for world-wide development.

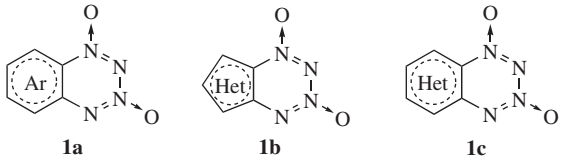
In this focus article, we describe a systematic integrated approach to organic and hybrid molecular systems. This interdisciplinary research includes four main complementary activities: (1) the design and preparation of organic molecules with high efficiency and selectivity; (2) the development of bioorganic molecular systems that address priority targets in medicine and which are useful in biological and environmental monitoring; (3) the development of new organic-inorganic hybrid systems and high-order materials for applications in catalysis, environment protection and the energy sector; and (4) research on complex molecular systems and mechanisms of chemical transformations through advanced physical and chemical methods.

Accordingly, the overall goal of this initiative is the design of new organic and hybrid molecular systems for critical technologies and sustainable development. The key point – being, in many respects, decisive in the overall success of this initiative – is the use of state-of-the-art physical and chemical methods in revealing chemical arrangements and spatial structures of organic, organoelement, and inorganic compounds and hybrid systems (ultimately, for systems of any chemical complexity). In this very brief review article, we focus on the areas of our research interests within the framework of the title initiative, 'organic and hybrid molecular systems'.

Design and preparation of organic molecules with high efficiency and selectivity

The first part of our initiative is focused on small organic molecules and the development of synthetic procedures. This area includes a vast number of research directions and applications, all of which are hardly possible to cover in detail. As a representative example, we consider the stereoselective and enantioselective synthesis of a specific class of molecules used in the preparation of neuromediators and enzyme inhibitors. Of particular interest are systems capable of releasing nitrogen oxide – a well-known gaseous molecule that plays an important role in nature as a powerful regulator of cardiovascular, central and periphery nervous systems in mammals[3] – under mild conditions. These systems can be used to develop new efficient medicines for curing cardiovascular problems, tumors and other widespread diseases. Furthermore, functionally substituted nitro compounds are precursors to valuable derivatives of γ-aminobutyric acid (GABA), which is an important natural neuromediator that can act as an antidepressant (phenibut,[4] baclofen[5]), and phosphodiesterase-IV inhibitors.[6] These substituted nitro compounds are also considered innovative drugs for the complex treatment of serious chronic obstructive lung disease. Notably, a number of N–O systems fall into the category of highly energetic compounds and may find applications not only in medicine but also in industry and technology. As a useful practical example, we consider the design of novel compounds bearing properly located *N*-oxide structural fragments: 1,2,3,4-tetrazene-1,3-dioxides, 1-alkoxytriazene-2-oxides, 1,2,5-oxadiazole-2-oxides (furoxans) and C- or N-nitro compounds.

1,2,3,4-Tetrazene-1,3-dioxides (**1**, TDO) represent a unique heterocyclic system developed by Tartakovsky and co-workers in 1995.[7] Since then, a number of TDOs (particularly, polynitrogen compounds **1a** fused with an (un)substituted benzene ring and heterocycles **1b** or **1c** that incorporate pyridine, furazan or 1,2,3-triazole moieties have been synthesized by the same research group (Scheme 1).[8]



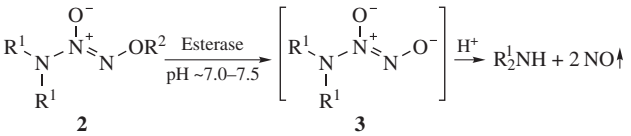
1a **1b** **1c**

Ar = (un)substituted benzene
Het = pyridine, furazan, 1,2,3-triazole

Scheme 1

These TDO derivatives were found to be a prospective class of thiol-dependent NO-donors with a wide spectrum of biological activities (*e.g.*, hypotensive, antithrombotic, and anticancer activities) and to act as H,K-adenosine triphosphatase inhibitors.[9] Furthermore, some of them are currently being investigated as extremely efficient components of modern explosives, propellants and powders.[10]

1-Alkoxytriazene-2-oxide derivatives **2** are also capable of generating nitrogen oxide under physiological conditions.[11] Compounds **2** are not inclined to spontaneous hydrolysis in an aqueous medium; however, in the presence of leukemic cells, they release a significant amount of NO because of an esterase-induced enzymatic cleavage of R^2–O bonds followed by the fragmentation of relatively unstable NONOates **3** (Scheme 2), thus inhibiting replication of the cells.[12] The data from *in vitro* biological testing allow compounds **3** to be considered as potential drugs for *in vivo* applications. Interesting NONOate-containing hybrid systems, particularly thromboresistant NO-releasing polymeric coatings, have been developed for this purpose.[13]



2 **3**

R^1 = alkyl, $R^1 + R^1$ = cycloalkyl
R^2 = (un)substituted alkyl, cycloalkyl, alkenyl

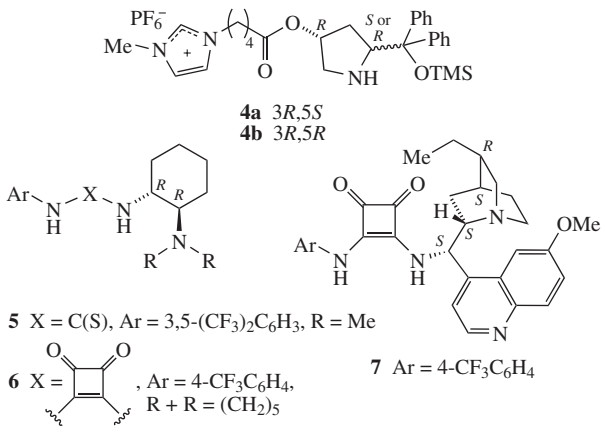
Scheme 2

Recently, Gasco and co-workers[14] reported that furoxan derivatives attached to praziquantel or entinostat (a moderately selective class I histone deacetylase inhibitor) generated nitrogen oxide in a solution buffered at pH 7.4 when L-cysteine or tyrosine was present. A remarkable contribution to the chemistry of furoxan derivatives has been made by Makhova and co-workers.[15] Among the elaborated compounds, amino, nitro, azo, azoxy and carboxyfuroxans, as well as bi- or polyheterocyclic systems bearing 1,2,3-triazole,[16] 1,3,4-oxadiazole[17] or even tetrazole units[18] along

with the furoxan ring, are considered potential NO-donors under physiological conditions.

In the last decade, aliphatic nitro compounds (ANC) and their derivatives have attracted considerable attention as precursors to pharmaceutical ingredients. Modern studies in the field of ANCs are focused in two primary directions: the development of nitro-group-mediating efficient methods for the formation of carbon–carbon and carbon–heteroatom bonds[19] and the elaboration of enantioselective, catalytic transformations of available nitro compounds into useful molecules.[20] In the framework of the first direction, an original approach to the reversal of traditional ANC polarity has been proposed by Ioffe and co-workers.[21] Their approach is based on an elegant conversion of the nitro group to active bis(oxy)iminium cations, which are an isostructural analogue of carbonyl groups, that readily participate in A_dN processes. Furthermore, interesting methods for the oxidative activation of remote C–H bonds in ANC under the action of metal (Ag^+) salts or even induced by the presence of a nitro group have been developed.[22] These methodologies allow one to perform relatively simple functionalization of commonly inactive β- and γ-positions of the ANC backbone.

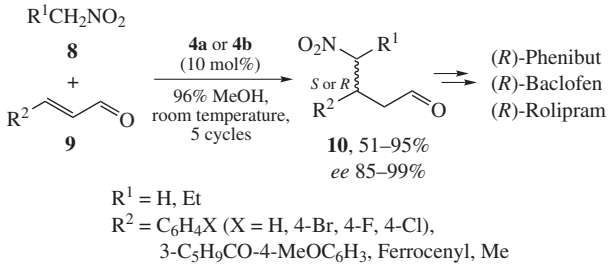
Extremely interesting results have been recently obtained in the area of asymmetric catalytic synthesis, including the synthesis of nitro compounds, in the presence of small chiral organic molecules (organocatalysts).[23] Among the most efficient organocatalysts for the enantioselective reactions of nitro alkanes and nitro alkenes are α,α-diarylprolinol silyl ethers[24] and bifunctional chiral tertiary amines containing thiourea[25] or squaramide units[26] (Scheme 3).



Scheme 3

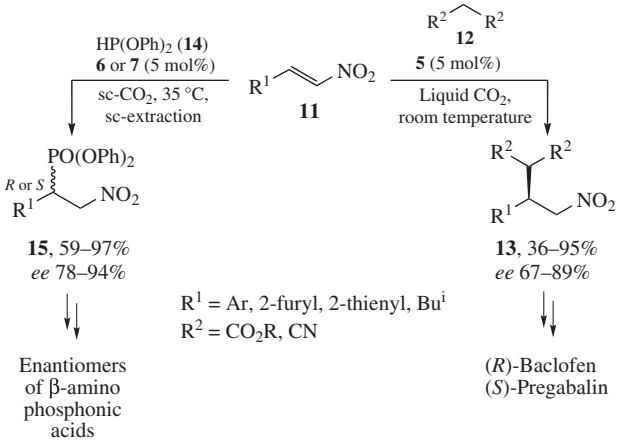
Zlotin and co-workers developed a unique recyclable hybrid organocatalyst **4** for asymmetric Michael reactions in which the diarylprolinol-derived core is attached to an ionic liquid unit.[27] In the presence of pseudo-enantiomeric catalysts **4a** or **4b**, nitroalkanes **8** and α,β-enals **9** stereo-divergently generated (*S*)- or (*R*)-enantiomers of γ-nitroaldehydes **10** with enantioselectivity of up to 99% *ee*. Compounds (*R*)-**10** serve as key intermediates for the preparation of the most active (*R*)-enantiomers of the drugs baclofen, rolipram, and phenibut, which are used to treat CNS disorders (Scheme 4).

The same research group suggested an approach to the recovery of precious chiral organocatalysts based on performing asymmetric reactions in liquid or supercritical (sc) carbon dioxide, which is an attractive substitute for non-renewable hydrocarbon-derived organic solvents and provides facile removal and recycling. Bifunctional-tertiary-amine-**5**-catalyzed reactions of α-nitroalkenes **11** with carbon acids **12** in liquid CO_2 enantioselectively afforded the corresponding Michael adducts **13**. Some of these products represent precursors of the therapeutically useful $GABA_B$



Scheme 4

receptor agonist baclofen and a chiral anticonvulsant pregabalin[28] (Scheme 5). The sc-CO_2 method was very useful in squaramide-catalyzed (**6** or **7**) asymmetric additions of P-nucleophiles **14** to α-nitroalkenes **11**, where both enantiomers of β-nitrophosphonate **15** precursors of bioactive β-amino phosphonic acids were generated with promising enantioselectivities (Scheme 5).[29] Importantly, products **15** were isolated from the reaction mixture by fractional extraction with sc-CO_2, indicating significant potential in terms of green chemistry.



Scheme 5

To summarize, N–O molecular systems open many possibilities in the development of new pharmaceutical ingredients whose biological action is based on their ability to generate nitrogen oxide or inhibit undesirable enzymatic reactions in living organisms. Monocyclic 1,2,3,4-tetrazene-1,3-dioxides, TDO, fused with pyridine or pyrazine structural fragments, and alkylidene- or arylidene-bis(1-alkoxytriazene-2-oxides) contain a significant amount of NO per unit mass and can be considered very promising NO donors. A possible life-science-oriented direction of furoxan chemistry involves the elaboration of carefully designed pro-drug molecules capable of releasing a precisely controllable amount of nitrogen oxide. Highly efficient and useful to industrial applications stereo- and enantioselective synthesis of polyfunctional nitro compounds (precursors of demanding drugs) still remains a challenge.

Bioorganic molecular and hybrid systems

The highest level of complexity and variable functionality is found in bioorganic frameworks. The structure of biomolecular systems is characterized by the presence of natural compound units such as proteins and oligopeptides, oligosaccharides and polysaccharides (often referred to as glycocompounds), steroids, and lipids, among others. The development of biomolecular systems is mostly stimulated by the demand for novel biomedical and pharmaceutical agents to satisfy the need for materials with improved functional properties. Carbohydrate-based molecular systems that contain glyco or glycomimetic[30] ligands are of

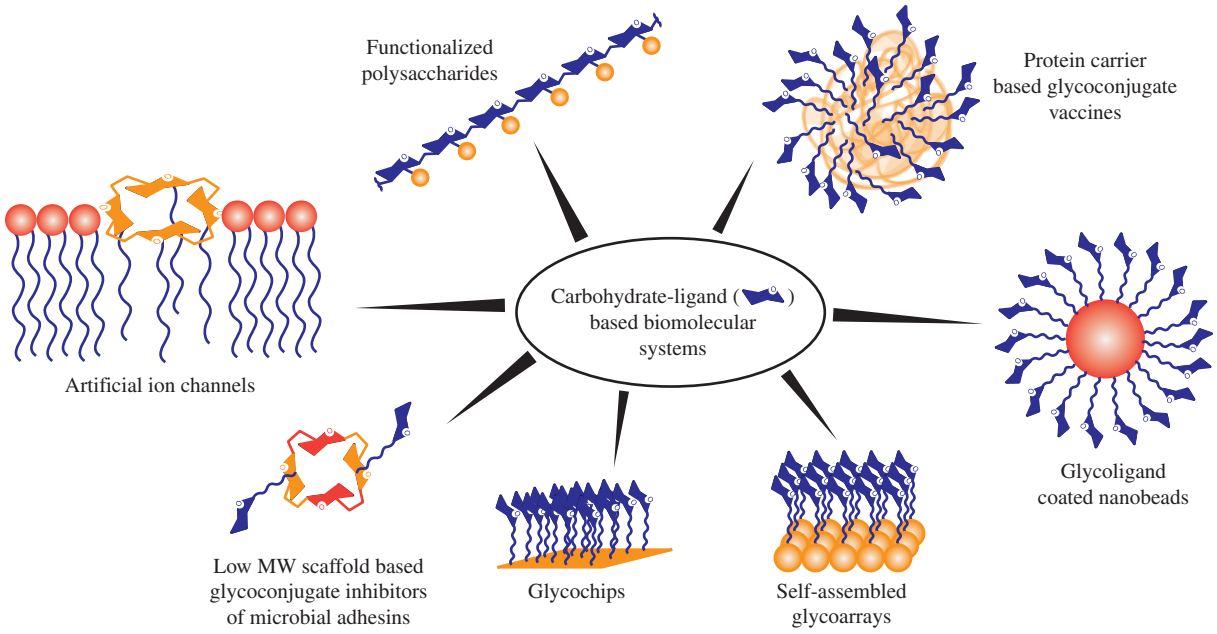


Figure 1 Examples of recently synthesized biomolecular systems containing function-specific carbohydrate ligands.

particular interest in current investigations. This interest is justified not only by the fact that carbohydrates are the most abundant class of natural molecules but also by the biological activity exhibited by extracellular carbohydrates and the key biological role they play in the course of a variety of known and new diseases.

The design and interdisciplinary study of different glycoclusters, glycopolymers and glycoassemblies are therefore being intensively pursued.[31] Numerous types of glycoconjugates are known (some of them are schematically depicted in Figure 1); they differ in their linking topology between various scaffolds (carriers) and carbohydrate ligands. In the case of molecular systems with a polymeric base, describing their precise spatial organization is difficult; therefore, they are evaluated as average structures. In contrast, the use of low-molecular-weight scaffolds enables the design of molecular systems with distinct structure and desired 3D architecture when appropriate carriers and connecting moieties (*i.e.*, spacers and linkers) are involved.

Artificial ion channels represent an example of recently synthesized biomolecular systems that enable ion-transport activity to be tuned by changing the size of their cyclooligosaccharide core.[32] Other exciting examples of biomolecular systems include protein-carrier-based glycoconjugate vaccines,[33] agents mediating protection of an organism against diverse prokaryotic and eukaryotic pathogens,[34] (carbohydrate ligand)-to-(α-galactosylceramide) conjugates as protein-carrier-free glycoconjugate vaccines,[35] multipartite oncovaccines,[36] glyco-clustered vectors for therapeutic siRNA delivery,[37] 3D pre-organized blockers of oligodentate bacterial adhesins,[38] stoichiometric[39] and polyanionic polysaccharide[40] chelators of ^{99}Tc and other tracers for tomography, coating ligands for nanobeads and glycoarrays[41] based on different technological platforms, artificial receptors for high-throughput screening (HTPS),[42] self-assembled ensembles,[43] asymmetric catalysts[44] and other high-technology drugs and materials. The further design of these and other sophisticated products is influencing future trends and challenges in the development of biomolecular systems.

Hybrid nanomaterials for catalysis and environment protection

In modern organic synthesis, the preparation of biologically active molecules and drugs is often based on selective catalytic approaches. Progress in catalysis and nanomaterials has changed the paradigm of modern chemical sciences toward cost-efficient and waste-free processes. The development of innovative, more efficient nanomaterials *via* molecular design is currently of great interest. Most of the available approaches to the preparation of nanomaterials (such as 'top-down' methods) are not capable of creating nano-engineered materials composed of a few hierarchical levels. In particular, materials that include sub-nanosized components built in the intrinsic architecture, which, in turn, may exhibit several levels of structural and functional organization, deserve attention. A wide range of hybrid materials, including purely inorganic systems as well as organo-inorganic materials and mixed organic structures, are being designed to satisfy the requirements of modern applications, including catalysis, energy conversion/harvesting, environmental protection, *etc.*[45,46] The application of such materials should result in further economy of energy, natural resources, and especially critical metals (noble metals, lanthanides, lithium), and the efficiency and functional properties of such materials should be enhanced because of the synergy between subnano- and nano-components and specific arrangements/organizations of structural units, modules and ingredients. The future use of hybrid nanomaterials should allow a leapfrog step forward in the robust and sustainable conversion of energy carriers (*e.g.*, biomass, hydrogen, electrochemical devices, photovoltaics). This advancement will, in turn, lead to socio-economic effects related to pollution control in air, water and soil, better waste utilization, and the production of environmentally safe fuels and energy to meet the growing needs of future generations.

The hybrid materials of great diversity are of particular interest for the application in catalysis and adsorption.[47,48] Here, we define hybrid materials as new architectures of one nano-engineered structure built in or intergrown with another nano-engineered structure. These structures may be a combination of two or more inorganic structures, two or more organic structures, or any combination of both. Following the above definition, a structure consisting of a strictly ordered system of nanopores built within an organized structure of mesopores may therefore also fit the definition of a hybrid material, even though the chemical composition of the material may be the same and uniform.

In the case of adsorption, we consider gas storage (CO_2, H_2, CH_4 *etc.*), the purification of air and water from ecotoxicants such as chlorinated compounds and heavy-metal ions, and membrane materials providing molecular recognition and selectivity capable

of distinguishing between very similar molecules (such as ethane/ethylene or CO/CO_2). Core-shell or decorated nanoparticles with tunable size and morphology, presumably encapsulated into hierarchical matrices or structured carriers, represent unique hybrid materials with great potential in these applications. Of particular interest is a new class of organo-inorganic hybrid materials known as metal-organic frameworks (MOFs), which exhibit zeolite-like structures with inorganic nodes linked to organic moieties. These unique materials can be 1D, 2D or 3D structures, including micro- and meso-porous systems with surface areas as high as 5500 m^2 g^{-1} and pore volumes up to 2 cm^3 g^{-1}, far beyond the parameters of zeolites (500–600 m^2 g^{-1}, 0.4 cm^3 g^{-1}) and carbon (~1000 m^2 g^{-1}, ~1 cm^3 g^{-1}).[49]

The literature contains numerous examples of the combination of two or more nanomaterials into one final hybrid system, resulting in synergy and an enhancement of useful properties (activity in catalysis, adsorption capacity, *etc.*) compared to those of the individual nanomaterials. The overall number of available organic building blocks suitable for the tailored design of hybrid materials is enormous; therefore, the number of combinations of inorganic and organic nano-sized moieties or structural units is beyond the limits of our imagination.

Although the chemistry of hybrid materials and their application to catalysis and adsorption is still in the early stages, several examples of fascinating performance from such materials have already been reported. For instance, MOFs have been evaluated in real on-board tests in methane-fueled cars[50] as methane storage adsorbents capable of holding up to 190 v/v (STP) of methane.[51] The same hybrid materials are being investigated for use in drug delivery,[52] hydrogen storage,[53] and CO_2 capture.[54]

Some hybrid materials composed of an inorganic matrix and encapsulated organic molecules or clusters can be used as photochromic or electrochromic materials (*i.e.*, materials that change color upon irradiation with light or upon the application of an electrical current), whereas others are used as coatings to improve mechanical properties, aerodynamic and hydrodynamic characteristics and resistance to thermal shock and mechanical impact. In some cases, such coatings exhibit hydrophobic properties. Another vast area of application for hybrid nanomaterials is medicine, specifically implants because of their excellent mechanical properties and good biocompatibility.

Hybrid materials can be (1) structurally hybridized, (2) functionally hybridized or (3) systems with chemical bonding between components. Quantum effects play a critical role in the manifestation of component synergy in hybrid materials. The morphology (shape and 3D architecture) of nanoparticles that compose hybrid systems is also of utmost importance in the design of effective materials. Their shape can range from spheres to discs, nanotubes, nanorods, or more complicated shapes (*e.g.*, stars, embedded cylinders, cones, *etc.*).

The application of hybrid systems containing metal or oxide nanoparticles in catalysis, adsorption, and environment protection, especially those with core-shell particles or nanoparticles decorated with subnanoparticles, is promising because proper design will result in the enhancement of activity, selectivity, and stability in addition to a decrease in production costs.

The preparation of hybrid materials can involve the entire toolbox of methods from organic, inorganic, and nanochemistry (the 'bottom-up' approach), including combinations of template synthesis, microwave-assisted processes, sol-gel chemistry, electrochemical processes, chemical vapor deposition, ionic liquids and supercritical fluids. This ongoing research is focused on the design and preparation of efficient and economically feasible hierarchical organo-inorganic hybrid materials and their application in catalysis, environmental protection, gas storage and many other areas.

Recently, monometallic and bimetallic nanoparticles of Fe, Cu, Ni, Ag, Au, Ru, Pt, Pd, Rh, and Ir, including core-shell and decorated nanoparticles supported on mesoporous and microporous carriers using diverse methods of preparation (*e.g.*, inter alia, microwave activation and the use of ionic liquids), have been studied.[55] The choice of carrier (MOF, MCM-41, SBA-15, sol-gel materials, hierarchical zeolites) plays a decisive role in the final performance of the catalysts.

A heuristic approach to the application of new designer materials allows a significant enhancement of the activity/selectivity in hydrogenation, hydroamination, ring-opening, and partial oxidation processes,[56] as well as in selective gas adsorption, storage, and the capture and separation of light gases (CH_4, CO_2, H_2, H_2S) using MOF-based nanomembranes.[57] The characterization of novel materials by structure-sensitive methods (SEM, TEM, EDS-SEM, HR-TEM, XPS, DRIFTS, XAFS, UV, plasmon resonance) and conventional adsorption methods (TPR/TPD, XRD, DTA/TG) has revealed the peculiarities and subtleties of the structures of synthesized hybrid materials.[58]

The use of microwave activation in the preparation of hybrid materials has proven to be efficient in our own research and in that reported in the literature.[59,60] Conventional thermal treatment typically leads to non-uniform materials, aggregates of nanoparticles and sintering. Microwave activation/reduction can result in milder pretreatment conditions and can be used to gently decompose metal complex precursors.

The use of resonance microwave mono-mode units and *in situ* treatments is of special interest. Conventionally, the operating frequency used for microwave treatments is 2.45 GHz, which is known to be not quite optimal for aqueous or organic solutions or for solid materials (oxides, carbonates, *etc.*). As a rule, the absorption efficiency of microwave energy is proportional to the square of the operating frequency; thus, increasing the operating frequencies to 4–11 GHz would enhance the microwave effects.[59]

Ionic liquids (low-temperature molten salts that typically contain an organic cation and an inorganic anion) have been used as benign solvents and reaction media for the production of unique hybrid nanomaterials. Most nanoparticles prepared in ionic liquids are monometallic (Pd, Cu, Au) and exhibit a uniform size and morphology. Ionic-liquid solvents provide outstanding stabilization possibilities for diverse nanomaterials because of the high solubility and compatibility of different types of precursors in ionic liquids. Furthermore, ionic liquids absorb microwave energy better than water, and this effect can be exploited to prepare hybrid materials. The combination of the unique properties of ionic liquids and the advantages of electrochemical methods have enabled the synthesis of original materials such as high-temperature metals (Re, W) deposited onto conductive polymers, also known as 'shark skin' materials (oxide nanotubes grown at the surface of a metal such as Ti, Ni, Cu, or steel).[61]

To summarize, innovative hybrid materials will definitely find roles in new material design, catalysis, and environmental protection, including the remediation of air, water and soil. Another intriguing area in the future commercialization of hybrid nanomaterials is medicine, including drug delivery, hyperthermia and cancer therapy (ferrite nanoparticles), and imaging (Au nanoparticles). A demanding market also exists for energy harvesting, conversion, and storage systems, where new, inexpensive nanomaterials (perhaps in combination with electrochemically stable ionic liquids as electrolytes) may be used in fuel cells, photovoltaics, supercapacitors, and photoelectrochemical devices.

Structure of complex molecular systems and mechanistic studies of chemical transformations

This part of our initiative is aimed at the development of a unified concept for studies of complex molecules and their trans-

formations. Real-time monitoring of molecular arrangements, structural dynamics and chemical reactions in organic and hybrid molecular systems will combine the techniques described in the aforementioned organic, bioorganic and nanomaterial investigations. To achieve this goal, an unprecedented comprehensive approach is required to investigate the structures of single molecules, molecular associates and complex molecular systems in liquid and solid states. Carefully designed experiments utilizing NMR spectroscopy, high-resolution mass spectrometry and electron microscopy are expected to provide the necessary level of structural insight. Such an approach will allow thorough investigations of chemical transformations (both in solution and on nanoparticle surfaces), dynamic processes in bioorganic and hybrid molecular systems, and interactions in bioorganic systems in a real time.

To achieve these challenging aims, we have undertaken the development of a target-oriented approach that combines the most powerful analytic tools (Table 1).[62] NMR spectroscopy is a well-known tool for the analysis of both liquid-state and solid-state samples. Mass spectrometry is a very powerful technique for the detection of ions in the gas phase, whereas ionization in solution and in the solid state is also a well addressed area. The combination of NMR/MS studies is standard in modern research, although care should be taken in mechanistic investigations because of large differences in the detected concentrations of reactive species.[63] In contrast, electron microscopy is mostly suitable for surface characterization, with only few exceptions for direct liquid-phase analysis. State-of-the art analytic measurements call for the development of a flexible NMR-MS-microscopy approach for the study of complex molecular systems and reaction mechanisms. Indeed, the evolution of analytical methods is one of the leading driving forces in the advancement of chemical science in recent decades.[62] An important point in this regard is the rapid progress in the miniaturization of analytic systems and enhancements of their detection limits.[64]

Table 1 Target-oriented map of areas of application for the considered analytical methods in molecular and hybrid systems.[62]

Chemical system	NMR Spectroscopy	Mass spectrometry	Electron microscopy
Gas-phase studies	Some applications	Many applications	—
Solution-phase chemistry	Many applications	Some applications	Limited applications
Solid-state systems	Many applications	Some applications	Many applications

Improvements to modern hardware have noticeably expanded the borders of structural investigations of complex molecular frameworks. The key achievements involve direct measurements in neat chemical systems, thus avoiding model approximations that often impose ambiguous speculation. Even highly complex reaction media, such as neat biological systems, ionic liquids, supercritical fluids, *etc*., are now within the range of capability of analytic measurements and mechanistic studies.

As a representative example, direct analysis of an ionic liquid has been carried out using NMR spectroscopy and mass spectrometry (Figure 2).[65,66] Ionic liquids represent a unique reaction media that combines several important advantages. However, as solvents, they are rather complex systems with known difficulties in carrying out high-precision analytic measurements.[67] The development of a special setup for sample preparation and the optimization of parameters for spectral measurements has led to high-resolution NMR and MS data. This mechanistic approach was successfully utilized for the in-depth study of biomass conversion to platform chemicals, including the monitoring of a reaction in neat ionic liquid (Figure 2). The structure and composition of a dynamic multi-component system was revealed at the molecular level for the first time. Using an improved analytic protocol, even a subtle change in molecular structure was clearly detected on standard NMR hardware. This example shows that thorough mechanistic studies can connect different scientific fields, including carbohydrate chemistry, biomass conversion and ionic-liquid solvent effects. Similar examples have also been demonstrated in the field of catalysis of organic reactions.[68] Interdisciplinary study is the key to promoting fundamental science and to carrying out the initiative highlighted in this brief article.

Undoubtedly, insights into the mechanistic data will guide the optimization of catalysts and reaction conditions to further

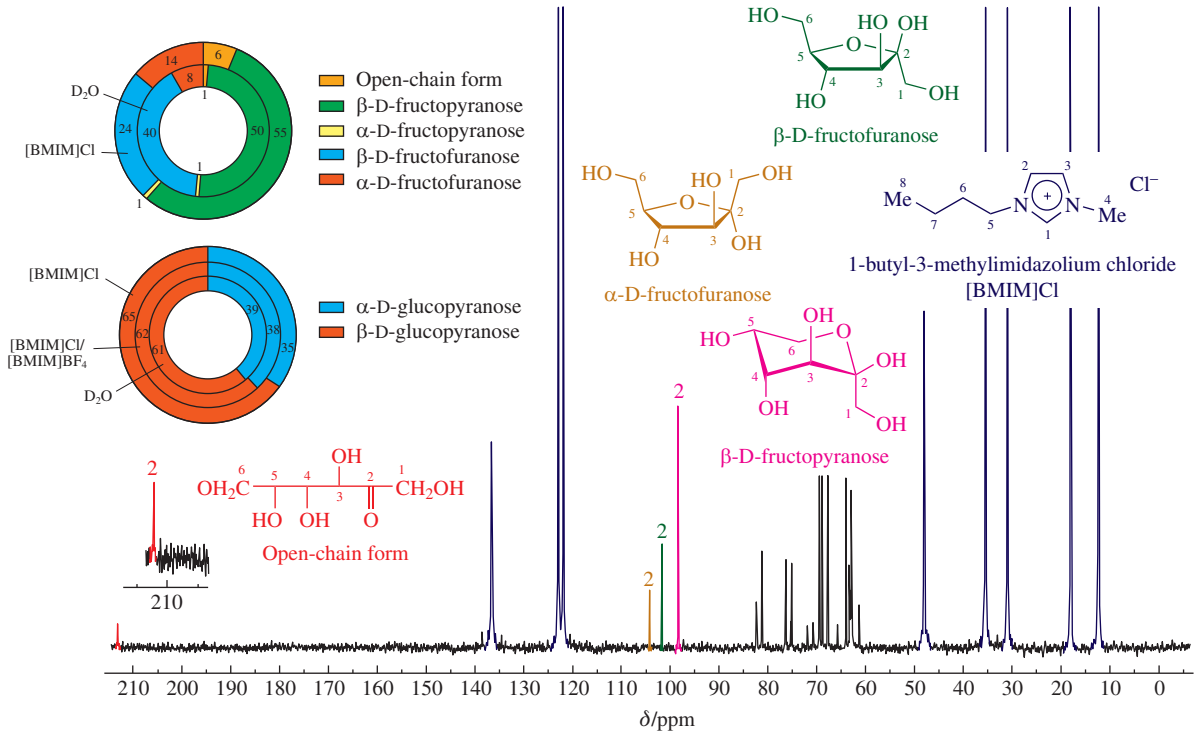


Figure 2 Structural study of complex molecular frameworks in neat ionic-liquid media.

improve their activity and selectivity. Structural studies in bio-organic systems will provide valuable information about three-dimensional molecular arrangements. The key point for bio-molecular systems concerns the estimation of binding efficiency between bioligands and receptors for the rational improvement of molecular architectures to obtain more selective binding.

Conclusions

Organic compounds will remain the fundamental core for the anticipated development and advancement of molecular sciences in the near future. The outstanding diversity of organic molecules and the flexibility of their synthetic methods will govern the efficient production of task-specific components for complex hybrid systems.

In biomolecular studies, the demand for further progress in the production of new materials and functional compounds encourages the development of new approaches in the design of 3D organized organic and hybrid substances. In particular, molecular systems with active components and a carrier whose spatial arrangement manages new and advanced functional properties are of great interest. The most efficient design of molecular systems is associated with the development of products for high-technology applications, including pharmaceutical substances, vaccines, bioligand-based chips and arrays, nano-sized tracers and beads, organic catalysts, and functionalized polymers, among others.

Hybrid nanomaterials and their applications in catalysis, gas capture, sensors, membranes, energy production and storage systems are expected to reach a point of cost-efficient commercialization. The rational application of such materials will have a substantial impact on industry and high-technology sectors, with all these features being translated into social, economical and environmental benefits.

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