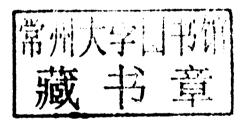
# Molecules at Work

Self assembly, Nanomaterials, Molecular Machinery GESELLSCHAFT RSC | Advancing the Chemical Sciences

### Edited by Bruno Pignataro

### Molecules at Work

Selfassembly, Nanomaterials, Molecular Machinery





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#### **Preface**

In addition to the traditional core areas of chemistry, the international trends record a growing development of those areas of chemistry that are multi- and cross-disciplinary, dealing more and more with recent challenges and opportunities in chemistry.

The aim of the most advanced meetings in chemistry is often to have a better quality of life for all people and to showcase knowledge, advanced products, and services that improve the efficiency of chemical professionals, the local and global environment, and our well-being. The central subject is chemistry, technology, and our global society for future "health" and sustainability. As shown in the last conference of the European Association for Chemical and Molecular Sciences – 3rd EuCheMs Chemistry Congress in Nuremberg (29 August to 2 September 2010) – chemistry is considered "a creative force" and the scientists are convinced that it will give shape to the future.

A particular trend of the general roadmap of chemistry (see, for instance, the document "Chemistry: Developing Solutions in a Changing World" produced by EuCheMs) is related to the fact that the advancement in molecular design and its control becomes more and more finished. Chemists engineer their synthetic products more and more on the molecular scale exploiting and guiding in an increasing controlled way not only the strong bond but also the weak bonds ( $\pi - \pi$  interaction, metal–ligand coordination, hydrogen bonds, hydrophobic interactions, van der Waals interactions, etc.). This often also aims to close the gap between synthetic and natural products. Nature, in fact, still has a lot of things to teach us for preparing useful chemical systems. This even if we must here stress the fact that those systems chemists can create may have characteristics or properties that are present or not in nature!

Present efforts are directed at overcoming self-assembling and obtaining a control on the kinetic instability of the covalent architectures going from the self-assembling to the far-from-equilibrium self-organization. This is in order to have molecular superstructures with particular well-defined conformations and, therefore, functions.

In agreement with another current development in chemistry, the advancements in understanding the phenomena and behaviors at the molecular level continue to increase the tendency to look, in a more and more different way, to the properties and reactions of the chemical systems. This helps to throw further bridges between Chemistry and other disciplines such as Molecular Biology, Electronics, or Material Science. The power of the synthetic methods in order to obtain, for example, new functional nanoparticles is now well documented and the products of such synthetic efforts embrace a large spectrum of sophisticated applications such as gene transfection, catalysis, lithium storage, or sensors and, in general, materials science and technology for a variety of applications.

In addition, learning also from the behavior of green plants, a research line is developing molecular photovoltaic devices having power conversion efficiencies of the order of 10%. This brings us closer to identifying "environmentally friendly" solutions for the world energy problem.

Another very important international trend follows from the fact that new discoveries and technological advancements improve our capacity to obtain better and better spatial, temporal, and energy resolutions. This is for one of these quantities alone or for these quantities in combination. In various fields we are close to the achievement of physical limits. One of the most astonishing recent achievements, which exploit these improved capacities, is, for instance, that reported by Paul Corkum, who launched at Ottawa the attosecond science. These researches have shown that we can measure electronic orbitals and we might film the orbital modification during a photochemical reaction. This area of research then passes from the femtochemistry led by Ahamed Zewail, allowing for the production of movies of the rupture and formation of chemical bonds, to this type of measures where theory and experiment are more and more interwoven. In addition, today we have the ability to measure smaller and smaller weights or other physical quantities. Indeed, picojoules, piconewtons, fractions of nanometer, femtograms, femtoamperes, and kilodaltons are quantities that are measured in our laboratories with always increasing facility and reliability.

Moreover, ongoing from the nanoscopic to the macroscopic and to complex systems, the number of data that computers are able to manage continues to increase in a dramatic way. The impact of computational methods has become extraordinarily important in the development of science and technology. Simulations that were unthinkable a few years ago are now possible and allow us to start thinking about extremely complex predictions.

Just as a reference, in the frontier area with Life Sciences the challenges that chemists had sought a few years ago seem less and less ambitious and it appears more and more clear that chemistry plays an essential role in understanding life itself.

This book is placed in this international scenario. In particular, it represents one of the two books comprising contributions of selected scientists from the last edition of the European Young Chemist Award (EYCA 2010) presented during the 3rd EuChemS Chemistry Congress. It is aimed to cover the generic area of functional molecular and supramolecular materials, while the other encloses contributions from the area of synthetic chemistry and is entitled "New Strategies in Chemical Synthesis and Catalysis."

As for EYCA 2010, it was the third time this Award has been given. The aim of EYCA is to showcase and recognize the excellent research being carried out by young scientists working in the chemical sciences. In particular, it is intended to honor and encourage younger chemists whose current research displays a high level of excellence and distinction. It seeks to recognize and reward younger chemists (less than 35 years old) of exceptional ability who show promise for substantial future achievements in chemistry-related research fields.

The applications presented by the best candidates during the two previous editions of the Award were so stimulating that together with Wiley, EuCheMs, SCI, RSC, and GDCh I decided to collect them into books. Thus, from the first edition of the Award was published the book "Tomorrow's Chemistry Today: Concept in Nanoscience, Organic Materials, and Environmental Chemistry" (Wiley 2009), and from the second edition the three books (Wiley 2010) entitled "Ideas in Chemistry and Molecular Sciences: Advances in Synthetic Chemistry," "Ideas in Chemistry and Molecular Sciences: Where Chemistry Meets Life," and "Ideas in Chemistry and Molecular Sciences: Advances in Nanotechnology, Materials and Devices."

The work from this third edition of the Award was once more very stimulating and again pushed by Wiley, EuCheMs, SCI, RSC, and GDCh, I planned to collect the best contributions into two other books.

The scientific standing of the award applicants was undoubtedly very high and their research achievements are remarkable, especially in relation to their young age. A few figures help to substantiate this point. About 45% of the applicants have been chosen to give an oral contribution to the Nuremberg Congress. In the CV of the participants one can find that the candidates have about 60 papers in peer-reviewed international journals and are guiding a group of more than 20 PhDs and Post Docs, or their work got more than 1500 citations. The publication lists of most applicants proudly noted the appearance of their work in leading general science/chemistry journals such as Science, Nature, Angewandte Chemie, Journal of the American Chemical Society, and so on or the best niche journals in the fields of organic, inorganic, organometallic, physical, analytical, environmental, and medicinal chemistry. Several participants have been granted different prizes, have been invited to give lectures, and achieved further recognitions such as front-end covers, hot articles, or highlights in top journals. Moreover, reading the application documents it comes out clearly that many of the competitors have different scientific interests and do have very exciting ideas for their future work. Further support for the applications, and a testament to the very high quality of the competitors, was apparent from the comments contained in the often very effusive recommendation letters from a number of eminent scientists. A flavor of these from the applications received can be found in the guest editorial published by Chemistry: A European Journal (vol. 16 (2010), pp. 13888-13893), where I reported many other details of the quality of the participants and of the whole Award Competition.

This is the pool from which I fished the contributors of this book.

In fact, the book gives an account of the most recent results of research in self-assembly, nanomaterials, and molecular machinery, based on a selection by upconversion, ligands of metal ions, substrates for self-assembly, or photoswitchable hosts.

Also, in connection with the fact that the approaching technology platforms for green fuel production require advanced molecular-separation processes for recovering liquid biofuels (biomethane, hydrogen), Chapter 9 reviews the state of the art and gives the perspectives for the fabrication and utilization of ultramicroporous silica membranes for gas-separation and pervaporation processes.

Chapter 10 reports on how nanotechnology can revolutionize both in vitro and in vivo cancer diagnostics, improving drug delivery in anticancer therapy. This chapter gives a historical approach to the development of metal-based drugs and hybrid materials consisting of nanostructured materials and metal complexes for anticancer therapy.

Part III consists of six chapters dealing with molecular machinery.

Chapter 11 is connected to the fact that the rate of diffusion of a species is of fundamental importance in the processes nurturing life since living organisms have evolved a complex intracellular machinery that relies on diffusion as the rate-determining step to bring chemicals together to meet the biological requirements. Thus, any changes in viscosity at both the cellular and the organism level can have catastrophic consequences, and many such changes can be directly linked to disease and malfunction in humans. This chapter shows the recent investigations using fluorescent molecular rotors as accurate tools to measure in vivo and in vitro viscosity in a wide range of biological environments, including those within a living cell.

In Chapter 12, the authors show the potential of chemically synthesized and organic-coated NCs in creating functional materials to be effectively integrated in systems and devices on the mesoscale. They have highlighted how the advancement of chemical routes in synthesizing NCs with unique optoelectronic properties and surface chemistry, together with their effective manipulation as macromolecules, has endorsed the increase in strategies for patterning them in mesostructures with defined properties on multiple length scales.

Chapter 13 gives an overview of the application of fullerene as a fluorescent sensor for oxygen and temperature, mainly in connection with the fact that there is a distinct lack of dual sensors covering high temperatures (above 70 °C) and ultralow oxygen concentrations (parts per billion).

Boronic acids and their tremendous potential as molecules at work in various fields of chemistry in the past 60 years is the subject of Chapter 14. Going beyond glucose sensing, this chapter addresses the problem of achieving selectivity for glucose with boronic acid receptors in solution-phase sensor arrays. These powerful sensor arrays have been established for neutral and anionic carbohydrates under physiological conditions. Finally, the use of these probes in novel, label-free fluorescent assays for carbohydrate-modifying enzymes demonstrates boronic acid molecules at work in a future biotechnology application.

In Chapter 15, different strategies to design iridium ionic transition-metal complexes (Ir-iTMCs) for highly efficient and stable light-emitting electrochemical cell (LEC) devices have been described. Indeed, the obtained results confirm that iTMC-based LECs are a promising technology for lighting applications. Nevertheless, these findings have been obtained by using different iTMCs in LECs. Hence, the main target for the future is to join all these strategies in only one iTMC.

The systems described in Chapter 16 show that, in the frame of supramolecular photochemistry, the design and construction of nanoscale devices able to perform useful light-induced functions can be attempted. Switches, logic gates, or molecular machines (threading-dethreading motions, molecular shuttles) are discussed there.

The readership of the book is aimed at the advanced and specialists level. It should be relevant to both readers from academia and industry since it deals with fundamental contributions and possible applications. I feel the audience that needs this book consists of chemists and also physicists and engineers interested in nanoscience, nanotechnology, materials, and devices.

As I have done for the other books in this series, I cannot finish this preface without acknowledging all the authors and all the persons who helped and supported me in the project. I thank Prof Giovanni Natile, Prof Francesco De Angelis, Prof Luigi Campanella who, as Presidents of the Italian Chemical Society and/or EuCheMs representatives, strongly encouraged me during the years in this activity. And of course, I thank all those Societies (see the book cover) that motivated and supported the book.

Palermo January 2012 Bruno Pignataro

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