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Ideas in Chemistry and Molecular Sciences

Advances in Synthetic Chemistry

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Bruno Pignataro



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Preface

The idea of publishing books based on contributions given by emerging young chemists arose during the preparations of the first EuCheMs (European Association for Chemical and Molecular Sciences) Conference in Budapest. In this conference I cochaired the competition for the first European Young Chemist Award aimed at showcasing and recognizing the excellent research being carried out by young scientists working in the field of chemical sciences. I then proposed to collect in a book the best contributions from researchers competing for the Award.

This was further encouraged by EuCheMs, SCI (Italian Chemical Society), RSC (Royal Society of Chemistry), GDCh (Gesellschaft Deutscher Chemiker), and Wiley-VCH and brought out in the book “Tomorrow’s Chemistry Today” edited by myself and published by Wiley-VCH.

The motivation gained by the organization from the above initiatives was, to me, the trampoline for co-organizing the second edition of the award during the second EuCheMs Conference in Torino. Under the patronage of EuCheMs, SCI, RSC, GDCh, the Consiglio Nazionale dei Chimici (CNC), and the European Young Chemists Network (EYCN), the European Young Chemist Award 2008 was again funded by the Italian Chemical Society.

In Torino, once again, I personally learned a lot and received important inputs from the participants about how this event can serve as a source of new ideas and innovations for the research work of many scientists. This is also related to the fact that the areas of interest for the applicants cover many of the frontier issues of chemistry and molecular sciences (see also *Chem. Eur. J.* 2008, **14**, 11252–11256). But, more importantly, I was left with the increasing feeling that our future needs for new concepts and new technologies should be largely in the hands of the new scientific generation of chemists.

In Torino, we received about 90 applications from scientists (22 to 35 years old) from 30 different countries all around the world (*Chem. Eur. J.* 2008, **14**, 11252–11256).

Most of the applicants were from Spain, Italy, and Germany (about 15 from each of these countries). United Kingdom, Japan, Australia, United States, Brazil, Morocco, Vietnam, as well as Macedonia, Rumania, Slovenia, Russia, Ukraine, and most of the other European countries were also represented. In terms of applicants, 63% were male and about 35% were PhD students; the number of

postdoctoral researchers was only a small percentage, and only a couple of them came from industry. Among the oldest participants, mainly born between 1974 and 1975, several were associate professors or researchers at Universities or Research Institutes and others are lecturers, assistant professors, or research assistants.

The scientific standing of the applicants was undoubtedly very high and many of them made important contributions to the various symposia of the 2nd EuCheMs Congress. A few figures help to substantiate this point. The, let me say, “*h* index” of the competitors was 20, in the sense that more than 20 applicants coauthored more than 20 publications. Some patents were also presented. Five participants had more than 35 publications, and, *h* indexes, average number of citations per publication, and number of citations, were as high as 16, 35.6, and 549, respectively. Several of the papers achieved further recognition as they were quoted in the reference lists of the young chemists who were featured on the covers of top journals. The publication lists of most applicants proudly noted the appearance of their work in the leading general chemistry journals such as *Science*, *Nature*, *Angewandte Chemie*, *Journal of the American Chemical Society*, or the best niche journals of organic, inorganic, organometallic, physical, analytical, environmental, and medicinal chemistry.

All of this supported the idea of publishing a second book with the contributions of these talented chemists.

However, in order to have more homogeneous publications and in connection to the great number of interesting papers presented during the competition, we decided to publish three volumes.

This volume represents indeed one of the three edited by inviting a selection of young researchers who participated in the European Young Chemist Award 2008. The other two volumes concern the two different areas of nanotechnology/material science and life sciences and are entitled “Ideas in Molecular Sciences: Advances in Nanotechnology, Materials and Devices” and “Ideas in Chemistry and Molecular Sciences: Where Chemistry Meets Life, respectively.”

It is important to mention that the contents of the books are a result of the work carried out in several topmost laboratories around the world both by researchers who already lead their own group and by researchers who worked under a supervisor. I would like to take this occasion to acknowledge all the supervisors of the invited young researchers for their implicit or explicit support to this initiative that I hope could also serve to highlight the important results of their research groups.

The prospect of excellence of the authors was evident from the very effusive recommendation letters sent by top scientists supporting the applicants for the Award.

A flavor of these letters is given by the extracts from some of the sentences below: “Excellent chemist, who has outstanding synthetic skill”; “He was a very creative and dedicated, but at the same time a highly practical and pragmatic researcher”; “The candidate was one of the best associates that I have had in my career”; “. . . has extraordinary laboratory skills and manages to obtain high quality data as a result of careful experimentation”; “The candidate is thoughtful, thorough, and insightful in chemical judgments”; “I believe that he will someday become a leader in the

field”; “The skills of the candidate are such that could contribute to many facets of organic chemistry”; “... has outstanding quality and intellectual capacity”; “I have no doubt about him to become a major contributor to the chemistry of the first half of the XXIst century”; “The candidate has proven to be a most dedicated, enthusiastic and productive chemist”; “He is a first rate organic chemist”; “... has a keen intellect”; “He is a leader and outstanding researcher”; “The work of the candidate is characterized by its quality as well as its breadth”; “He has an exceptionally strong publication record and has already won several awards”; “The candidate was an exceptional talented young scientist”; “The pioneering research of the candidate resulted in a number of paper in top journals”; “He performed the research in a professional and highly independent manner and was highly capable of guiding young students during their research projects”; “The exceptional talent is further illustrated in the large number of projects and grants he was involved in”; “It is my firm opinion that he has the capabilities to soon become one of the leaders of the new generation of chemists in Europe”; “One of the most promising young scientists of his generation worldwide. I believe that he has the drive, creativity, and track record of accomplishment that suggest the candidate himself is highly worthy of the European Young Investigator Award”; “Is a very brilliant young researcher”; “With such diversified capability he is able to create and expand the research topic of own interest.”

The content of the first part of the volume is largely dedicated to catalysis and catalytic processes including the very important and hot field of organocatalysis. For example, taking into account that the oxidation of organic compounds is one of the most important transformations of chemistry with fundamental involvements in many areas (general synthesis, industrial processes, materials, energy, biology, etc.) and that nowadays, the ecological standards require the development of new catalytic processes characterized not only by oxidant economy, but also by environmental benignity under mild conditions, one contribution (Punta *et al.*) refers to the case of *N*-hydroxyderivatives as organocatalysts for the selective free radical aerobic oxidation of organic compounds. Following the author’s suggestion it is hopeful that this synthetic route will soon become a “winning industrial process.” In another chapter (Fernández Rodríguez) the gold-catalyzed reactions of push–pull conjugated diene are highlighted, while the lithiation of tertiary amines as a powerful tool for the building block processes in organic synthesis (Gessner) is the theme of another stimulating chapter. In particular, this last chapter gives an overview of nitrogen ligands in the coordination chemistry of organolithium compounds with special focus on the direct deprotonation of tertiary amines to α -lithiated species. A combination of structure elucidation and computational studies gives insight into mechanistic features and observed selectivity. The process and selectivities are explained by means of the spatial proximity of reactive groups in intermediate, precoordinated adducts of the amine, and the organolithium compounds according to the complex-induced proximity effect.

A further contribution (Díez-González) is dedicated to the field of copper-catalyzed transformations using *N*-heterocyclic ligands. In particular,

recent results concerning Click Chemistry along with related mechanistic studies are highlighted in this chapter.

In the last paper of this area (Giacalone *et al.*) the following cases are reviewed: (i) L-proline or H-Pro-Pro-Asp-NH₂ supported on ionic liquid-modified silica gels as recyclable catalysts for aldol reaction; (ii) polystyrene-supported proline as versatile and recyclable organocatalyst; and (iii) prolinamide-supported polystyrenes as highly stereoselective and recyclable organocatalysts for the aldol reaction.

In connection to the increasing relevance of the field, the second section of this volume is dedicated to the study of chemical interactions and reactions by predictive tools.

A chapter in this section (Marcelli) exploits the computational methods for the study and development of the organocatalysis field. This chapter, in particular, features a gallery of recent examples unraveling important mechanistic aspects of double hydrogen bonding organocatalysis in synthetically relevant transformations. In addition, some recent striking results in the development of novel types of double hydrogen bonding organocatalysts are briefly discussed. I am particularly happy to have a chapter like this in the book since, in agreement with the author, it seems reasonable to assume that, in the coming years, the importance of computational tools in the development of new catalytic systems is destined to grow. The results described in these pages significantly improved our understanding of organocatalytic reactions, often by pointing out important aspects that had been overlooked in the initial catalyst design. Together with the inexhaustible source of inspiration represented by enzymatic processes, the use of these mechanistic insights in catalyst design will likely result in significant progress toward the development of truly biomimetic organocatalytic systems.

Another stimulating chapter (Prins) in this section is dedicated to the molecular recognition area and the emerging strategy of the dynamic covalent capture. This very general concept is potentially applicable for different purposes. An important role of dynamic covalent capture is envisioned in areas where subtle noncovalent interactions are crucial, for example, in protein-protein interactions as well as in catalytic pathways and therefore for catalyst discovery.

Taking into account that (see also above) one of the most important challenges of synthetic chemistry lies in combining efficiency, reduced costs, and environmental impact in the production of relevant molecules for application in different areas such as pharmaceutical, food, agrochemistry, material chemistry, and energy resources, some contributions are particularly dedicated to this area.

The first chapter in this area (Dias *et al.*) deals just with the theme of environmentally important reactions. In this paper, after an overview of the applications of furfural and the reaction mechanisms of dehydration/hydrolysis of polysaccharides into furfural, some of the most relevant results on the use of solid acid catalysts in the conversion of saccharides (in particular, xylose) into furfural are discussed.

The second chapter (Coquerel *et al.*) in this area deals with ecocompatible organic synthesis, which, by the way, for the authors means being both economically as well as ecologically compatible. In this last chapter the idea that the next major evolution

in synthetic organic chemistry might be the control of multiple bond-forming transformations (MBFTs) is underlined and in particular the nonconcerted MBFTs are presented as reactions whose control would nicely combine with the now required criterion of *ecocompatibility*.

Given the great present concern on environment as mentioned above, a further chapter on modeling of the photochemical reactions in surface fresh water (Vione *et al.*) is dedicated to the ecology theme.

A modeling approach was presented to describe the indirect photolysis processes that can take place in surface waters, with particular emphasis on the reactions that involve OH, CO_3^- , and $^3\text{CDOM}^*$ (triplet states of photoexcited colored dissolved organic matter). The model allows the important assessment of the lifetime of dissolved compounds in water bodies, including hazardous xenobiotics, as far as the indirect photochemical processes are concerned.

The last contributions to the volume can be considered as a bridge between organic synthesis and material chemistry. In particular, the first one (Peña) deals with alternant polycyclic aromatic hydrocarbons (PAHs) that contain more than 10 fused benzene rings and have been prepared through organic synthesis. These bottom-up approaches used to obtain nanographene should now be addressed to prepare larger nanosized polyarenes and nanographenes with potential outstanding electronic properties.

In the second chapter of this section (Baudron), it is shown that the synthetic challenge that represents the elaboration of heterometallic architectures can be faced using a sequential construction strategy. The used ligands can be tuned with respect to the nature and relative arrangement of the coordination poles, having therefore a direct influence on the structure of the architectures. As it is underlined by the author, beyond the structural beauty of these systems, their physical properties (such as the optical and electronic properties) are of prime importance.

In the last chapter (Schmidt), the general properties and applications of perylene dyes are summarized. In this chapter, after an overview of water-soluble perylene dyes and their applications, chiral water-soluble perylene dyes are presented. Particularly interesting is the noncovalent strategy of SWNT functionalization. This strategy has the advantage of implementing multifunctional groups without compromising the main properties of SWNTs as opposed to usual covalent functionalization of this system, in the sense that the sp^2 carbon backbone is not altered.

The chapters of this book show, *inter alia*, that, as is written in one of the contributions (Coquerel and coworkers), “the only limitations to the exploration of the molecular world are the creativity of the chemist, and most importantly on a practical point of view, the major limitation is the current knowledge of the science of synthesis. In the current era, however, it is assumed that any three-dimensional molecular architecture, providing it is sufficiently stable, can be prepared by total synthesis (i.e., the laboratory construction of naturally occurring or designed molecules by chemical synthesis from simple starting materials) if the chemist has enough experience, knowledge, time, and money.”

I cannot end this preface without acknowledging all the authors and the persons who helped me in the book project together with all the societies (see the book cover) that motivated and sponsored the book. I'm personally grateful to Professors Giovanni Natile, Francesco De Angelis and Luigi Campanella for their motivation and support in this activity.

Palermo, October 2009

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