Edited by Bruno Pignataro

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Tomorrow's Chemistry Today

Concepts in Nanoscience, Organic Materials and Environmental Chemistry

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Edited by
Bruno Pignataro

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The Editor

Professor Bruno Pignataro
Department of Physical Chemistry
University of Palermo
Valle delle Scienze
90128 Palermo
Italy

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Preface

Contrary to the general image that chemistry has in public opinion, chemists are great observers, admirers, and lovers of Nature. Chemists have a relationship with Nature at a molecular level, learn from it, and attempt to copy its perfection and harmony. In their activities, chemists work to find solutions for human health; to widen the range of sustainable processes and materials; to prevent pollution and maintain the quality of climate; to devise clean, renewable energy sources; to preserve and restore the cultural heritage; and to develop new technologies for improving everyday life. Using synthetic processes and discovering and manipulating molecules, chemists are increasingly establishing a primary role within prominent interdisciplinary scientific and technological fields such as those of nanoscience, nanotechnology, and biotechnology. Alluding to precisely this great potential, "Long life to chemistry" said Jean Marie Lehn at the end of his plenary during the 1st European Chemistry Congress held in Budapest on 27–31 August 2006. This sentiment has to be related also to the fact that young chemists are producing new paradigms opening up excellent perspectives for future research.

The plan for this book was originated during the preparation of the European Young Chemists Award that I had the honor to chair and that was held during the First European Chemistry Congress. At that congress a number of young chemists showed the results of their research, presenting fascinating ideas and original conclusions and proposing radically new materials, molecules, supramolecules, and superstructures. About 120 chemists from all over the world, and all less than 34 years old, participated in the Award. According to the supporting letters, there were several excellent candidates. Just to give you an idea of the type and level of assessments contained in those letters, let me cite few of them: "outstanding scientist, who in spite of the young age has already accomplished a lot"; "unusually talented chemist"; "this rapid rise through the academic ranks is almost unprecedented and is testament to extraordinary talent"; "particularly bright and full of original ideas and also hard working"; "totally reliable and highly professional, gives continuous input of original solutions"; "truly outstanding synthetic organic chemist with a glittering future ahead"; "the mobility and international cooperation experience of the candidate are great examples for the future generation of scientists not only in Europe but also outside"; "ambitious, successful

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young scientist who is goal oriented on challenging scientific topics." About half of the participants were judged top level by the Award jury.

Most of the candidates presented fundamental research issues, although possible applications were almost always also considered. They dealt with a variety of problems in keeping with chemical tradition.

I was then encouraged to collect in a book what I felt to be the most interesting topics by different candidates for the Award. *Tomorrow's Chemistry Today* is therefore a book intended to showcase excellence in chemistry by inviting a selection of young chemists each to write a chapter on their research field, their main results, and the perspectives they envision for the future.

Many of the 18 contributions are interdisciplinary and involve interfaces such as:

- organic-synthesis/polymer science/supramolecular science;
- supramolecular chemistry/material science and nanotechnology/optoelectronics;
- bioorganic chemistry or inorganic chemistry/medicinal chemistry;
- organic synthesis/analytical chemistry/protein biochemistry;
- biology/nanoscience/physical chemistry;
- biology/supramolecular chemistry.

Reading the book, one will find many new ideas and innovations. It is clear that important steps forward, at the forefront of modern chemical science and technology, are made in several area with the contributions of these talented authors. These concern at least the following fields:

- New synthetic procedures, reaction routes, and schemes intended to give supramolecular motifs.
- Development of real bottom-up molecular technology as well as nanotechnology through supramolecular chemistry.
- New chemical products or materials with unusual properties for potential applications in various devices.
- Hybrid nanomaterials involving organic, inorganic, as well as biological systems or assemblies.
- Molecular systems having intense industrial interest in medicine.
- Structure–property relationship and biomimetic chemistry.
- New "green" catalysts for environmentally friendly industrial processes.
- Advanced characterization methods.

The book has been divided into three main parts:

1. Self-organization, Nanoscience, and Nanotechnology
2. Organic Synthesis, Catalysis, and Materials
3. Health, Food, and Environment

In the first part, emphasis is given to the efforts made in the exploitation of improved knowledge of noncovalent interactions to synthesize new molecules having hierarchical structure, possibly to mimic Nature. Molecules are often designed to utilize precisely these noncovalent interactions and molecular recognition processes, particularly those based upon hydrogen bonding, metal–ligand coordination, π–π interactions, hydrophobic interaction, ion pairing, and van der Waals interactions. This is in order to stabilize well-defined conformations and therefore function.

Powerful methods for the synthesis of elaborate and intricate supramolecular systems and the technique of *subcomponent self-assembly* for the creation of increasingly complex structures are presented. Particular strategies of synthesis are described such as *"self assemble, then polymerize, and then fold into hierarchical structures"* or vice versa, as well as successful strategies involving the incorporation of aromatic heterocycles into the backbone of π-conjugated systems for the design and assembly of structures having desired properties. In some cases the parameters controlling the exact nature of the observed hierarchical structures are discussed. Fascinating architectures, or molecular topologies if you like, are demonstrated that have an almost unmatched range of physical properties involving different types of molecules such as polyoxometallates, co-oligomers alternating phosphole and thiophene and/or pyridine rings, catenanes, rotaxane, naphthalenediimides, and so on. Their potentialities in everyday life as catalysts, sensors, molecular machines, switches, photoactive or electroactive components for optoelectronics as well as light-emitting diodes, thin-film transistors, photovoltaic cells, nanodevices, and so on, are discussed. Reading these works it is easily understood that, as one of the contributors says, "Chemists are in an ideal position to develop such a molecular approach to functional nanostructures because they are able to design, synthesize, investigate, and organize molecules– i.e., make them react or bring them together into larger assemblies. And at the end a better understanding of the rules and principles guiding a self-assembly process can allow one to utilize these rules synthetically, creating new structures possessing new functions for engineering at the molecular level."

The book continues with other contributions in the area of materials and catalysis. Important concepts are treated, like that of exploiting nonlinear optical behavior of certain classes of materials which emit in the short wavelength region, such as the visible region, when excited by another region such as the infrared. This property leads to many advantages, especially in biological studies, telecommunications, and three-dimensional optical storage, and it is potentially important for bioimaging. The bottom-up approach is again amply exploited to prepare nanostructured materials with hierarchical organization, leading to properties which can be tuned by judicious modification of their synthesis conditions. New synthetic techniques based again on weak interactions are continually being developed to gain more precise control over the organization of solids. In particular, template-assisted synthesis, self-assembly, and biomimetic methods are highlighted as likely to become widely used in the fabrication of materials with controlled porosity. The important method of spatially constrained synthesis is

described. The bottom-up nanoengineering approach is used in another contribution dealing with the preparation of light-emitting aggregates from functionalized *para*-quaterphenylene. This work ends with the question: "which chemically functionalized oligomers would still undergo a similar self-assembly process and allow creation of quantitative amounts of crystalline nanofibers with tailored morphologies and optical, electrical, mechanical and even new properties?"

Moving to other contributions, one can readily appreciate that Nature still has plenty of things to teach us for engineering at molecular level and preparing useful materials. This motif is present, for example, in a contribution reporting the study of bio-inspired models of copper proteins elucidating model compounds of the copper-containing enzyme catechol oxidase and aiming to understand its mechanism of action.

Nature has always been a source of inspiration for chemists and materials scientists. In addition to the inspiration, Nature is also giving us "materials" useful for nanotechnology. This concept is vividly and beautifully presented in a further contribution in which plant viral particles are used as programmable nanobuilding blocks. The focus of this chapter is in the area of nanobiotechnology and the exploitation of biomolecules for technological applications. A new field is emerging, says the author: "a highly interdisciplinary area which involves collaborations between virologists, chemists, physicists, and materials scientists. It is exciting at the virus–chemistry interface."

The book collects contributions in the field of characterization of materials also, and these are reported in various chapters. In addition to this, a particular chapter is dedicated to interesting new calorimetric approaches to the study of soft-matter three-dimensional organization intended to demonstrate methods able to make a contribution to our understanding of hierarchical porous structures in which matter and void are organized in regular and controlled patterns.

Studies in the catalytic-organic chemistry area are enriched here by an elegant contribution on selective hydrogen transfer reactions over supported copper catalysts leading to simple, safe, and clean protocols for organic synthesis.

Contributions to organic synthesis, in some respects more traditional than those previously mentioned and concerning different areas from those potentially important for nanotechnology, materials, or catalysis, are also reported.

In one of these contributions, organic synthetic procedures regarding nucleophilic radical addition under mild conditions is described, underlining and confirming the idea that high reactivity is not necessarily associated with low selectivity.

In the last part of the book some examples are reported on the importance of the contribution of chemical studies to fields that are of increasing concern for the public opinion such as health, food, and the environment. One of these describes investigation of the protein–tannin interaction in order to better understand organoleptic properties of foodstuffs, and in particular those of red wine.

Two other chapters give an overview of the analogues and derivatives of cisplatin and the alternatives for it, the ruthenium-based drugs reported in the last 30 years for tumor biology, and present both future perspectives of medicinal chemistry

for speeding up discovery chemistry in the field and future strategies for drug design. Last but not least, a chapter is devoted to the important photochemical transformation processes of environmental significance and their possible influence on climate change.

The contributions reported in this book clearly show that chemistry is not a static science and that this is because it is continuously developing its knowledge base, techniques, and paradigms, adapting its potentialities to the demands of society, implementing its own tradition and collaborating with other scientific areas to open up entirely new fields at the interface with physics or life sciences to generate hybrid systems. It is important to stress that the systems chemists can create may have characteristics or properties that are not even present in Nature. Either exploiting the synthetic arts such as those presented in many chapters of this book or creating hybrid systems with living organisms, chemists are, as stated at the beginning, in the ideal position to contribute to our civil and societal development. The perspective for this science and for the products that it can give to society are therefore excellent, considering especially that a number of talented young researchers are very active in the area.

In conclusion, I hope that such a book, directed to a broad readership, will be a source of new ideas and innovation for the research work of many scientists, the contributions covering many of the frontier issues in chemistry. Our future is undoubtedly on the shoulders of the new scientific generation, but I would like to express the warning that in any case there will be no significant progress if – together with the creativity of young scientists and their will to develop interdisciplinary and collaborative projects – there is not established a constructive political will that takes care of the growth of young scientists and their research.

I cannot finish this preface without acknowledging all the authors and the persons who helped me in the book project. I am very grateful to Professor Natile (President of the European Association for Chemical and Molecular Sciences) and Professor De Angelis (President of the Italian Chemical Society) for their stimulation and suggestions. And of course, I thank all the Societies (see the book cover) that motivated and sponsored the book.

Palermo, August 2007
Bruno Pignataro

Author List

Mohammed Baba
Laboratoire de Thermodynamique des Solutions et des Polymères, CNRS UMR 6003, TransChiMiC, Université Blaise Pascal, Clermont-Ferrand 2 24 Avenue des Landais, Bâtiment Chimie 7, 63 177 Aubière, France
E-mail: mohammed.baba@univ-bpclermont.fr

Sheshanath Vishwanath Bhosale
School of Chemistry, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
E-mail: shehanath.bhosale@sci.monash.edu.au

Elisabete Barros de Carvalho
Centro de Investigação em Química, Universidade do Porto, Faculdade de Ciências, Departamento de Química, Rua do Campo Alegre, 687 4169-007 Porto, Portugal
E-mail: elisabete.carvalho@fc.up.pt

Matteo Colombo
NiKem Research srl, via Zambeletti, 25, 20021 Baranzate (Milan), Italy
E-mail: matteo.colombo@nikemresearch.com

Leroy Cronin
Department of Chemistry, The University of Glasgow, Glasgow, G12 8QQ, UK
E-mail: L.Cronin@chem.gla.ac.uk

Holger Frauenrath
Eidgenössische Technische Hochschule Zürich, Department of Materials, Wolfgang-Pauli-Str. 10, HCI H515, CH-8093 Zürich, Switzerland
E-mail: frauenrath@mat.ethz.ch

Victor Armando Pereira de Freitas
Centro de Investigação em Química, Universidade do Porto, Faculdade de Ciências, Departamento de Química, Rua do Campo Alegre, 687 4169-007 Porto, Portugal
E-mail: vfreitas@fc.up.pt

Cristian Gambarotti
Politecnico di Milano, Materiali ed Ingegneria Chimica "Giulio Natta", Via Mancinelli 7, I-20131 Milano, Italy
E-mail: cristian.gambarotti@polimi.it

Patrick Gamez
Leiden University, Leiden Institute of Chemistry, P.O. Box 9502, 2300 R.A. Leiden, The Netherlands
E-mail: p.gamez@chem.leidenuniv.nl

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Javier García-Martínez
Molecular Nanotechnology Laboratory, Department of Inorganic Chemistry, University of Alicante, Carretera San Vicente s/n. E-03690, Alicante, Spain
E-mail: j.garcia@ua.es

Muriel Hissler
Université de Rennes I Sciences Chimiques de Rennes UMR 6226 CNRS-IR1 263 avenue du Général Leclerc 35042 Rennes, France
E-mail: muriel.hissler@univ-rennes1.fr

Eike Jahnke
Eidgenössische Technische Hochschule Zürich, Department of Materials, Wolfgang-Pauli-Str. 10, HCI H515, CH-8093 Zürich, Switzerland
E-mail: jahnke@mat.ethz.ch

Iryna A. Koval
TNO Quality of Life, P.O. Box 718, Polarisavenue 151, 2130 A.S. Hoofddorp, The Netherlands
E-mail: i.koval@chem.leidenuniv.nl

Ga-Lai Law
Department of Chemistry, The University of Hong Kong, Chong Yuet Ming Chemistry Building, Pokfulam Road, Hong Kong
E-mail: galai_law@hotmail.com

Christophe Lescop
Université de Rennes I Sciences Chimiques de Rennes UMR 6226 CNRS-IR1 263 avenue du Général Leclerc 35042 Rennes, France
E-mail: christophe.lescop@univ-rennes1.fr

Palanisamy Uma Maheswari
Leiden Institute of Chemistry, Leiden University, P.O. Box, 9502, 2300 R.A. Leiden, The Netherlands
E-mail: p.maheswari@chem.leidenuniv.nl

Nuno Filipe da Cruz Batista Mateus
Centro de Investigação em Química, Universidade do Porto, Faculdade de Ciências, Departamento de Química, Rua do Campo Alegre, 687 4169-007 Porto, Portugal
E-mail: nbmateus@fc.up.pt

J.M. Nedelec
Laboratoire des Matériaux Inorganiques, CNRS UMR 6002, TransChiMiC, Université Blaise Pascal, Clermont-Ferrand 2 & Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, 24 Avenue des Landais, 63 177 Aubière, France
E-mail: j-marie.nedelec@univ-bpclermont.fr

Jonathan R. Nitschke
University of Cambridge, Department of Chemistry, Lensfield Road Cambridge, CB2 1EW, United Kingdom
E-mial: jrn34@cam.ac.uk

Ilaria Peretto
NiKem Research srl, via Zambeletti, 25, 20021 Baranzate (Milan), Italy
E-mail: ilaria.peretto@nikemresearch.com

Carlo Punta
Politecnico di Milano, Dipartimento di Chimica, Materiali ed Ingegneria Chimica "Giulio Natta", Via Mancinelli 7, I-20131 Milano, Italy
E-mail: carlo.punta@polimi.it

Nicoletta Ravasio
Università di Milano, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Via Venezian, 21, 20133 Milano, Italy
E-mail: n.ravasio@istm.cnr.it

Jan Reedijk
Leiden University, Leiden Institute of Chemistry, P.O. Box 9502, 2300 R.A. Leiden, The Netherlands
E-mail: reedijk@chem.leidenuniv.nl

Manuela Schiek
University of Southern Denmark Mads Clausen Institute, NanoSYD, Alsion 2, 6400 Sonderborg, Denmark
E-mail: Manuela.Schiek@uni-oldenburg.de

Andreea R. Schmitzer
Department of Chemistry, Université de Montréal, 2900 Edouard Montpetit, succursale Centre ville CP 6128, Montréal H3C 3J7, Canada
E-mail: ar.schmitzer@umontreal.ca

Nicole F. Steinmetz
The Scripps Research Institute, Department of Cell Biology, CB262 La Jolla CA 92037, USA
E-mail: nicoles@scripps.edu

Davide Vione
Dipartimento di Chimica Analitica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy
E-mail: davide.vione@unito.it

Federica Zaccheria
Università di Milano, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Via Venezian, 21, 20133 Milano, Italy
E-mail: federica.zaccheria@unimi.it

Member Societies

A
Society of Albanian Chemists (SAC)
University of Tirana
Faculty of Natural Sciences
Tirana
Albania

GÖCH – Gesellschaft Österreichischer Chemiker
Nibelungengasse 11/6
1010 Vienna
Austria

ASAC – Austrian Society for Analytical Chemistry
Universitaet Linz
Altenbergerstrasse 69
4040 Linz
Austria

B
KVCV – Koninklijke Vlaamse Chemische Vereniging
Celestijnenlaan 200F
3001 Herverlee
Belgium

Société Royale de Chimie
Université Libre de Bruxelles
CP 160/07
Av F.D. Roosevelt 50
1050 Bruxelles
Belgium

Union of Chemists in Bulgaria (UCB)
108 Rakovski Street
PO Box 431
1000 Sofia
Bulgaria

C
Croatian Chemical Society
Horvatovac 102a
10000 Zagreb
Croatia

Pancyprian Union of Chemists (PUC)
P. O. Box 28361
2093 Nicosia
Cyprus

Czech Chemical Society
Novotného lávka 5
116 68 Praha 1
Czech Republic

D
Danish Chemical Society
Universitetsparken 5
2100 København Ø
Denmark

Kemiingeniorgruppen
Ingeniørforeningen i Danmark
Kalvebod Brygge 31-33
1780 København V
Denmark

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E
Estonian Chemical Society
Akadeemia tee 15
12618 Tallinn
Estonian

F
Association of Finnish Chemical Societies
Urho Kekkosen katu 8 C 31
00100 Helsinki
Finnland

Société Française de Chimie
250, rue Saint-Jacques
75005 Paris
France

G
Dechema
Gesellschaft für Chemische Technik und Biotechnologie e.V.
Theodor-Heuss-Allee 25
60486 Frankfurt am Main
Germany

Gesellschaft Deutscher Chemiker e.V. (GDCh)
Postfach 90 04 40
60444 Frankfurt am Main
Germany

Deutsche Bunsen-Gesellschaft (DBG) für Physikalische Chemie
Postfach 150104
60061 Frankfurt am Main
Germany

VAA
Geschäftstelle Köln
Mohrenstraße 11-17
50670 Köln
Germany

Greece
Association of Greek Chemists
info@eex.gr

H
The Hungarian Chemical Society (MKE)
Fö utca 63
1027 Budapest
Hungary

I
Institute of Chemistry of Ireland
PO Box 9322
Cardiff Lane
Dublin 2
Republic of Ireland

The Israel Chemical Society (ICS)
P.O. Box 26
76100 Rehovot
Israel

Societa Chimica Italiana
Viale Liegi 48c
00198 Roma
Italy

Consiglio Nazionale dei Chimici (CNC)
Piazza San Bernardo, 106
00187 Roma
Italy

L
Latvian Chemical Society
21 Aizkraukles Street
1006 Riga
Latvia

Lithuanian Chemical Society
G A Gostauto
Vilnius LT 2600
Lithuania

Association des Chimistes
Luxembourgeois (ACHIL)
16 rue J. Theis
9286 Diekirch
Luxembourg

Society of Chemists and Technologists
of Macedonia (SCTM)
Faculty of Technology and Metallurgy
Rudjer Boskovic
1000 Skopje
Macedonia

Chemical Society of Montenegro
(CSM)
Hemijsko Drustvo Crne Gore
Tehnolosko-metalurski fakultet
Cetinjski pu bb
81000 Podgorica,
Republic of Montenegro

N

Royal Netherlands Chemical
Society–KNCV
Vlietweg 16
2266 KA Leidschendam
Netherlands

Norwegian Chemical Society
President: Tor Hemmingsen
Universitetet i Stavanger
4036 Stavanger
Norway

P

Polish Chemical Society (PCS)
ul. Freta 16
00-227 Warszawa
Poland

Portuguese Electrochemical Society
(SPE)
University of Coimbra
Department of Chemistry
3004-535 Coimbra
Portugal

Sociedade Portuguesa de Química
Av. Republica, 37, 4
1050-187 Lisboa
Portugal

R

Romanian Society of Analytical
Chemistry
13 Bulevardul Republicii
70346 Bucharest
Romania

Romanian Chemical Society
c/o The Romanian Academy
Calea Victoriei nr. 125
71102 Bucharest
Romania

Mendeleev Russian Chemical Society
The Federation of Mendeleev Chemical
Societies (FCS)
Prof N. N. Kulov (Vice President)
Department of International Relations
Kurnakov Institute of General and
Inorganic Chemistry of the Russian
Academy of Sciences
31 Leninskii prospekt
119991 Moscow
Russia

Russian Scientific Council on Analytical
Chemistry
Council Secretariat
Institute of General and Inorganic
Chemistry
31 Leninskii prospekt
119991 Moscow
Russia

S

Serbian Chemical Society
Karnegijeva 4
11120 Belgrade
Serbia

Slovak Chemical Society (SCS)
Radlinského 9
81237 Bratislava
Slovakia

Slovenian Chemical Society
Hajdrihova 19
p.p. 660
1000 Ljubljana
Slovenia

National Chemical Association of Spain (ANQUE)
C/ Lagasca, 27
28001 Madrid
Spain

La Real Sociedad Española de Química (RSEQ)
Secretary General
Facultade de Quimica
Universidad Complutense
28040 Madrid
Spain

Spanish Society of Analytical Chemistry (SEQA)
Universidad Complutense de Madrid
Dra. Carmen Cámara
Dpto de Química Analítica
Facultad de Químicas
Universidad Complutense de Madrid
Madrid
Spain

Swedish Chemical Society
Wallingatan 24 3 tr
11124 Stockholm
Sweden

Schweizerische Chemische Gesellschaft (SCG)
Schwarztorstrasse 9
3007 Bern
Switzerland

T

Chemical Society of Turkey
Halaskargazi Gad No. 53 D 8
Harhiye
80230 Istanbul
Turkey

U

Ukranian Chemical Society
ul. Murmanskaya 1
02094 Kiev
Ukraine

Royal Society of Chemistry, Cambridge
Thomas Graham House
Science Park
Milton Road
Cambridge CB4 0WF
United Kingdom