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Geoffrey A. Ozin

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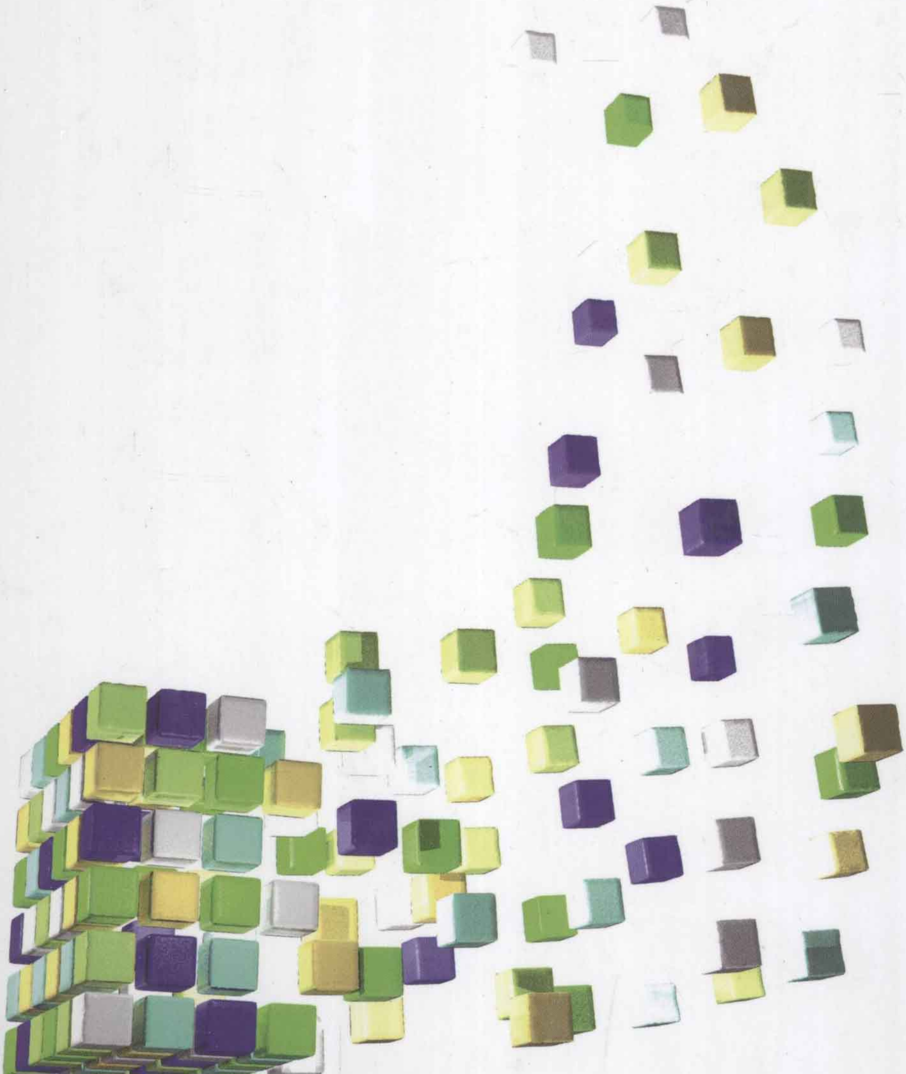
With a Foreword by Jean-Marie Lehn



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To our wives Rebecca and Linda

Foreword

The emergence of nanotechnology in the past fifty years has been accompanied by the parallel development of the chemistry of nanotechnology: "nanochemistry".

The conceptual foundation of this discipline is the hypothesis that with clever chemistry it is possible to design and to synthesize building blocks, possessing particular properties and able to undergo self-assembly from the molecular scale to the nanoscale to form hierarchical structures with additional hierarchical functions.

The miniaturization of materials to a scale where size-dependent effects operate poses challenges to the chemistry community, not only from a technical perspective but also from a conceptual perspective. It requires to think of broader capabilities for chemistry and the notions of size and shape entered the mainstream lexicon of the community, along with self-assembly, promoted by supramolecular chemistry.

The origin of nanotechnology is difficult to identify, as it is a field that expanded across the scientific landscape in various forms, usually not immediately recognized as related. This mosaic of discoveries and areas of research is still persisting and makes teaching the subject to a multidisciplinary group of students a demanding prospect.

In the present textbook, the authors bring all the pieces of nanochemistry together under one umbrella, using the unifying concepts as glue and key materials as case histories.This unique organization of the subject matter is to be appreciated for how it conveys the subtle relations between topics in a way that is not only correct and educational but also stimulating.

This approach to writinga textbook strikes a remarkable balance between the effectiveness and rigor of teaching through concepts and the vividness of examples, case histories and an accessible language. It will be appealing not only to students interested in the chemistry of nanotechnology, but also to those, across scientific disciplines, who want to understand how nanochemistry impacts their field.

The present volume can be warmly recommended to teachers and students alike. It will be very useful to many in finding their way in this blossoming field.

Jean-Marie Lehn

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About the Authors

Ludovico Cademartiri was born in Parma, Italy, in 1978. He was among the first students to graduate from the University of Parma with a Laurea Magistrale (*summa cum laude*) in Materials Science in 2002, defending a thesis on colloidal self-assembly conducted under the mentorship of Prof. Gianluca Calestani. In 2003 he ventured overseas to start a PhD degree in Interdisciplinary Chemistry at the University of Toronto, under the inspired supervision of Prof. Geoffrey Ozin. His thesis was entitled "Colloidal Nanostructures: A Curiosity Driven Investigation" and was defended in April 2008.

After a couple of months as a postdoctoral fellow in the Ozin labs, he moved to Boston, Massachusetts, where he is currently a postdoctoral fellow at the Department of Chemistry and Chemical Biology of Harvard University, in the group of Prof. George M. Whitesides.

He has coauthored 16 scientific publications, 2 textbooks, and is the recipient of several awards, among which two Materials Research Society Graduate Student Awards (twice in a row, in 2005 and 2006), the ACS DIC Young Investigator Award, the Canadian Society of Chemistry DIC Prize for Graduate Work in Inorganic Chemistry, the Canadian Society of Chemistry CCUCC Chemistry Doctoral Prize, and the Governor General Gold Medal, granted yearly to the three graduate students with the highest academic standing in the whole University of Toronto.

Geoffrey A. Ozin, born 23rd August 1943, obtained his undergraduate degree at Kings College London and his graduate degree at Oriel College Oxford. Following post-doctoral research as an ICI Fellow at Southampton University he joined the University of Toronto where he is now a Tier 1 Government of Canada Research Chair in Materials Chemistry and Nanochemistry and Distinguished University Professor. He is also Honorary Professor at The Royal Institution of Great Britain and University College London, an External Associate of the London Centre for Nanotechnology, a Guest Professor at Karlsruhe Institute of Technology, the Centre for Functional Nanostructures Karlsruhe Institute of Technology and the Institute for Nanotechnology Forschungszentrum Karlsruhe.

His work has enabled a fusion of "top-down" solid-state physics ways of making structures and "bottom-up" molecular-chemistry methods of making materials. His approach of integrating materials chemistry and self-assembly, templating and

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patterning strategies, traversing nanometer to micron length scales, has inspired generations of researchers in university, industry and government laboratories around the world, to imagine and make entire new classes of nanomaterials and nanostructures, having useful properties and functions, well suited to a range of nascent technologies.

He has delineated some of the most important Nanochemistry principles that underpin a chemical approach to nanomaterials. Since the seventies he has made ground-breaking contributions to several areas of Nanochemistry, the most noteworthy of which include his *early career work* on metal atom and metal cluster chemistry (chemistry from the atom-up) and advanced zeolite materials science (chemistry of microporous crystals) to his *mid-career work* on biomimetic inorganic materials chemistry (learning from nature), hybrid materials (inorganic-organic nanocomposites) and inclusion chemistry (host-guest nanomaterials) to his *most recent work* on mesochemistry (materials with intermediate dimensions), photonic crystal materials chemistry (chemistry control of the flow of light and structural color) and nanolocomotion (chemically powered nanomotors).

His work has had a major influence on shaping contemporary Nanochemistry, a dynamic multidisciplinary field helping to drive the nanotechnology industrial revolution. A hallmark of his recent work is "*materials self-assembly over all scales*". He has shown how to organize nanometer to micron scale building blocks into unprecedented structures with remarkable form, and how they can serve as functional materials for a myriad of uses. He has shown that structure at "*all*" levels of construction from the nanoscale to the overall macroscopic form, determine materials properties and functions and ultimately utility in diverse application, his "*panoscopic*" vision of Nanochemistry.

Nanomaterials that have emerged from his work have proven to be interesting in areas as diverse as catalysis and (bio)chemical sensing, drug delivery and bone implants, full color tuneable displays, banknote anti-counterfeit protection and product authentification devices, optical telecommunications and microelectronic packaging. His recent discovery of the chemically powered nanorotor bodes well for the practical realization of purposeful nanomachines.

The significance of his materials chemistry and nanochemistry research has been recognized in various ways. Recently he was awarded a Government of Canada Research Chair in Materials Chemistry and Nanochemistry (2000–2014) and the inaugural Natural Sciences and Engineering Research Council of Canada NSERC Brockhouse Interdisciplinary Prize for his pioneering work on photonic bandgap materials with Sajeev John University of Toronto 2005. He was also recipient of the Society of Chemical Industry Le Sueur Award, 2008, Alexander von Humboldt Senior Scientist Prize 2005, the Canadian Society of Chemistry E. W. R. Steacie 2002 CSC Award in Chemistry, the Royal Society of Chemistry Great Britain 2002 RSC Award in Materials Chemistry, ISI Highly Cited Researcher in Materials Science 2002, the Canadian Institute of Chemistry 2001 CIC Medal, a Canada Council Isaac Walton Killam Research Fellowship 1997–1995, and the Royal Society of Canada inducted him as a Fellow in 1992. Amongst his other honours are the Pure or Applied Inorganic Chemistry Award from the Canadian Society for Chemistry;

Rutherford Memorial Medal in Chemistry from the Royal Society of Canada; Alcan Award for Inorganic Chemistry from the Chemical Institute of Canada. Others include the Coblentz Memorial Prize for Molecular Spectroscopy from the American Spectroscopy Society; Meldola Medal for Physical-Inorganic Chemistry from the British Royal Institute of Chemistry. He was a Sherman-Fairchild Fellow at California Institute of Technology and he received three University of Toronto Connaught Special Research Awards, reserved for top rank institutional scientists. He is Founding Fellow of the Canadian Institute for Advanced Research, CIFAR Nanoscience team.

Two of his graduate students Hong Yang and Mark MacLachlan were awarded the 1999 and 2000 NSERC Doctoral Prize in recognition of the top PhD. Thesis research in the Canadian Natural Sciences. Two other of his graduate students won the coveted Governor General Gold Medal, Nicolas Tetreault in 2005 for his PhD. thesis research on silicon photonic band gap materials and Ludovico Cademartiri in 2008 for his PhD. thesis research on nanocrystals and nanowires. Another of his graduate students Ben Hatton won the NSERC Innovation Challenge Award in 2005 for his PhD. thesis research on low dielectric constant periodic mesoporous organosilica films for next generation microelectronic packaging materials. Graduate student Andre Arsenault won the top NSERC graduate student award in Canada 2004–2006 as well as the NSERC Innovation Challenge Award for his PhD. thesis research in 2008. Graduate student Friederike Fleischhaker was awarded the German Chemical Society graduate student fellowship for 2005–2006. Graduate student Jennifer Chen won the prestigious International Chorafas Foundation Prize and FE Beamish Prize in Inorganic Chemistry in 2006 and graduate student Ludovico Cademartiri won the Canadian Society of Chemistry DIC Prize for Graduate Work in Inorganic Chemistry, the Division of Inorganic Chemistry American Chemical Society Young Investigator Award in Inorganic Chemistry in 2008, and the Chemical Institute of Canada Chemistry Doctoral Prize in 2009.

He has published 591 articles in top rank refereed international journals. These papers have garnered over 22,409 citations. He has been granted 12 patents and has 35 patents filed, many in different countries. His ISI Hirsch Index h = 68, a measure of the significance of his careers work, places him in a global elite group of researchers. He was named an ISI Top-Ten Materials Scientist (1996–2006). He has also made significant contributions to teaching, research and technology through the training of a large cadre of undergraduate, graduate and postgraduate students in materials chemistry and nanochemistry, and through his long-standing research collaborations with industry. His close ties with industry have resulted in numerous inventions and technology transfer licensing agreements. It is noteworthy that 31 of his former co-workers hold Professorial positions in Universities in Canada and other parts of the world, four are Heads of chemistry departments and one is a Dean of Science. Of his papers 22 are published in Nature and Science, graphical illustrations from 33 of his papers have been used as covers of top rank scientific journals and commentaries on his work appear frequently in the scientific media.

In the context of education, he has just completed the Second Edition of "Nanochemistry: A Chemical Approach to Nanomaterials" by Ozin, Arsenault and Cademartiri published by the RSC January 2009. In the second edition, written just three years after the global success of the initial edition, the authors have included the latest breakthroughs in the field with more than eighty new case histories, more problem sets, and more teaching principles. The authors are looking forward with excitement to more Nanochemistry discoveries for continued updated editions of this widely accepted textbook in the years ahead.

Acknowledgments

Ludovico Cademartiri

I thank God for the life He has given me, the greatest gift, and indeed a very funny one!

Only few years ago I was throwing myself like a wet towel towards a life of little perspective and increasingly gloomy solitude. I am now happily married, I am traveling the world, I can pay for my own food and shelter (not for much else, I admit), I work with people more gifted than me, and, at the end of the day, I come home to find an angel waiting for me, whose smile makes even the blackest of days shine.

I have a supporting and loving family, friendships that resisted years of distance, and a job that fills my days with some hope that I might one day do something helpful for somebody other than myself and my family.

Somebody said that life is what you make of it. What I make of this is that life is the greatest storyteller. And one of its most surprising stories is this book, a book I could coauthor with a friend, a supervisor, an advisor, and a true mentor. I couldn't have been more lucky than to be accepted in his group.

And in this time of economic uncertainty I have had the privilege to be hired as a postdoctoral fellow by one of the most illustrious chemists of our time, a true teacher.

Life proceeds then, like a train on ill-defined rails, and I mostly sit back and try to relax, enjoying the ever-shifting view with the marvelous companionship I've been granted.

Geoffrey A. Ozin

At the outset I wish to express my deepest appreciation to the number one love of my life, my wife Linda Ozin, for her strong and sustained support, wise and insightful advice throughout the writing of this textbook. The second love of my life is Nanochemistry, a field to which I have dedicated four decades of my life, helping to grow it from just an idea through an amorphous state to the beautifully crystallized form described between the covers of this introductory textbook, On the Concepts of Nanochemistry. Having earlier co-authored an advanced undergraduate and graduate level treatise on Nanochemistry with one of my co-workers André Arsenault, the first edition of which was published in 2005, it became abundantly

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clear that a new textbook was urgently required to teach the principles of nanochemistry upon which the advanced textbook was based, to satisfy the growing appetite of undergraduates in their first three years for an introduction to the subject. Another co-worker Ludovico Cademartiri rose to the challenge and together we brainstormed and wrote Concepts of Nanochemistry. The elegance of his words and aesthetics of his graphical illustrations are indelibly imprinted on the pages of this book. They define his love of nanochemistry, science and life. And Sue Mamiche, my personal assistant, deserves very special praise for her extraordinary support, in the midst of helping manage my large and active research group, to assist Ludovico and I with various key aspects that made the completion of this book possible. I also wish to acknowledge the strong and sustained financial support of my Nanochemistry research program from the Natural Sciences and Engineering Research of Canada (NSERC) who believed in my ideas from the beginning of my career as an Assistant Professor in 1969 when this field was just emerging until the present time where there are scientific breakthroughs on a daily basis and much anticipation that Nanotechnology will likely power the next industrial revolution. The award of a Canada Research Chair in Materials Chemistry from NSERC also enabled my group to continue its work at the leading edge of Nanochemistry. Being a Founding Fellow of the Canadian Institute for Advanced Research (CIFAR) Nanoscience Team has had a most positive impact on the research of me and my group. The strong backing of all my past and present Chairs, Deans, Provosts and Presidents, as well as the professional support from the Technology Transfer Group and Innovations Foundation at the University of Toronto, has been pivotal in facilitating the research and development work undertaken by my group. I also recognize my industrial colleagues, who over the years have provided my group with the financial incentive and personal encouragement to undertake adventurous Nanochemistry research. None of this would have been possible without the contributions of all of my co-workers and collaborators, who excited and challenged me every day of my career with creative and insightful ideas and questions – they have profoundly influenced my way of thinking and writing about the wonderful world of Nanochemistry. At the close, I wish to say that each day in my academic career has been an exhilarating learning experience. I have tried to instill some of this excitement and knowledge into the pages of our textbook, On the Concepts of Nanochemistry.

Joint Acknowledgments

Both authors would like to thank the instrumental people who made the monumental task of publishing a book seem easy. Thanks for fooling us!!!

We thank Sue Mamiche for being such a stable, relaxing, and productive influence on the whole process. We wouldn't even started this book if we wouldn't have known she was at our side.

We thank Mike Brook (!!!), Leonardo Bonifacio, Ilia Auerbach-Ziogas, Vladimir Kitaev for their most competent and valuable suggestions and criticism which improved readability and accuracy of our manuscript.

We thank Jennifer Chen, Kun Hou, Jennifer Lofgreen, Vladimir Kitaev, Wendong Wang for providing important material for the figures.

We thank Gudrun Walter, Peter Gregory, Karen Grieve, Bernadette Gmeiner, Yvonne Eckstein, Heike Noethe and all the people at Wiley who clearly showed us the love and care they feel for their work. We are privileged to have them as our partners in this venture. The whole scientific community should be grateful that such professionalism is still available in scientific publishing.

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Introduction

Nanochemistry – Why Should We Care?

There have been times in history when a scientific paradigm shift has been chiefly responsible for major changes in society: iron, the engine, the transistor, optical fibers, and the internet are famous examples. This happens because these discoveries question major assumptions we live with, and they transform our culture by defeating them.

Nanotechnology is touted to be at the core of the next paradigm shift, the next industrial revolution; mastering its possibilities is thought to be a key to the future competitiveness of nations. But what is the promise of nanotechnology? How is it going to improve our lives, create new businesses, solve any of the big problems facing the planet?

Many scientists think that it will empower the developing nations with cheaper solutions for their problems, leading their people to healthier and longer lives; many think it will bring better solar cells, smaller and faster computers, environmental remediation solutions, and the next cure for cancer; many think that it will help to solve the problem of global warming.

It is important for you to understand that besides the hype that surrounds it and that many discoveries enjoy, there is something unique about nanotechnology which truly makes it a paradigm shift: it is not just the discovery of a better solution to a problem or of a smarter way to tackle an issue, but a new way of thinking about solutions, a new and broader set of game rules.

One of the consequences of the hype is the concern about the toxicity of nanomaterials. The memory of asbestos (which is certainly a nanomaterial) is still vivid in our minds, as its cost for society is still being paid. This growing concern is drawing the attention of governments, which are now increasingly funding research into the toxicity of nanomaterials. This is especially motivated since one of the most promising areas of application is in medical diagnostics and therapeutics.

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What governments around the world also seem to understand is the disruptive potential of nanotechnology in terms of creation of new businesses: at every paradigm shift in history the existing businesses were often unable to adjust to the new rules of the game. They were overtaken by smaller, younger, more adaptable, and nimbler ventures. It is then understandable how nobody wants to miss this phase that will set the stage for many years to come.

It should not come as a surprise that the same governments are also pushing for an earlier introduction of nanotechnology in the academic curriculum. Degrees in nanoengineering, nanotechnology, and nanoscience are spawning around the world, and the pace of this transformation is taking its toll on the teaching staff, which, in most cases, was not specifically trained in nanoscience. These changing necessities create a demand for teaching resources at every level of the curriculum and for every background: while traditional subjects are limited in their scope, nanoscience is by definition interdisciplinary and crosses the boundaries between chemistry, physics, biology, medicine, and materials science and engineering.

The motivations for teaching nanoscience at earlier stages of the academic curriculum are many. On the one hand, it is important to get the new generations accustomed to nanoscience concepts; on the other hand, from a more pedagogical point of view, bringing the teaching of nanoscience to the freshman years would have a profound effect on the mindset of its recipients. It is a widely held fact that the freshman years define a scientist's mindset: students trained as chemists for the first two years of their undergraduate degree will often remain chemists forever, at least in their problem-solving approach. This explains why many chemistry PhD graduates have difficulties in getting "into" nanochemistry, and also explains why it is often easier for a chemist to branch into a completely different area of chemistry than to enter a closely related sub-discipline of physics.

Teaching nanoscience at the freshman years would give the students the tools necessary to tackle this subject in the most effective and interdisciplinary way.

While creating the right mindsets is definitely an important goal of policy-makers and educators, there is a probably bigger challenge in which nanoscience could help. In a world that is rushing towards a knowledge-driven approach to business and wealth creation, and where great changes in the needs and habits of people will likely be required, a lack of student performance in the sciences could be devastating. In North America this has become one of the priorities, as high-tech companies are forced to hire from abroad to fill their ranks.

It is a widely held hope that introducing nanoscience at early stages of the undergraduate curriculum would help increase the interest of students in the sciences. For too long the rationale for explaining the