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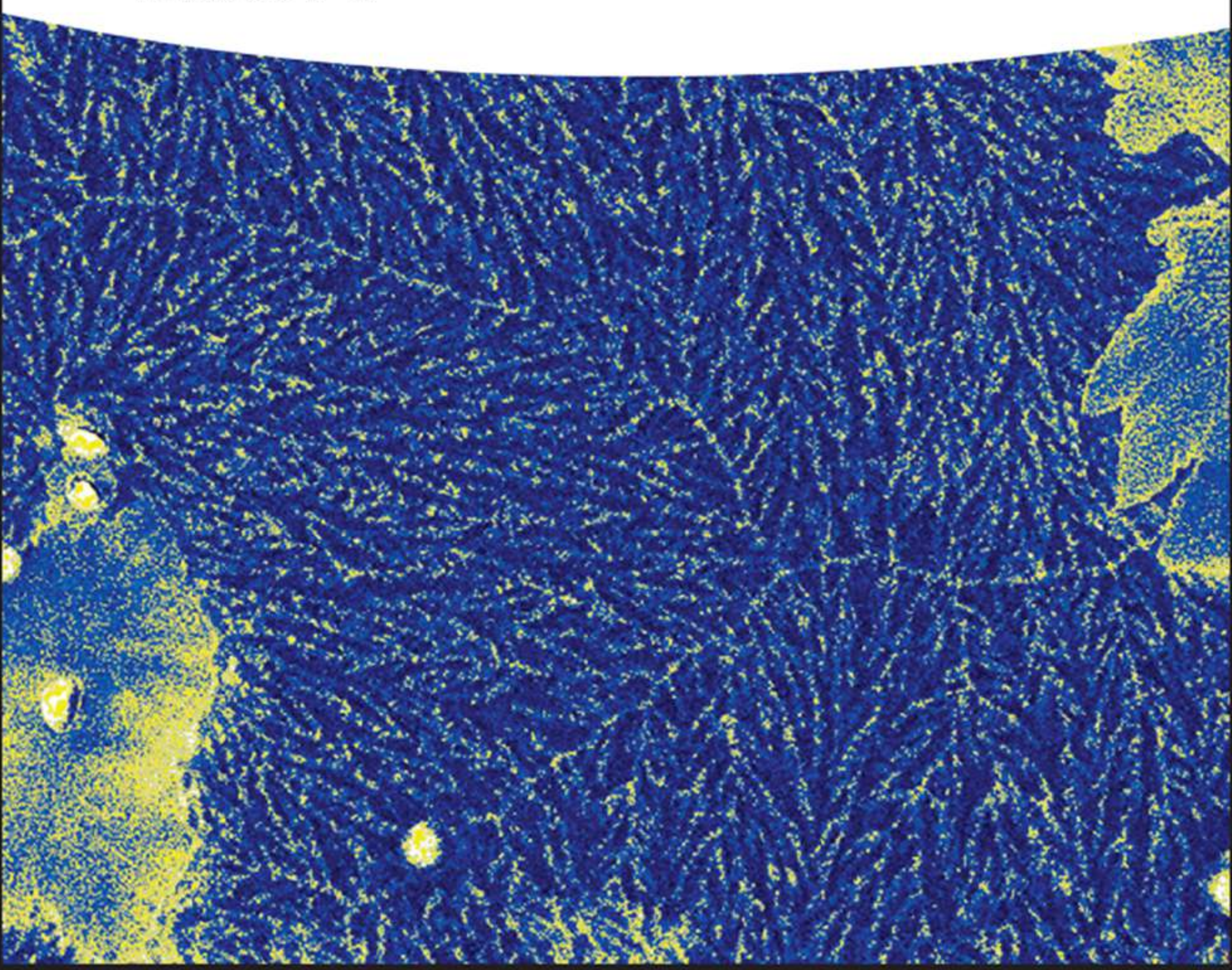
Edited by
Omar Azzaroni and Martin Conda-Sheridan

Supramolecular Nanotechnology

Advanced Design of Self-Assembled Functional Materials

Foreword by Jean-Marie Lehn and
Epilogue by Sir Fraser Stoddart

Volumes 1–3



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Volume 1

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Editors

Dr. Omar Azzaroni
INIFTA-CONICET-UNLP
Diagonal 113 y 64
1900 La Plata
Argentina

Dr. Martin Conda-Sheridan
University of Nebraska
Department of Pharmaceutical Sciences
4040 Emile St.
68198 Omaha NE
United States

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This book is dedicated to Dante and Ivo, and to Lucia, Elisa and Esteban

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Preface

If we were to ask any scientist (or any person in general) "what is the biggest mystery of all time?" one likely response would be "how did life start?" Origin-of-life research seeks to answer this inquiry by understanding how the molecules that are essential for life – amino acids, nucleosides, sugars, lipids – came to be. However, from those simple building blocks to life itself, there are nano-, micro-, and macromolecular gaps. Thus, understanding how key molecules originated is just part of the matter. Arguably, the answer cannot be complete without knowing how those molecules combine and how the obtained compounds interact with each other in order to achieve the shape, size, and function that are necessary to achieve life itself.

It is likely that any satisfactory response will be found within the field of self-assembly. This is the process by which disorganized molecules spontaneously assemble into organized patterns. For millennia, nature has used inter- and intramolecular interactions to create the systems that support life: cells and cell membranes (made of molecules such as phospholipids and cholesterol), peptides and proteins (both made of amino acids), polysaccharides (derived from simple sugars), and the nucleic acids (made up of nucleobases, five-carbon ribose sugars, and phosphate groups) which form deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

Given the importance of self-assembly in human life and also in medicine, electronics, and many other areas, we considered it necessary to assemble a group of experts able to introduce and discuss the field to a wide audience of researchers and science enthusiasts. We identified several experts whose contributions could offer a solid perspective of what self-assembly is today. The identification of these scientists can be considered the origin of this work, which we titled *Supramolecular Nanotechnology: Advanced Design of Self-Assembled Functional Materials*.

When discussing self-assembly, there are several hallmarks that can be identified as the foundation of the field (disregarding all the initial work done by Nature, God, or whomever the reader considers to be the driver of life). Among them we can identify Langmuir and Blodgett's 1935 paper describing the arrangement of amphiphilic molecules into closed-packed structures on liquid and solid surfaces [1]. Bigelow, Pickett and Zisman's key study of alkylamine monolayers on platinum surfaces appeared in the following decade [2]. Besides these works, the famous lecture "There's Plenty of Room at the Bottom" [3] given by the

Nobel Laureate Richard Feynman in 1959 has been identified as a landmark in nanotechnology, which by extension, can be connected to self-assembly itself (although it is likely he did not foresee atomic and molecular self-assembly in a true chemical sense [4]). During that decade, a magnificent achievement took place: the discovery of the DNA double helix with key contributions by Watson, Crick, Stokes, Franklin and Wilkins [5–7]. This work is key to our book in two ways. Firstly, DNA is a self-assembled molecule widely investigated by different groups, and secondly, it showed the power of one of the main techniques to study these systems: X-rays. The 1950s are also highlighted by the crystallographic characterization of two self-assembled protein structures: hemoglobin and myoglobin determined by Perutz and Kendrew and their groups, respectively [8, 9].

Those early works paved the way, directly or indirectly, for several giants. Every discussion of self-assembly may start with three names: Charles Pedersen, Donald Cram, and Jean-Marie Lehn who received the 1987 Nobel Prize [10]. Almost 30 years later (2016), Ben Feringa, Jean-Pierre Sauvage, and Sir Fraser Stoddart received the same award for the discovery of molecular machines, a related field [11]. And so, here we are today, where self-assembly is a thriving field with various branches, champions (which will be too many to name), structures, and properties, including systems formed by DNA, peptides, proteins, sugars, polymers, and dendrimers, and their hybrids (i.e. metal–organic frameworks or MOFs).

Given the depth and breadth of the field, we provide here a glimpse of what is possible by presenting work written by some of the pioneers of the field, some of the current trailblazers, and some of the up-and-coming stars of self-assembly. The coverage spans from polyelectrolytes and polymers to peptides and porphyrins along with the extended material systems that they form. Their chapters highlight the influence of self-assembly in electronics, tissue engineering, drug delivery, and catalysis. The content also includes discussion of the theoretical approaches to study the formed systems and the imaging techniques that are key to understand them. We hope that the information presented here will be as valuable to the readers as it was and is to us.

We want to immensely thank the 45 main authors and their colleagues for providing fantastic chapters full of depth, knowledge, and insights. The authors are from all over the globe (see the map below), thus ensuring that many points of view from all continents are covered. We also feel very honored to have a foreword by Jean-Marie Lehn and concluding remarks from Sir Fraser Stoddart. Having two legends, and personal heroes of ours, opening and closing our book is a treasure and a source of joy. We hope you will find the content inspiring and that new ideas will be born because of it. Our goal is that the inspiration for new directions in the field can be found within these pages. If even a single spark, resulting in new knowledge, can be struck after reading any of the chapters, we will feel the book has accomplished its objective.

Omar Azzaroni & Martin Conda-Sheridan

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Foreword

Supramolecular Chemistry in the Nanodomain

Supramolecular chemistry may be considered to cover two areas extending beyond the molecule: discrete entities and extended entities. Discrete supramolecular nanostructures, supermolecules of nanometric size, consist of well-defined associations of molecules held together by intermolecular forces akin to molecules formed by a well-defined set of atoms and covalent bonds. Extended entities cover large assemblies of different sizes, which may reach beyond nanometric dimensions consisting of different numbers and types of molecular components, such as supramolecular polymers and functional supramolecular materials, gels, liquid crystals, mesophases, layers and films, and membranes. Both categories contribute to the definition of supramolecular nanotechnology, the theme of the present book. Thus, supramolecular chemistry is making fundamental contributions to nanoscience and nanotechnology. A major feature resides in the spontaneous but molecular information controlled generation of well-defined, complex, and functional supramolecular architectures from their molecular components by self-organization in equilibrium as well as nonequilibrium conditions. It represents a powerful complement, and might well become a possible alternative, to present-day nanofabrication and nanomanipulation, spanning from the nanoscale to the macroscale up the ladder of dimensions. It makes possible the passage from fabrication, the need to make, to self-fabrication where the object, the device, or the material builds itself up by the selection of the correct molecular building blocks in a sequential and hierarchical fashion: the ultimate fabrication! Finally, and most significantly, supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the noncovalent interactions connecting the molecular components of a supramolecular entity and the resulting ability to exchange, incorporate, and rearrange its components. Therefore, supramolecular nano-objects may undergo constitutional variation, i.e. changes in constitution by association/dissociation processes in a given set of conditions. Supramolecular materials are thus dynamic materials. They may in principle select their components in response to external stimuli or environmental factors and as a consequence behave as adaptive entities. In particular, supramolecular polymers are dynamic polymers, dynamers, that may be generated by the polyassociation of multiple molecular components/monomers interconnected through complementary recognition groups. They may undergo modifications of their properties (mechanical, optical, etc.) via incorporation, exchange, and recombination of their monomeric components. These features give access to higher levels of behavior, such as healing and adaptability in response to external stimulants (heat, light, medium, chemical additives, etc.). As a result, the objects of supramolecular nanochemistry are thus dynamic in their constitution and capable of adaptation in response to physical stimuli (such as heat, pressure, electric field, etc.) and chemical effectors (protons, metal cations, anions, etc.). They define a *dynamic and adaptive nanochemistry* of supramolecular nature in line with the active development of adaptive chemistry. The present book assembles a set of chapters by expert practitioners on topics that represent a cross section of the various areas of supramolecular nanotechnology. It will be of much interest to all those pursuing basic research in the field as well as for the development of a wide range of potential applications.

Jean-Marie Lehn