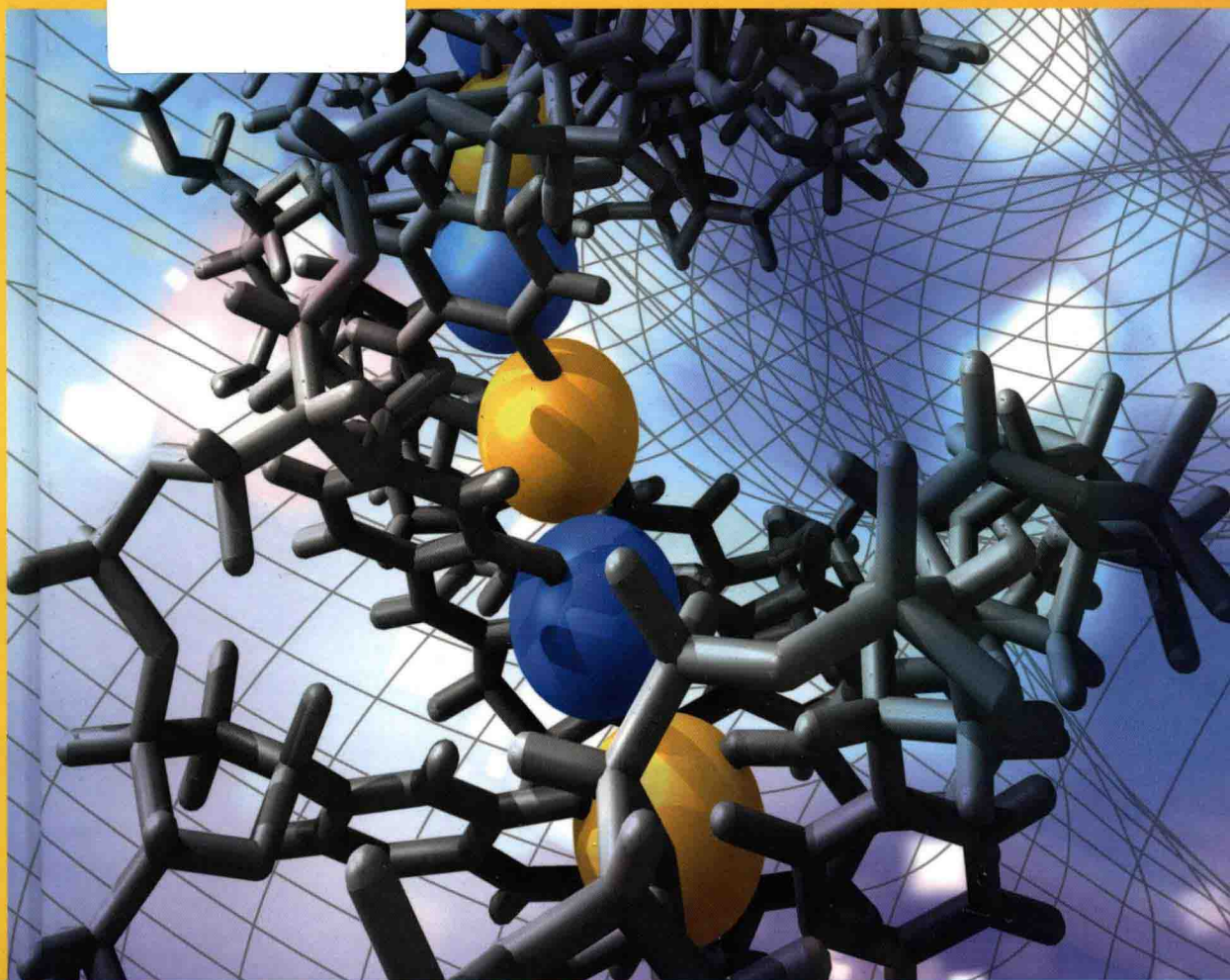


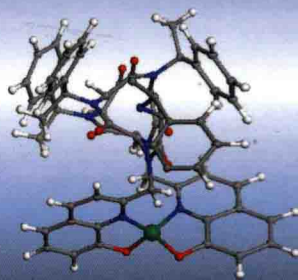
EDITORS | GALIA MAAYAN | MARKUS ALBRECHT

Metallofoldamers

Supramolecular Architectures
from Helicates to Biomimetics



 WILEY



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Edited By

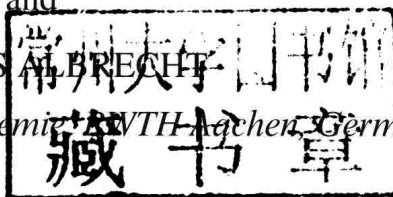
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Metallofoldamers

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Foreword

Since their initial presentation 25 years ago, helicates, helical metallosupramolecular architectures, have received wide attention and been subject to numerous investigations. Much of the fascination they exerted and continue to exert on chemists results from their helical structure, and in particular the relationship of double helicates with the emblematic entity, double-stranded DNA. Although this feature was part of our initial motivation, the goal and the impact were much wider. Indeed, as pointed out earlier, the generation of double helicates from designed ligands and suitable metal ions had for us a much broader significance as it marked the start of the implementation of self-organization processes in supramolecular chemistry via metalloarchitectures. It represented an important first step in the formulation of supramolecular self-organization as the outcome of programmed chemical systems, whereby information stored in the structural features of the ligand molecules is processed by the metal cations via their coordination algorithm. In a further extension, the self-sorting processes occurring in mixtures of equilibrating helicates and the generation of anion-dependent circular helicates became the starting points of our studies that were to evolve into constitutional dynamic chemistry.

From double-stranded to multiple stranded, from two centers to multiple centers, from identical metal ions to different ones, the field of helicates developed extensively, exploring structural features, physical properties and coding schemes, and reaching beyond towards a great variety of other metallosupramolecular architectures. Its expansion demonstrated once again that, without claiming to imitate what biology has so powerfully achieved in the DNA molecule, chemistry is exploring a much wider scene, generating entities entirely imagined and fabricated by chemists, exerting the power of chemistry over the expressions of matter.

The present volume displays a selection of the various aspects of the chemistry of helicates and related entities. It takes stock of achievements, but also suggests numerous exciting developments to the imagination of chemists, at the triple interface of organic, inorganic and biological chemistry, as well as, from a more general perspective, towards the precise control of the self-organization of chemical entities through appropriate programming.

The editors have to be congratulated for assembling a remarkable roster of active players in the field, who deserve our warmest thanks for their expert contributions.

Jean-Marie Lehn

Preface

Nature's examples of functional molecular entities are highly versatile. The living world as we know it only exists due to the specific properties and selective interactions of molecules. Hereby, the observed broad functionality of biological systems is mainly based on the structure of biomacromolecules (proteins or DNA), which strongly relies on an intra- or intermolecular connection between polymer strands. This occurs either in a covalent (e.g., –S–S– bridges) or in a noncovalent fashion. In the latter case H-bonding is probably the most prominent bonding motif. In many cases, however, metal ions have a significant role in the structure and function of biopolymers, being able to bind them and consequently to control their overall structural and thus functional features. It is now well established that the identity of the metal-binding ligands and their coordination mode, as well as side chain interactions, have a crucial role in governing metal binding and selectivity in proteins. The coordination of metal ions to proteins and peptides results in conformational changes, which lead to important functions such as catalysis, interactions with specific receptors or target proteins and the inhibition of biochemical or biophysical processes.

The effect of metal ions on conformational changes in proteins and peptides and thus on their function, which is widely discussed in Chapter 1, has inspired the design and synthesis of “metallofoldamers” – synthetic oligomers that fold upon interactions with metal ions to give various stable architectures in solution. Metallofoldamers are one class of “foldamers”, which are unnatural oligomers that fold into well defined three-dimensional structures in solution via noncovalent interactions. The design, synthesis, structures and applications of foldamers, as thoroughly described in several reviews and a book, are summarized in Chapter 2. We distinguish between three types of metallofoldamers: helicates (Chapters 3–8), metallo-nucleic acids (Chapters 9–10) and metallo-peptidomimetics (Chapter 11).

The term “helicate” was introduced 25 years ago by J.-M. Lehn and describes a rigid oligomer that spontaneously folds into helical structure upon binding of metal ions to its backbone. The self-assembly principles of helicates are presented in Chapter 3. Due to their simplicity, helicates are the ideal “supramolecular *Drosophila*” to be investigated. Indeed, in the years following their introduction, the chemistry of helicates was intensely studied. This included looking into their structural aspects (Chapter 4) and exploring new ways to construct helicates with various structures and features using unique oligomer backbone chelators (Chapter 5) or nontransition metal ions (Chapter 6). Although the majority of studies were based on the helicate model character, some functional helicates were developed. Thus, liquid-crystalline helicates were designed as supramolecular materials (Chapter 7). In the quest for the creation of more biomimetic helicates, a new generation of helicates is being developed, which includes the use of biopolymers such as peptides and DNA as backbones (Chapters 8–10). This new direction in the field of helicates leads the way to new trends in the field of foldamers – the generation of synthetic

oligomers which are peptide and nucleic acid mimics and can fold upon metal coordination to produce various three-dimensional structures stable in solution (Chapters 9–11). It is important to note that, while in helicates the metal ions template a helical structure via self-assembly, in biomimetic oligomers the metal ions nucleate the formation of a three-dimensional structure in a controlled manner. These biomimetic metallofoldamers are therefore macromolecular coordination compounds in which the overall structure of the macromolecule is influenced by its coordination to metal ions (Chapter 11). This copies nature's example of metallaproteins and opens the door to developing novel functional materials (Chapter 12).

The present book covers the whole field of structure control in oligomeric, polymeric, biomimetic and biological systems spanning the bridge from the simple helicates to polymers and natural or artificial peptides or DNA. This directly leads to prospective applications. We believe that the presented aspects are of interest and we hope that many scientists will be inspired and motivated as we are to do research in this fascinating field of chemistry.

Finally, we would like to deeply acknowledge the authors of the individual chapters for their singular and extraordinary contributions. We are also thankful to our coworkers and colleagues for introducing us to this fascinating field of chemistry, for fruitful discussions and for sharing our interest and passion. We also want to express our gratitude to the Wiley team, especially Paul Deards, who initiated the production of this book, as well as Sarah Tilley and Rebecca Ralf for their professional assistance during the editing and publishing process.

August 2012
Galia Maayan
Markus Albrecht

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