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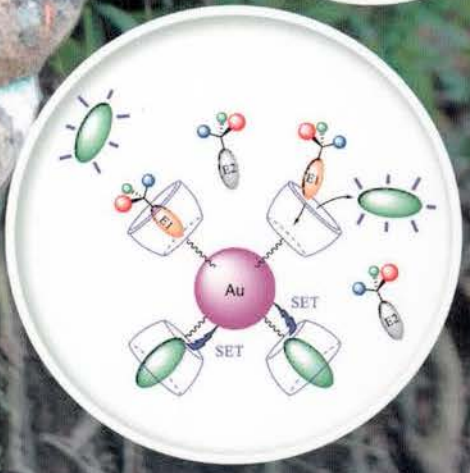
F. RICHARD KEENE

Chirality in Supramolecular Assemblies

Causes and Consequences



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Causes and Consequences

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Preface

The origins of what is now called *supramolecular chemistry* have been somewhat disparate, arising in part from studies of the chemistry of macrocycles (a development of naturally occurring analogues), spherands and carcerands, and cryptates . . . but the award of the 1987 Nobel Prize to Donald Cram, Charles Pedersen and Jean-Marie Lehn in many ways gave it a consolidated focus and led to its emergence as a field that retains vigorous and distinctly multidisciplinary activities. Supramolecular chemistry – defined by Lehn as "the chemistry of molecular assemblies and of the intermolecular bond" – deals with the organization of molecules into defined assemblies using noncovalent interactions, including weaker and reversible associations such as hydrogen bonds, π-π interactions, dispersion interactions, hydrophobic and solvophobic effects, and metal-ligand interactions. The aspect of stereochemistry within such chemical architectures, and in particular *chirality*, is of very special interest as it impacts on considerations of molecular recognition, the development of functional materials, the vexed question of homochirality, nanoscale effects of interactions at interfaces, biocatalysis and enzymatic catalysis, and applications in organic synthesis.

This book is intended to address the nature of the phenomenon of chirality in its broadest sense, noting the change in its nuances and subtlety in the progression from simple individual molecules to molecular assemblies, and to show the manifestations of chirality in the synthesis, properties, and applications of supramolecular systems, emphasizing their multidisciplinary importance.

The book is essentially divided in to four broad parts. The first constitutes an introduction to chirality: Chapter 1 develops the concept of chirality from rigid isolated molecules through to assemblies of molecules (in supramolecular entities), to topological chirality. Chapter 2 discusses chirogenesis and the phenomenon of homochirality (loss of parity) in the development of naturally occurring polymers (including nucleic acids and polypeptides) – and its consequences for the formation of artificial supramolecular

aggregates. Chapter 3 provides an overview of chiral aspects arising in the crystallization of small organic molecules – principles that are applicable to all classes of molecules, including supramolecular assemblies.

The second part is predominantly (but not exclusively) centered on metallosupramolecular chemistry. By the use of examples, Chapter 4 addresses the diversity of supramolecular assemblies – and in particular metallosupramolecular assemblies – and describes the complexity of chiral structures and their construction through self-assembly procedures. Chapter 5 describes the role of chirality in molecular recognition and host-guest systems. Chapter 6 develops the notion that unique characteristics can be built into supramolecular assemblies because of features of chirality – characteristics that can lead to functional properties of such materials. Chapter 7 addresses bulk homochiral solids formed using chiral reagents – either by direct incorporation, or by templating or induction, during synthesis. Chapter 8 considers the basic design principles that underpin the construction of metallosupramolecular polyhedra.

The third part is devoted to chirality at interfaces. Chapter 9 focuses on chirality expression and amplification at solution / solid-state interfaces, and applications such as heterogeneous catalysis and chiral separations. Chapter 10 addresses the initiation of chiral suprastructures on surfaces, and their modeling by high-resolution experimental methods and theoretical calculations.

The fourth part addresses chirality in organic hosts, and in biological / enzymatic systems: organic hosts are used in analytical chemistry to separate racemic guest mixtures or simply to distinguish enantiomers, and chiral hosts can function as catalysts in asymmetric reactions – Chapter 11 reviews particular features and applications of chiral organic host systems based primarily on cyclodextrins, calixarenes, and crown ethers in this regard. Chapter 12 stresses the enormous potential of microorganisms and enzymes as catalysts in asymmetric synthesis for controlling the stereochemical outcome of reactions, and discusses the use of whole cells and isolated enzymes as an attractive option for the chemical industry.

It is always understood that supramolecular chemistry is so diverse that one book cannot be totally equitable in its coverage of all aspects of the field. This book attempts to address some of the major aspects authoritatively and highlight important current thrusts. It will be useful to researchers working with chiral supramolecular assemblies, and will hopefully draw others with an existing interest in supramolecular systems to a further appreciation of the importance of chirality in the field, as seen through contributions of experts in their respective parts of that firmament.

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