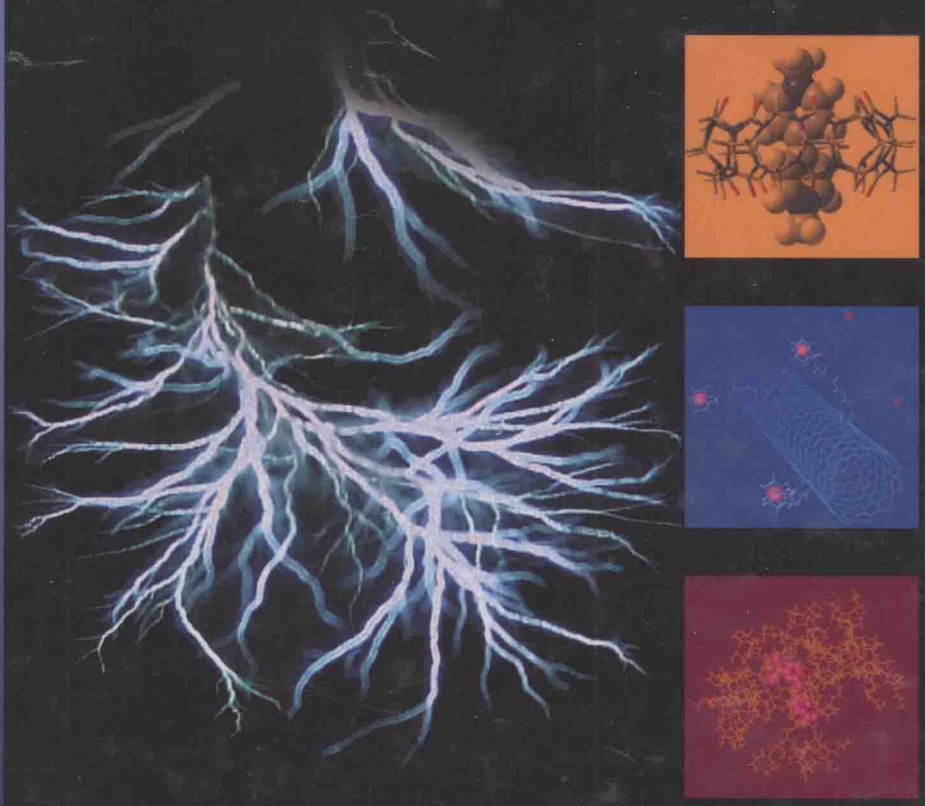
Electrochemistry of Functional Supramolecular Systems

Edited by

Paola Ceroni, Alberto Credi and Margherita Venturi



With a Foreword by Allen J. Bard

WILEY

ELECTROCHEMISTRY OF FUNCTIONAL SUPRAMOLECULAR SYSTEMS

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The Wiley Series on Electrocatalysis and Electrochemistry

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PREFACE to the Wiley Series on Electrocatalysis and Electrochemistry

This series covers recent advances in electrocatalysis and electrochemistry and depicts prospects for their contribution to the present and future of the industrial world. It illustrates the transition of electrochemical sciences from a solid chapter of physical electrochemistry (covering mainly electron transfer reactions, concepts of electrode potentials, and structure of the electrical double layer) to the field in which electrochemical reactivity is shown as a unique chapter of heterogeneous catalysis, is supported by high-level theory, connects to other areas of science, and includes focus on electrode surface structure, reaction environment, and interfacial spectroscopy.

The scope of this series ranges from electrocatalysis (practice, theory, relevance to fuel cell science and technology) to electrochemical charge transfer reactions, biocatalysis, and photoelectrochemistry. While individual volumes may look quite diverse, the series promises updated and overall synergistic reports on insights into further the understanding of properties of electrified solid/liquid systems. Readers of the series will also find strong reference to theoretical approaches for predicting electrocatalytic reactivity by such high-level theories as DFT. Beyond the theoretical perspective, further vehicles for growth are the sound experimental background and demonstration of significance of such topics as energy storage, syntheses of catalytic materials via rational design, nanometer-scale technologies, prospects in electrosynthesis, new instrumentation, surface modifications in basic research on charge transfer, and related interfacial reactivity. In this context, readers will notice that new methods that are being developed for a specific field may be readily adapted for application in others.

Electrochemistry has benefited from numerous monographs and review articles due to its unique character and significance in the practical world (including electroanalysis). Electrocatalysis has also been the subject of individual reviews and compilations. The Wiley Series on Electrocatalysis and Electrochemistry is dedicated to the current activity by focusing each volume on a specific topic of choice. The chapters also demonstrate electrochemistry's connections to other areas of chemistry and physics, such as biochemistry, chemical engineering, quantum mechanics, chemical physics, surface science, and biology, and illustrate the wide range of literature that each topic contains. While the title of each volume informs of the specific focus chosen by the volume editors and chapter authors, the integral outcome offers a broad-based analysis of the total development of the field. The progress of the series will provide a global definition of what electrocatalysis and electrochemistry are concerned with now and how they evolve with time. The purpose is manifold,

mainly to provide a modern reference for graduate instruction and for active researchers in the two disciplines, as well as to document that electrocatalysis and electrochemistry are dynamic fields that expand rapidly and likewise rapidly change in their scientific profiles.

Creation of each volume required the editor's involvement, vision, enthusiasm, and time. The Series Editor thanks all Volume Editors who graciously accepted his invitations. Special thanks are for Ms. Anita Lekhwani, the Series Acquisition Editor, who extended the invitation to the Series Editor and is a wonderful help in the Series assembling process.

ANDRZEJ WIECKOWSKI

Series Editor

FOREWORD

Like the currently popular area, called "nanoscience", the field of "supramolecular chemistry" has rather hazy boundaries. Indeed, both areas now share much common ground in terms of the types of systems that are considered. From the beginning, electrochemistry, which provides a powerful complement to spectroscopic techniques, has played an important role in characterizing such systems and this very useful book goes considerably beyond the volume on this same topic by Kaifer and Gómez-Kaifer that was published about 10 years ago. Some of the "classic" supramolecular chemistry topics such as rotaxanes, catenanes, host–guest interactions, dendrimers, and self-assembled monolayers remain, but now with important extensions into the realms of fullerenes, carbon nanotubes, and biomolecules, like DNA.

These topics lead to considerations of supramolecular devices, for example for use as sensors, and to molecular machines. Not only is electrochemistry an excellent way of characterizing such systems, for example, via cyclic voltammetry, but in the world of molecular machines, it is also the most straightforward approach to providing the energy to power such devices. These topics then naturally lead to consideration of the conversion of electricity to light (electrochemiluminescence) and light to electricity (dye-sensitized solar cells) via electrochemical devices. While the latter are not fundamentally supramolecular systems, their design could certainly benefit from the considerations in the very detailed and authoritative treatments in this volume. The idea of integrated chemical systems, based on nanoscience and nanotechnology, was proposed a little over 20 years ago and was the subject of my 1994 monograph, but, so far, few such systems have reached widespread practical utilization. Nevertheless, the principles of such systems, for example for synthesis, analysis, and perhaps computation remain of interest, and supramolecular electrochemistry can play a major role in their development. I hope this important volume will go a long way toward introducing such principles to a wide audience, especially to the young people who are less burdened by impressions of what is impossible.

The University of Texas at Austin *Allen J. Bard*

PREFACE

Supramolecular chemistry is a highly interdisciplinary field that has been developed at an astonishingly fast rate during the last three decades. In a historical perspective, as pointed out by Jean-Marie Lehn, supramolecular chemistry originated from Paul Ehrlich's receptor idea, Alfred Werner's coordination chemistry, and Emil Fischer's lock-and-key image. It was only after 1970, however, that fundamental concepts such as molecular recognition, preorganization, self-assembly, and self-organization were introduced to chemistry; supramolecular chemistry then began to emerge as a well-defined discipline and was consecrated by the award of the Nobel Prize in Chemistry to Charles Pedersen, Donald Cram, and Jean-Marie Lehn in 1987.

Supramolecular chemistry, according to its most popular definition, is "the chemistry beyond the molecule, bearing on organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces." As the field developed, it became evident that a definition strictly based on the nature of the bond that links the components would be limiting. Many scientists, therefore, started to distinguish between what is molecular and what is supramolecular based on the degree of intercomponent interactions. In a general sense, one can say that with supramolecular chemistry there has been a shift in focus from molecules to molecular assemblies or multicomponent structures driven by the emergence of new functions.

In the frame of research on supramolecular systems, the idea began to arise in a few laboratories that the concepts of "device" and "machine" could be applied at the molecular level. In other words, molecules might be used as building blocks for the assembly of multicomponent structures exhibiting novel and complex functions that arise from the cooperation of simpler functions performed by each component. This strategy, encouraged by a better understanding of biomolecular devices, has been implemented on a wide variety of chemical systems, leading to highly interesting results. As a matter of fact, the molecular bottom-up construction of nanoscale devices and machines has become one of the most stimulating challenges of nanoscience.

Such achievements have been made possible because of the substantial progresses obtained in other areas of chemistry and physics—particularly concerning the synthesis and characterization of complex chemical systems, and the study of surfaces and interfaces. In this perspective, electrochemistry is a very powerful tool not only for characterizing a supramolecular system, but also for operating the device. Indeed, molecular devices, as their macroscopic counterparts, need energy to operate and signals to communicate with the operator. Electrochemistry can be an interesting

answer to this dual requirement: it can be used to supply the energy needed to make the system work, and, by means of the various electrochemical techniques (e.g., voltammetry), it can also be used to "read" the state of the system, controlling and monitoring the operation performed by the device. Furthermore, electrodes represent one of the best ways to interface molecular-level systems to the macroscopic world, a feature that is important for future applications. Hence, it is not surprising that the marriage of electrochemistry and supramolecular chemistry has produced a wealth of very interesting devices and functions, thereby generating new scientific knowledge and raising expectations for practical applications in energy conversion, information and communication technologies, advanced materials, diagnostics, and medicine.

Our aim with this book is to provide the reader with an overview of current electrochemical research applied to multicomponent chemical systems, with particular attention to properties and functions, and to strengthen the contacts between the electrochemical community and the researchers engaged in the field of nanoscience. Although the text covers a wide range of topics with contributions from leading authorities in their respective fields, it does not even attempt to be a comprehensive book on supramolecular electrochemistry. Rather, we would like to give the reader a flavor of the level of creativity and ingenuity reached by scientists working in this area. We hope that the book will be useful as a reference not only for experienced researchers, but also for graduate students and postdoctoral fellows who are interested in exploring electrochemistry at its frontiers with supramolecular chemistry, materials science, and biochemistry. It may also be a useful complement for students attending nanoscience and nanotechnology courses.

The 17 chapters of the book are not grouped in sections but they are somehow logically ordered. The initial contributions, describing basic science investigations on systems in solution, are followed by chapters dealing with less conventional multicomponent architectures and/or environments. The final part contains contributions on devices and systems of high complexity and/or applicative interest. Although the book does not include introductory or tutorial sections, most chapters begin with a discussion of the basic concepts that are relevant for the presented topics. We hope that these sections will make the book comprehensible also to nonspecialists.

We would like to express our gratitude to the distinguished colleagues and friends who contributed the chapters: their commitment is indeed a fundamental ingredient of this initiative. We also thank people at Wiley for their assistance during the various phases of the editorial work. Finally, we would like to thank our families because their love and patience are an invaluable support for our professional activity.

Bologna, June 2009

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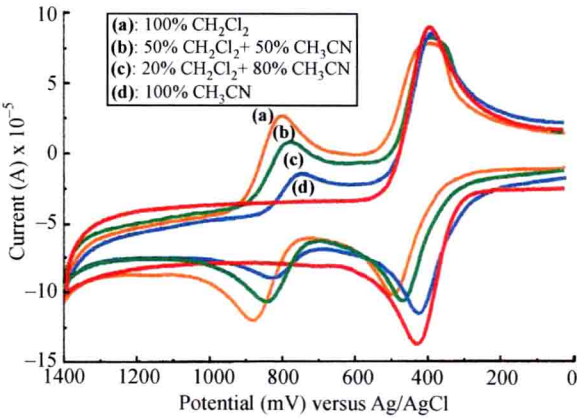

Figure 1.5 CVs of 1 mM **40** in 0.1 M NBu_4PF_6 with different ratios of CH_2Cl_2 and CH_3CN: (a) 100% CH_2Cl_2, (b) 50% CH_2Cl_2, 50% CH_3CN, (c) 20% CH_2Cl_2, 80% CH_3CN, and (d) 100% CH_3CN. 100 mV/s scan rate.[67]

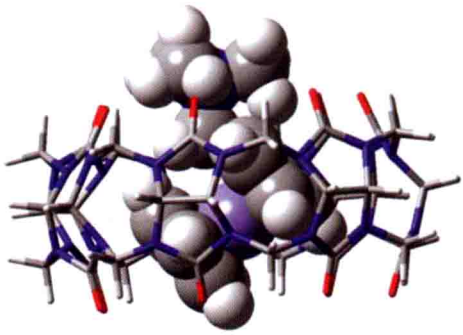

Figure 3.7 Energy minimized structure (PM3 method) of the CB7 • **2** complex.

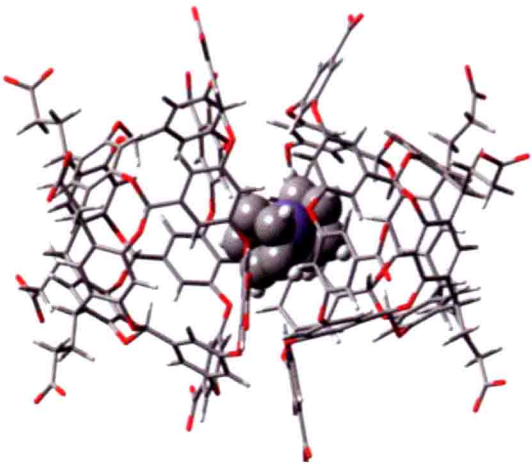

Figure 3.11 Energy-minimized (PM3 method) structure of the Fc@$\mathbf{5}_2$ molecular assembly.

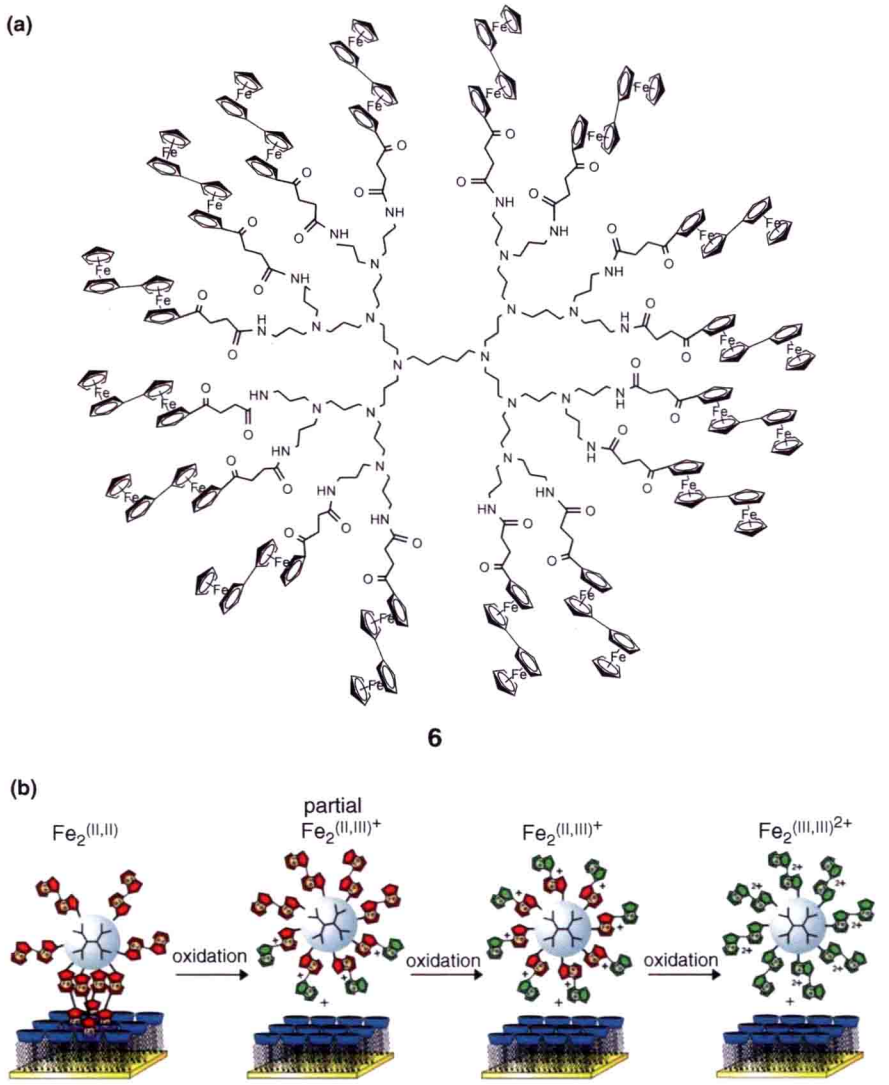

Figure 6.6 (a) Structural formula of dendrimer **6** containing at its periphery 16 biferrocene units; (b) schematic representation of the proposed oxidation mechanism (at low scan rate) of dendrimer **6** in solution and immobilized at the β-CD host surface.[40] Reproduced with permission from Ref. 40.

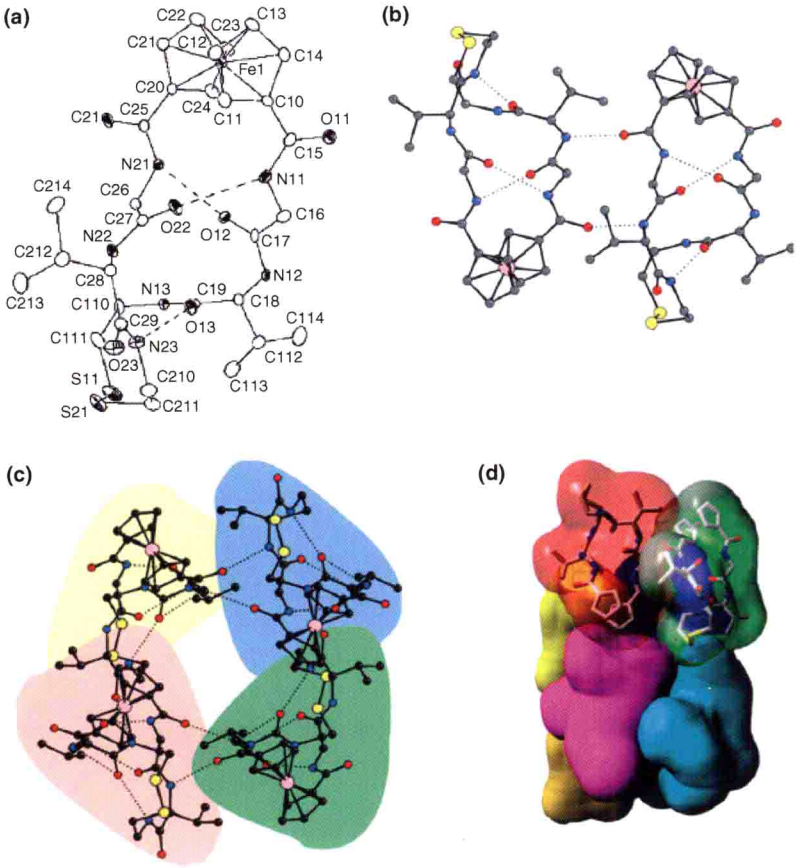

Figure 10.4 Schematic representation of the formation of the pseudo-β-barrel formed from molecular building blocks by tiling. (a) Molecular structure of Fc[Gly-Val-CSA]$_2$, (b) formation of β-sheets through intermolecular N(H)O=C hydrogen bonding, (c) H-bonding interactions between four molecules to form a β-barrel, and side view molecular-surface representation showing barrel.

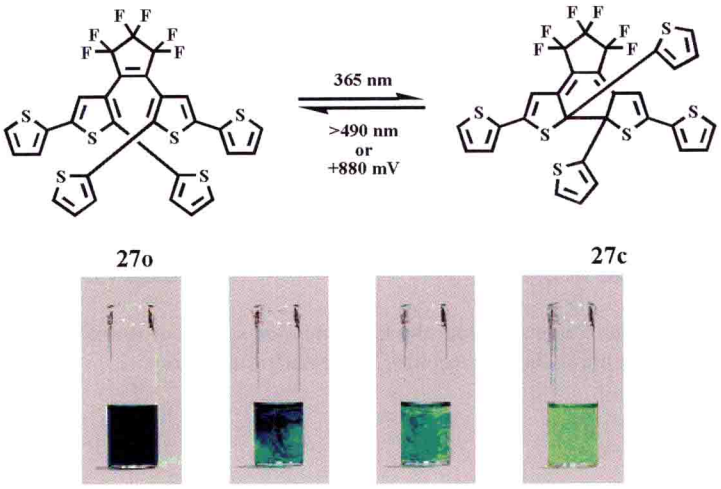

Figure 15.2 Gradual color change of a CH_2Cl_2 solution of compound **27** containing 75% of the ring-closed isomer **27c** when treated with a catalytic amount of $[(4\text{-}BrC_6H_4)_3N][SbCl_6]$.