Electrochemistry of Functional Supramolecular Systems

Supramolecular chemistry has been an ever-growing subject since the mid-1980s and has benefited from some spectacular advances in analytical chemistry and molecular spectroscopy. The main concepts behind supramolecular chemistry, although dating back to Emil Fischer's celebrated "lock and key" principle, were outlined in the classical text of Jean-Marie Lehn.[1] It has to be stressed that supramolecular chemistry is a highly multidisciplinary field that deals with complex systems held together by relatively weak interactions. A particular strength of the topic is that it relates to all areas of molecular science, including biology and biochemistry, and seeks to understand molecular properties in terms of local topology and organisation.

From the onset, supramolecular chemistry has been strongly linked to function and there have been numerous elegant demonstrations of cooperative behaviour between subunits assembled by way of non-covalent forces. To some degree, it can be argued that the future exploitation of novel chemical systems intended to operate on a large scale and at the molecular level must be constructed around supramolecular concepts in order to overcome problems of cost, repair, and regeneration. Such systems include selective catalysis, solar energy conversion, molecular recognition, and bio-inspired networks. To examine the function of supramolecular entities, many new spectroscopic tools have been developed and modern electrochemical practices have been hugely successful in advancing our knowledge of intercompartmental interactions in assembled conjugates. The present volume adds substantially to this knowledge base and provides deep insight into many supramolecular systems. The emphasis of the book lies with the functional properties of the assemblage, as probed by electrochemical methodology. There is a wealth of critical and sophisticated artistry within the 600 pages and much to enjoy.

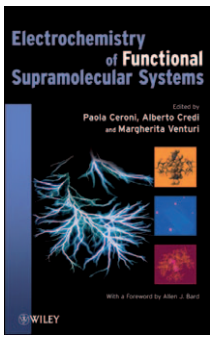
The foundation of this volume lies with 17 self-contained chapters, each contributed by a different research group, and with little or no overlap. The ordering of chapters is somewhat haphazard but this only adds to the value of the book. There is no easy introduction and it is assumed that the reader is already familiar with both basic electrochemical methodology and the general principles of supramolecular chemistry. The book forms part of the *Wiley Series on Electrocatalysis and Electrochemistry* but stresses the special considerations appropriate to the electrochemistry of multicomponent molecular systems. In terms of instrumentation, the text is dominated by applications of cyclic voltammetry.

Chapter 1 provides a concise review of the electrochemistry of hydrogen-bonded ensembles, including many host–guest complexes, and illustrates the way in which such binding can change during the electrochemical step. Chapter 2 is an ambitious review of molecular motions driven by electrolysis and covers a wide variety of examples. Here, electrochemistry is used as the stimulus for the translational migration of subunits and emphasis is placed on the logic behind the design of putative molecular-scale machines. The opposite approach forms the basis of Chapter 3, which is concerned with the trapping of redox-active guests by a suitable host. Here, differential complexation patterns are discerned by virtue of the oxidation/reduction state of the guest. This theme is continued, to some extent, in Chapter 4 where the accent is placed on the use of dendrimers to encapsulate redox-active moieties from solution. This latter chapter is meticulously referenced and contains some thought-provoking ideas about how electrochemistry can be useful for unravelling complex processes occurring in non-natural polymers.

The general concept of dendrimers is sustained in Chapter 5 which deals with accretions of metal-poly(pyridine) complexes and their ensuing electrochemistry. Such materials exhibit a bewildering array of electrochromic properties that evolve according to the molecular architecture of the dendrimer. In principle, dendrimers could replace redox-active polymers as vehicles for storing electronic charge and this notion is expanded upon in Chapter 6. Several disparate types of dendrimer are considered in terms of their capability to undergo successive charge-transfer steps, leading to the accumulation of charge within a relatively small volume. Both organic and inorganic materials are considered and attention is drawn resolutely towards device manufacture using dendrimers as the charge-storage medium.

Chapter 7 describes recent advances in the electrochemistry of self-assembled monolayers formed from thiol linkages. The electrochemistry of carbon nanoparticles forms the basis of Chapter 8, with emphasis on doped fullerenes that display intricate multielectron voltammograms during reduction. This chapter is nicely complemented by an up-to-date survey of carbon nanotubes bearing intercalated residues, forming the basis for Chapter 9. This is a rapidly advancing field and some highly elaborate molecular architectures have been synthesized, often with porphyrin chromophores incorporated into the array.

Chapter 10 switches attention to electro-active biomolecules, including peptides and nucleobases. Many of the reported systems include a covalently



Electrochemistry of Functional Supramolecular Systems
Edited by Paola Ceroni, Alberto Credi and Margherita Venturi. John Wiley & Sons, Hoboken 2010. 598 pp., hardcover € 132.00.—ISBN 978-0470255575

attached ferrocene moiety as the redox-active component. Functional nanoparticles can be used as catalysts for certain processes and such realisations form the main premise advanced in Chapter 11. Here, gold nanoparticles are used as the central core by which to assemble redox-active clusters that can be attached to macroscopic electrodes. The appendage can be doctored with redox-active units, thereby leading to the generation of multifunctional clusters with a rich electrochemistry.

Several of the chapters appearing towards the end of the volume describe state-of-the-art supramolecular systems that might offer promise for the construction of molecular-scale devices. Thus, Chapter 12 delivers a comprehensive and exclusive account of bio-hybrid systems driven by electrochemical means. The text covers an inordinately wide range of redox-active materials attached to electrode surfaces and used for analytical purposes. This is a most impressive chapter, slightly flawed by a few poor figures, that spans the entire field in an authoritative manner. Chapters 13 and 14 describe different aspects of the electrochemistry of rotaxanes and catenanes, emphasizing their usefulness as prototypes for molecular-scale machines. The role for supramolecular chemistry in the area of molecular electronics is further expounded upon in Chapter 15, specifically in the context of redox-controlled molecular switches. The final chapters deal with electrochemiluminescence and with the electrochemical properties of dye-injection solar cells. Both subjects are highly topical at present.

The book is edited by three well-acknowledged specialists in the field, each coming from the University of Bologna, which itself has been highly prominent in the field of functional supramolecular chemistry. There is a total of 41 contributing authors. Presentation is universally excellent, with most chapters being well researched, nicely referenced and decorated with informative figures. The index is satisfactory, without being great, while the cover is pretty much uninspiring but hefty. Most chapters end with a summarizing conclusion that also serves as an abstract. Overall, the book is very good value for money and should serve to inspire new researchers to try their hand at applying electrochemical techniques to complex molecular organisations. It is highly recommended to all researchers in the field.

Anthony Harriman
Molecular Photonics Laboratory
School of Chemistry, Newcastle University (UK)

DOI: 10.1002/anie.201005968

[1] J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, **1995**.

