

1 Introduction

Interfacial Supramolecular Assemblies comprise an electrochemically addressable solid surface functionalized with a film which incorporates molecular components that can be addressed electrochemically or photochemically. In these assemblies, specific bonding interactions exist between the surface and film and they are generally in contact with a solution. Typical of a supramolecular assembly, the individual building blocks retain much of their molecular character, but the overall assembly exhibits new properties, or is capable of performing a specific function beyond that possible when using the individual components.

1.1 Introductory Remarks

The development of chemistry is continuously reinvigorated by discovery and innovation. Following the discovery of atoms in the 18th century, synthetic techniques were developed and, since the beginning of the 19th century, molecular chemistry involving covalent bonding has been dominant. These synthetic capabilities were complemented by theoretical understanding and structural characterization, e.g. the correct structure of benzene was proposed by Kekule in 1865. At the beginning of the 20th century, coordination chemistry was added to the armor of the chemist when Werner defined the coordination bond and this development greatly promoted the development of inorganic chemistry. At around this time, progress was also made in the development of spectroscopic techniques and the discovery of the spectroscopic lines for the various elements led to the development of quantum chemistry.

During the 1970s, the picture of chemistry was that of a sophisticated science built on a good understanding of bonding and of the physical properties and behavior of compounds. In addition, many synthetic methods had been developed and a number of powerful techniques for their characterization were available. Without techniques such as X-ray diffraction, nuclear magnetic resonance spectroscopy, infrared spectroscopy, mass spectrometry and UV–visible spectroscopy, much of today's chemistry would be unthinkable. Other important developments have been the emergence of separation science, electrochemistry and photophysics. As will be shown below, the latter two techniques are of prime importance for the development of interfacial supramolecular chemistry. With this powerful array of techniques and knowledge, chemists started to consider more and more complicated systems, and as a result, interest in the molecular aspects of biological systems developed rapidly.

This has led to a well-developed biochemistry, and has resulted in a much improved understanding of the properties of enzymes, natural photosynthesis, respiration, etc. These studies revealed that the structure of natural systems is controlled by intermolecular forces and the importance of organization and self-assembly was soon recognized.

It is against this background that the interest in intermolecular interactions has developed. The term *supramolecular chemistry* was introduced in 1978 by Jean-Marie Lehn in an article in the journal *Pure and Applied Chemistry* and was defined as *chemistry beyond the molecule*. This definition implies that supramolecular chemistry deals with intermolecular interactions and with molecular assemblies. The central concept of supramolecular chemistry is that of *organization*. In biological systems, molecular assemblies are able to carry out specific functions because they are arranged in an appropriate manner. For example, in natural photosynthesis, it is not just the spectroscopic and redox features of the components that allow for effective charge separation, but more importantly, their relative orientation and intersite separation. It is this idea of utilizing and understanding organization and interaction that has attracted so many scientists into the area of supramolecular chemistry.¹

One of the fascinations of scientists has long been the ability of nature to use supramolecular forces to create molecular assemblies for carrying out particular functions. As a result, one of the ultimate aims of supramolecular chemistry is to create molecular devices.

1.2 Interfacial Supramolecular Chemistry

From high-speed molecular computers to optoelectronic switching, technological advances in speed and miniaturization drive the search for novel materials with enhanced electronic properties. Supramolecular chemistry has played a major role in progressing research in this area, leading to novel classes of materials which are capable of light or electrically stimulated chemistry and long-range electronic communication.

Interfacial supramolecular assemblies use well-characterized redox centers and chromophores as building blocks to create assemblies on surfaces that are purposefully structured on the molecular level, while at the same time extending over supramolecular distances. Figure 1.1 illustrates how a surface can play an important, often decisive, role in dictating the overall structure and function of a molecular component. In terms of structure, a high degree of molecular organization can be best achieved by developing supramolecular architectures at solid interfaces. The surface impacts the supramolecular system in three important ways. First, the surface provides a platform for extended two-dimensional organization of the supramolecular adsorbate. Secondly, the packing density of the molecular species on the surface allows the extent and strength of lateral interactions to be controlled so that intermolecular communication, which may be individually weak, can collectively drive the assembly of defect-free structures. Finally, since the surface itself becomes

¹ A selection of suitable texts for further reading on this subject are presented at the end of this chapter.

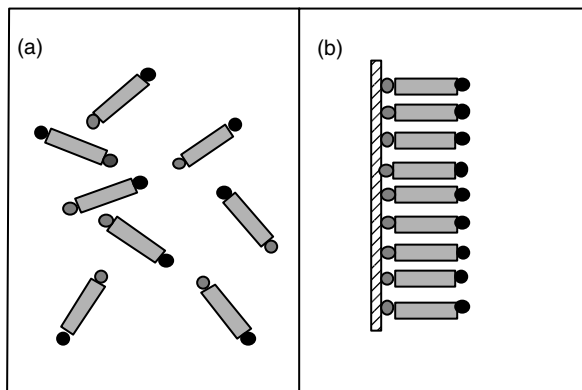


Figure 1.1 Schematic representations of (a) supramolecular and (b) interfacial supramolecular assemblies

a component of the supramolecular assembly, it participates in supramolecular function without eliminating the identity of each moiety in the structure.

A surface also provides a communicable interface, through which the adsorbate can be addressed directly. In doing so, it provides a powerful means of directing processes within the assembly. For example, if the surface is conducting it may be used to induce vectorial electron transfer.

Creating organized structures is an important goal in interfacial supramolecular chemistry. The Langmuir–Blodgett technique is important for the production of macroscopic materials that are organized on the molecular length scale. This approach allows amphiphilic molecules to be oriented at the air–water interface and then transferred sequentially onto a solid support. Despite the very elegant research conducted in this area, it seems unlikely that this approach will produce materials with the thermal, mechanical, and chemical stability required for practical applications. For this reason, Langmuir–Blodgett monolayers are not considered in this present book.

Synthetic flexibility is one of the most significant advantages of self-assembly allowing organic, inorganic and biological components to be used as building blocks. Organized molecular films deposited on solid surfaces are of great conceptual interest because their small thickness makes them ‘quasi-ideal’ two-dimensional systems. They constitute a novel ‘bottom-up’ approach to creating nanoscale structures. This approach contrasts with ‘top-down’ approaches that entail making existing devices so small that they eventually finish up as nanosized objects, with dimensions of no more than a few hundred nanometers. The top-down approach is typified by the manufacture of transistors on computer chips. Currently, such transistors are only ca. 200 nm in size and it is widely anticipated that they will break the 100 nm barrier in the near future. The bottom-up approach, in which interfacial supramolecular assemblies (ISAs) play an intimate part, involves constructing nanodevices from their constituent parts, i.e. atoms or small molecules. Fabrication is achieved by either physical relocation of the building blocks into their required locations, or by using molecular self-assembly. The former route involves techniques such as the use of laser tweezers or atomic force microscopy. However, the process is laborious and molecules occasionally stick to the substrate and break

apart. Chemical manipulation of the kind described in this book is more elegant and vastly more subtle because it relies on instructions programmed into the system to determine the ultimate location of each building block.

The parallels with nature are obvious. Biotechnology is the only fully functional nanotechnology and life itself is intrinsically interfacial. Atomic-scale construction and information processing are mediated on the surfaces of protein and nucleic acid catalysts. Biological systems excel at atom-by-atom or molecule-by-molecule manipulation. Take, for example, the origins of life itself, namely a fertilized ovum, which is programmed to build, molecule-by-molecule, the most complex of self-assembled constructs, a living organism. In the laboratory, nothing even remotely as complex could be attempted in the foreseeable future, although it does not prevent scientists from deriving their inspiration from such complex functions. Simple instructions such as switchable lateral interactions, site-selective functionalization to create surface patterns, as well as self-healing and replication, can currently be encoded. These advances allow ISAs to be created that exist in the solid (ordered) regime, but are close to an order–chaos phase boundary, i.e. their structure is influenced by external factors. For example, permeation into an ISA can be switched on and off by the presence of key molecules in solution.

1.3 Objectives of this Book

The primary goal is to provide a molecular-level understanding of how ISAs are designed for specific functions, created, characterized and then used to address fundamental issues such as the distance dependence of energy and electron transfer, as well as applications such as molecular switching. This objective will be achieved by examining how the interplay of the physical and electronic structure, morphology and dynamical properties of an ISA influence its overall properties and functioning.

The intention is not to comprehensively review the literature that describes the multidisciplinary efforts of researchers to create interfacial supramolecular assemblies. The literature in this area is vast and involves research programs in chemistry, physics and biology, as well as analytical, materials and surface sciences. Rather, key examples of advances that have significantly influenced the field and will direct its future development are presented. In addition, some of the analytical methods, theoretical treatments and synthetic tools, which are being applied in the area of interfacial supramolecular chemistry and are driving its rapid development, will be highlighted.

1.4 Testing Contemporary Theory Using ISAs

Supramolecular chemistry has provided an experimental platform for testing many modern theories on bonding, molecular organization, photochemistry, and in particular, electron transfer theory. For example, in 1956, Marcus predicted that highly exoergonic electron transfer reactions actually slow down with increasing driving force. Numerous bimolecular electron transfer reactions were studied

in order to test this prediction, but slow diffusional mass transport inevitably limited the range of conditions under which rate measurements could be made. Supramolecular chemistry provided the first rigorous proofs of the validity of these contemporary theories by linking donor and acceptor species within a single electronically communicating entity. This approach allows the electron transfer rate-limiting reactions to be studied over a much wider range of driving forces.

Electron transfer remains one of the most important processes explored when using interfacial supramolecular assemblies and given the emerging area of molecular electronics, this trend is set to continue. Therefore, Chapter 2 outlines the fundamental theoretical principles behind the electrochemically and photochemically induced processes that are important for interfacial supramolecular assemblies. In that chapter, homogeneous and heterogeneous electron transfer, photoinduced proton transfer and photoisomerizations are considered.

1.5 Analysis of Structure and Properties

Modern surface analytical tools make it possible to probe the physical structure as well as the chemical composition and reactivity of interfacial supramolecular assemblies with unprecedented precision and sensitivity. Therefore, Chapter 3 discusses the modern instrumental techniques used to probe the structure and reactivity of interfacial supramolecular assemblies. The discussion here is focused on techniques traditionally applied to the interrogation of interfaces, such as electrochemistry and scanning electron microscopy, as well as various microprobe techniques. In addition, some less common techniques, which will make an increasing contribution to supramolecular interfacial chemistry over the coming years, are considered.

1.6 Formation and Characterization of Interfacial Supramolecular Assemblies

Chapter 4 discusses the formation and properties of spontaneously adsorbed monolayers, self-assembled monolayers and thin polymer films. This chapter considers how molecules can be immobilized on a surface in a controlled manner to create a useful ISA. The structural features of the layers are also considered. Self-assembled and spontaneously adsorbed monolayers offer a facile means of controlling the chemical composition and physical structure of a surface. These monolayers can exhibit low defect densities and high degrees of structural order over supramolecular distances. In contrast, polymeric ISAs tend to exhibit poorly defined primary structures, but their secondary structure is strongly influenced by external factors such as temperature, contacting solvent, ionic strength, etc. The possibility of controlling this secondary structure to achieve a specific function, e.g. exclusion of an interference in a chemical sensing application, is one of the most attractive features of these ISAs. Finally, Chapter 4 considers likely developments in the future, in particular, the role of molecular self-assembly in developing nanotechnology.

1.7 Electron and Energy Transfer Properties

Understanding those factors that control electron and energy transfer is not only of fundamental interest, but is vital for creating molecular electronic devices. Chapter 5 describes selected case studies which illustrate the key factors that control electron and energy transfer within interfacial supramolecular assemblies and especially across solid–film interfaces. In doing so, it seeks to identify those approaches that provide key fundamental insights and show the greatest promise for creating electrochemically and photochemically triggered molecular switches, sensors and biomimetic systems. It also considers the major challenges for the future and barriers to progress in the area.

Interfacial monolayer, multilayer and polymer species which exhibit interesting examples of light and electrically stimulated functions such as isomerization and proton transfer in ISAs are also presented in this chapter. Such materials may represent the precursors for electrooptic switches and addressable molecular-based machines.

1.8 Interfacial Electron Transfer Processes at Modified Semiconductor Surfaces

The development of functional supramolecular devices remains mainly conceptual. However, photovoltaic devices are one of the few exceptions. Dye-sensitized nanocrystalline semiconductor materials have received significant interest as a result of their application in solar energy conversion.

Chapter 6 takes the much studied supramolecular dye-sensitized TiO₂ as an example of an operational supramolecular interfacial device. The fundamental operation of these devices are discussed, including their mechanism of operation. The application of modified semiconductor surfaces as electrochromic devices is also considered.

In conclusion, this book is intended as an overview of the principles behind and state-of-the-art in interfacial supramolecular chemistry. The book is suitable for researchers and graduate students and focuses on assemblies that demonstrate at least the potential to produce useful devices such as solar cells, electrochromic devices, molecular wires, switches and sensors which are addressable by using electrochemical and optical stimuli. Molecular materials for nanoscale molecular devices remain an intriguing conceptual possibility.

Further Reading

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