Macromolecules Containing Metal and Metal-Like Elements

Volume 9

Supramolecular and Self-Assembled Metal-Containing Materials

Edited by

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Contents

Preface

This book series, *Macromolecules Containing Metal and Metal-Like Elements*, is our attempt to bring to the chemical community new concepts and developments in the titled area of research. Volume 9 focuses attention on the area of supramolecular chemistry, supramolecular architecture, and supramolecular self-assemblies that involve materials containing metals and metal-like elements and the potential applications of these interesting hybrid materials.

Supramolecular chemistry may be defined as the formation of large complex assemblies (i.e., clusters) of species composed of two or more small, intermediate, and/or large molecules that are held together by noncovalent bonds. By noncovalent bonds we essentially mean hydrogen bonds, van der Waals interactions, metal coordination (donor–acceptor) interactions, π–π interactions, hydrophobic interactions, electrostatic forces, and/or combinations of these forces. Such interacting complex species are characterized by their spatial features, which include their architecture, as well as by the interactions, which hold the various components into a superstructure. The intermolecular interactions may be *weak,* as in hydrogen bonding, or *strong,* as in the case of metal-ion coordination. Very simple examples of the former are the vapor phase dimerization of acetic acid, which is held together by two hydrogen bonds; clathrates, which consist of one type of molecule that traps and contains a second type of molecule (i.e., host–guest complexes, inclusion compounds); and catenanes and rotaxanes, which are composed of two or more macrocyclic molecules that form a mechanically interlocked molecular architecture. An example of a strong intermolecular interaction is ferritin, which is a natural, iron-containing, globular complex of 24-protein subunits arranged as a hollow sphere with six channels that are used for intracellular storage and mobility of iron.

Supramolecular science has grown considerably over the past several decades, particularly with the pioneering discoveries by D. J. Cram, C. J. Pederson and Jean-Marie Lehn.[1,2] The field is now highly interdisciplinary and has developed to such an extent that it presently encompasses all the subdisciplines of chemistry in addition to significant contributions from the other physical and biological sciences and numerous engineering technologies. It is important that supramolecular systems are beginning to display valuable commercial applications in catalysis, nanotechnology, electro-optical devices, molecular sensing and recognition, and biomedicine. For example, several inventions involving supramolecular assemblies have recently been reported in the patent literature.[3] Some scientists have proposed that supramolecular systems will be the chemical *building blocks* of the future, thereby affecting everything from quantum dots to artificial intelligence.[4] For those who wish to learn more about the field, we recommend the several recent reviews[5] in addition to the series, *Advances in Supramolecular Chemistry*, edited by G. W. Gokel.[6]

In this volume we have collected 10 review chapters from distinguished scientists who have contributed extensively to the study and development of supramolecular assemblies that contain metals and metal-like elements with unusual structures and morphologies and possess potentially useful (and applicable) physical and biological properties. The first chapter by K. Ariga et al. is a general discussion of supramolecular structures that contain inorganic building blocks for hybrid lipid thin films, layer-by-layer assemblies, structure transcription, and functional mesoporous hybrids. This is followed by two chapters, the first by M. L. Kistler et al., who describe the self-assembly of hydrophilic polyoxometalate (POM) macro-anions and examine the structure and behavior of POM macro-ions in solution. This is followed by a chapter by S. K. Das, who provides an overview of the supramolecular features of POM-supported transition metal complexes, POM-crown ether complexes with supramolecular cations, and supramolecular water clusters associated with POMs.

Chapter 4, by G. K. H. Shimizu et al., discusses work using metal-containing sulfonates and phosphonates as building blocks (linkers) to supramolecular networks. They describe the disruption of layered solids to form open-framework solids and examine the structure and dynamic behavior of these porous materials.

In Chapter 5, M. Majumdar and J. K. Bera describe the properties of and synthetic protocols for preparing extended linear metal (Cr, Co, Ni and Cu) chain compounds that contain at least three metal ions and are supported by ligand systems. In addition, they describe bent Pd chains that are sandwiched between unsaturated hydrocarbons and unsupported linear metal chain compounds.

In Chapter 6, B. M. Rombo et al. delve into the formation of boronate-linked supramolecular architectures based on boronate ester formation—for example, small molecule diesters form supramolecular self-assemblies in the solid state based on a phenyl-boron-phenyl sandwich motif in which these small oligomers link together to generate macrocycles and other polymers. The polymeric macrocyclics and linear structures demonstrate self-repair capabilities and constitute a new class of wide band-gap semiconducting materials. Through the incorporation of polyvalent boronates, covalent organic frameworks are described, which create highly crystalline, porous network materials.

In Chapter 7, S. M. Arachchige and K. J. Brewer concentrate on the coupling of light-absorbing metal centers to reactive Rh(III), Pt(II), and Pd(II) centers. This chapter highlights the recent progress and basic methods used to study such reactive metal-containing assemblies. The authors examine different structural motifs and their chemical and photo-physical properties, which give rise to the coupling of ruthenium and osmium light absorbers because recent findings indicate their promise in solar energy conversion, emission-based sensing, spectroscopic probes of biomolecules, DNA modification, DNA photo-cleavage agents, anticancer drug development, and photodynamic therapy.

In Chapter 8, R. Martínez-Máñez et al. discuss the use of supramolecular and hybrid organic–inorganic systems in the development of novel sensing and signaling concepts through a shift or intensity change in color, fluorescence, or redox wave. The chapter highlights the general concept of supramolecular signaling as applied to the development of chromo-fluorogenic chemosensors and focuses attention on new functional sensing concepts that have an improved level of performance with special attention to hybrid systems that show synergic functional effects that are not found in molecular-based systems or with unmodified nanoscopic solids.

O. Castillo et al. in Chapter 9 provide an overview of various aspects of molecular recognition that takes place between nucleobases and artificial receptors. The authors focus attention on metal-oxalato frameworks that are involved in the molecular recognition process. These metal-oxalato fragments present great efficiency by acting as receptors of neutral and cationic nucleobases and even supramolecular nucleobase aggreates; where anchoring to these receptors takes place by coordinative bonding to the metal centers through endocyclic nitrogen atoms or by means of hydrogen bonding interactions between the organic bases and the inorganic fragments.

Finally, in Chapter 10, M. Andruh and C. Ruiz-Pérez discuss synthetic approaches to the crystal engineering of coordination polymers. They address important questions concerning architecture and packing arrangements; i.e., cavities or channels, because such empty spaces may be filled by host anions, solvent molecules, uncoordinated ligand molecules—and interpenetration in which voids associated with one framework are occupied by one or more independent frameworks.

Thus, Volume 9 covers a wide array of subjects in the titled area. The discussions along with the plethora of references in each chapter should enable the reader to obtain a basic understanding of this frontier area of research.

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Series Preface

Most traditional macromolecules are composed of less than 10 elements (mainly C, H, N, O, S, P, C1, F), whereas metal and semi-metal-containing polymers allow properties that can be gained through the inclusion of nearly 100 additional elements. Macromolecules containing metal and metal-like elements are widespread in nature with metalloenzymes supplying a number of essential physiological functions including respiration, photosynthesis, energy transfer, and metal ion storage.

Polysiloxanes (silicones) are one of the most studied classes of polymers. They exhibit a variety of useful properties not common to non-metal-containing macromolecules. They are characterized by combinations of chemical, mechanical, electrical, and other properties that, when taken together, are not found in any other commercially available class of materials. The initial footprints on the moon were made by polysiloxanes. Polysiloxanes are currently sold as high-performance caulks, lubricants, antifoaming agents, window gaskets, O-rings, contact lens, and numerous and variable human biological implants and prosthetics, to mention just a few of their applications.

The variety of macromolecules containing metal and metal-like elements is extremely large, not only because of the large number of metallic and metalloid elements, but also because of the diversity of available oxidation states, the use of combinations of different metals, the ability to include a plethora of organic moieties, and so on. The appearance of new macromolecules containing metal and metal-like elements has been enormous since the early 1950s, with the number increasing explosively since the early 1990s. These new macromolecules represent marriages among many disciplines, including chemistry, biochemistry, materials science, engineering, biomedical science, and physics. These materials also form bridges between ceramics, organic, inorganic, natural and synthetic, alloys, and metallic materials. As a result, new materials with specially designated properties have been made as composites, single- and multiple-site catalysts, biologically active/inert materials, smart materials, nanomaterials, and materials with superior conducting, nonlinear optical, tensile strength, flame retardant, chemical inertness, superior solvent resistance, thermal stability, solvent resistant, and other properties.

There also exist a variety of syntheses, stabilities, and characteristics, which are unique to each particular material. Further, macromolecules containing metal and metal-like elements can be produced in a variety of geometries, including linear, two-dimensional, three-dimensional, dendritic, and star arrays.

In this book series, macromolecules containing metal and metal-like elements will be defined as large structures where the metal and metalloid atoms are (largely) covalently bonded into the macromolecular network within or pendant to the polymer backbone. This includes various coordination polymers where combinations of ionic, sigma-, and pi-bonding interactions are present. Organometallic macromolecules are materials that contain both organic and metal components. For the purposes of this series, we will define metal-like elements to include both the metalloids as well as materials that are metal-like in at least one important physical characteristic such as electrical conductance. Thus the term includes macromolecules containing boron, silicon, germanium, arsenic, and antimony as well as materials such as poly(sulfur nitride), conducting carbon nanotubes, polyphosphazenes, and polyacetylenes.

The metal and metalloid-containing macromolecules that are covered in this series will be essential materials for the twenty-first century. The first volume is an overview of the discovery and development of these substances. Succeeding volumes will focus on thematic reviews of areas included within the scope of metallic and metalloid-containing macromolecules.

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CHAPTER 1

Supramolecular Structures and Functions with Inorganic Building Blocks

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CONTENTS

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I. INTRODUCTION

Fabrication of nanometer-scale structures for ultra-small devices has been paid a great deal of attention because small machines could provide many societal benefits, such as optimization of energy consumption and waste discharge. Several excellent top-down approaches, including photolithography and electron-beam lithography, have been so far used to provide fine microstructures. However, these methods have several drawbacks, including size limitation and the paucity of applicable materials. Therefore, an alternate means, known as the bottom-up approach, has been recently intensively investigated. Methods of bottom-up fabrication rely on molecular self-assembly in supramolecular processes. Supramolecular chemistry, which was originally a branch of fundamental science, has now become an important concept in nanotechnology.

Most of the well-known or well-investigated supramolecular objects are assembled from organic molecules. The class of organic molecules possesses huge structural diversity and thus can exhibit many interesting chemical, physical, and biological functions. Probably the main drawback presented by organic species is their relative physical instability under the harsh conditions currently required for precise fabrication. This is in contrast to the high mechanical strengths and stabilities of most inorganic substances, which make them suitable for material applications. Unfortunately, inorganic materials have not been well investigated in terms of their potential in supramolecular chemistry. A combination of the two worlds of organic supramolecular chemistry and inorganic materials science should create useful nano-structured materials concurrently possessing various functionality, fine structural precision, and high mechanical stability. Supramolecular nanofabrication with inorganic building blocks, including organic–inorganic nano-hybrids and structure-transcribed materials, could be one of the most powerful methodologies for satisfying the current demands of nanotechnology.

As has been widely reported, metal-organic complexes, including metal-organic framework materials, are representative examples of supermolecules containing inorganic building blocks.[1,2] Because this subject has been extensively discussed in many forms, we here concentrate on supramolecular objects consisting of inorganic building blocks that are based on soft supramolecular assemblies. In this chapter, various recent topics in hybrid lipid thin films, layer-by-layer assemblies, structure transcription, and functional mesoporous hybrids are described (Fig. 1). Of course, not all of the recent work can be introduced here but the reader should be able to sense the essential recent trends in the corresponding fields from those examples that have been selected.

II. HYBRID LIPID THIN FILMS

Lipid thin films have been used in many applications, such as permeation control, drug delivery, and other medical applications because of their

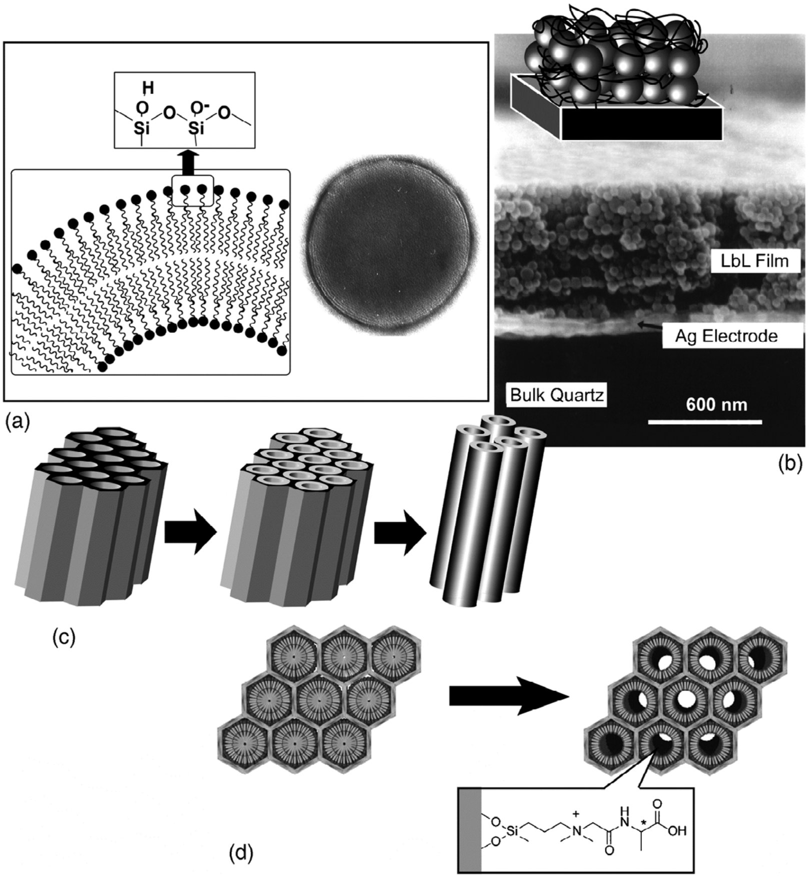

FIGURE 1. Supramolecular objects consist of inorganic building blocks mainly based on soft supramolecular assemblies. (a) Hybrid lipid thin films. (b) Layer-by-layer assemblies. (c) Structure transcription. (d) Functional mesoporous hybrid.

biocompatibility and ease of control under physicochemical conditions. However, a limited mechanical strength is sometimes apparent so that the hybrids of lipid thin films and strong inorganic frameworks are anticipated. In this section, several examples of lipid-inorganic hybrid thin films are described.

As stable lipid monolayer structures, self-assembled monolayers (SAMs) have been used widely where covalent bonding between the monolayer and the substrate afford a satisfactory mechanical strength. Typically, organosilane compounds such as *n*-octadecyltrichlorosilane (OTS) have been used for the preparation of SAM structures through the formation of covalent Si—O—Si linkages between hydrolyzed silane moieties and solid surfaces, such as glass plates or metal oxide layers. For example, Okahata and co-workers prepared a SAM of dialkylorganosilane on a porous glass plate, and successfully regulated

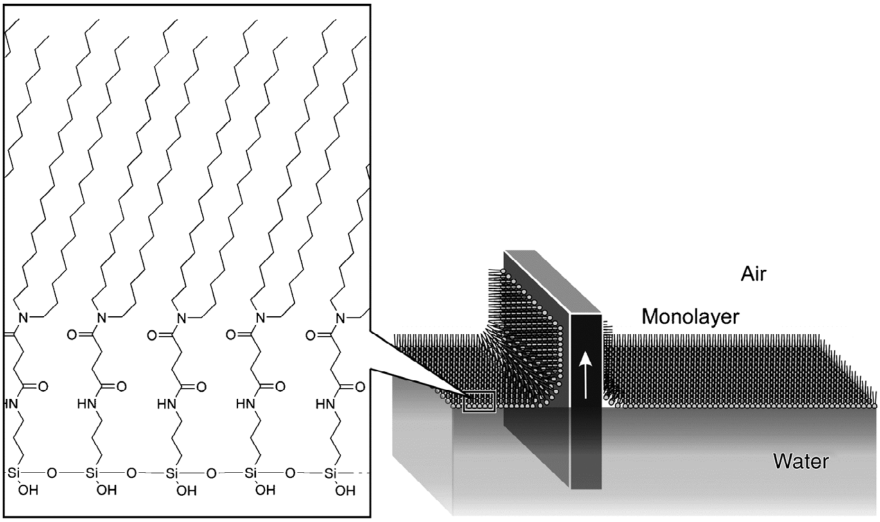

FIGURE 2. Technique for use of organosilane compounds.

material permeation through the glass.[3] The SAM structures developed deeply within the pores, where permeation of molecules dissolved in water could be regulated by variation of the physical state of the SAM structure.

The same research group developed a more sophisticated technique to realize the first example of permeation control through a single monolayer.[4,5] To immobilize a single monolayer on a porous glass surface, the SAM concept and the Langmuir-Blodgett (LB) technique were combined (Fig. 2). An organosilane monolayer was first prepared and polymerized on an air–water interface and was then transferred for immobilization on a solid substrate. The surface pressure-molecular area (π-A) isotherm of dialkylalkoxysilane depended significantly on the pH condition of the water subphase. Condensation at acidic pH 2 induced the formation of a well-condensed monolayer with a limiting area of 0.54 nm^2, which is rather close to the corresponding values from the conventional monolayers of dialkyl compounds such as phospholipids. The LB films that were prepared under acidic conditions showed peaks in the infrared spectra at 1026 and 1095 cm^{-1}, which are assignable to Si—O—Si and indicate the presence of an acid catalyst in the subphase, enabling the monolayer to polymerize.

For permeation control experiments, the polymerized monolayer was transferred onto a porous glass with 5-nm-diameter pores. From the unit area and degree of polymerization, the area occupied by a single polymer molecule was estimated to be $\sim$150 nm^2, which is apparently larger than the pore area of the 5-nm glass (20 nm^2). The transferred monolayer was covalently immobilized on the porous glass plate by heat treatment. As illustrated in Figure 3, the glass plate with the immobilized monolayer was attached to the bottom of a polyethylene tube and soaked in a 1-cm quartz cell. Permeation of a water-soluble

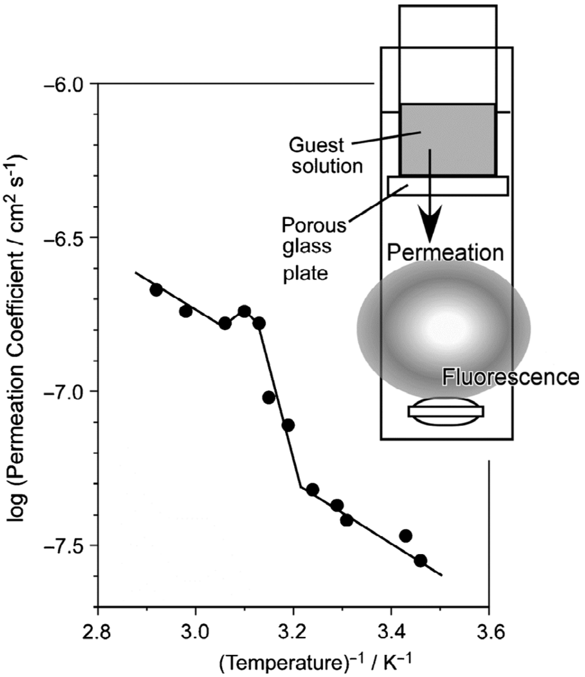

FIGURE 3. Permeation of water-soluble fluorescent probe through a glass plate with the immobilized monolayer.

fluorescent probe was estimated by the increase in fluorescence intensity of the lower solution. It is interesting that permeation through the monolayer exhibited a discontinuity at around 45°C (Fig. 3), which is very close to the phase transition temperature (crystal state to liquid crystalline state) of the polymerized monolayer. This was the first example of permeation control using a 2-nm-thick monolayer, and so far, it is the thinnest lipid film that operates as a permeation valve. This demonstration of control of organic thin film permeation became possible only through hybridization of the fragile monolayer with the mechanically stable inorganic substrate.

Permeation control through monolayer structures has also been demonstrated using electrochemical means (Fig. 4). The same research group similarly immobilized monolayers of dialkyl organosilane compounds on SnO_2 electrodes by forming covalent linkages; permeability of an electrochemically active probe ($Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$) through the monolayer was monitored.[6] This monolayer-hybridized electrode suppressed dramatically the redox response of the Fe probe and was hardly affected by repeated measurements. In sharp contrast, the electrode covered noncovalently with monolayers of conventional fatty acids could not continuously block permeation of the probe molecule. Permeation profiles of $Fe(CN)_6^{4-}$ /$Fe(CN)_6^{3-}$ probe were evaluated at different temperatures, indicating that the redox response of the probe increased

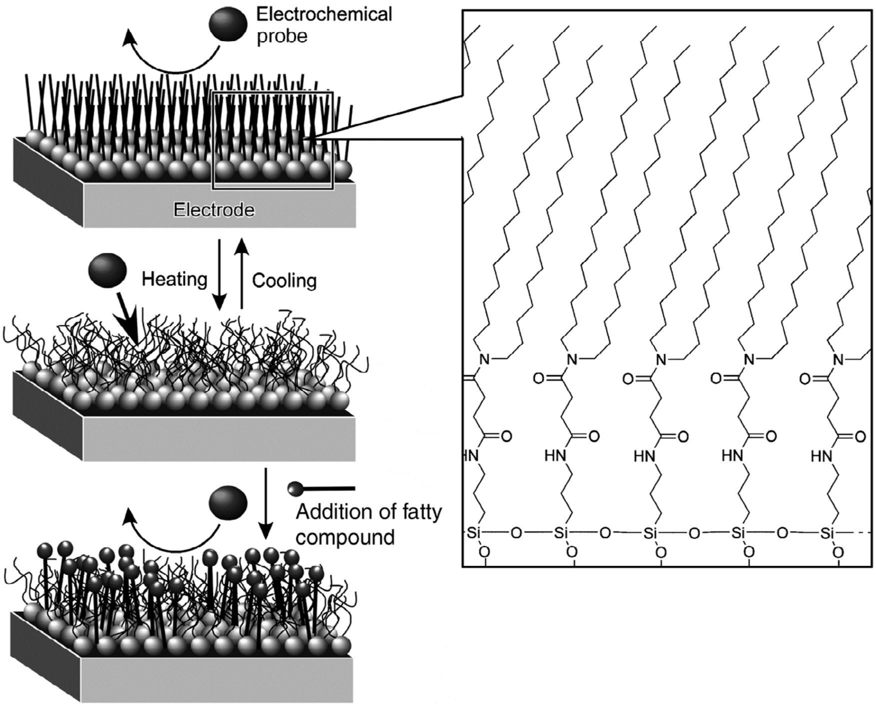

FIGURE 4. Electrochemical investigation of permeation control through monolayer structure.

drastically near the phase transition temperature. Maximum permeability to the probe molecule near the phase transition temperature was probably due to alkyl chain disorder during a period of unstable coexistence of crystalline and liquid crystalline states of the monolayer phase. It is interesting that the addition of alcohol molecules to the solution blocks the permeation of probe molecules, with a significant dependence on the identity of the added alcohol. It is likely that the alcohol molecules fill the pinholes formed on the monolayer and shape discrimination occurs upon alcohol insertion into the monolayer.

The concept of the hybrid electrode was extended to a vitamin-immobilized system by Hisaeda and co-workers (Fig. 5), in which heptapropyl and heptaoctyl esters of vitamin B_{12} derivatives with a Co(II) or Co(III) center were used.[7] Investigation of π-A isotherms of these compounds with the alkoxysilane monolayers suggested that stable accommodation of the vitamin B_{12} functionality in the lipid monolayer can be achieved by the introduction of long chains at the vitamin B_{12} core. The mixed monolayers of the long chain–substituted vitamin B_{12} and organosilane amphiphile were transferred as an x-type LB film onto a quartz plate and showed reasonable UV absorbance. Monolayers similarly immobilized on an indium-tin-oxide (ITO) electrode possessed a