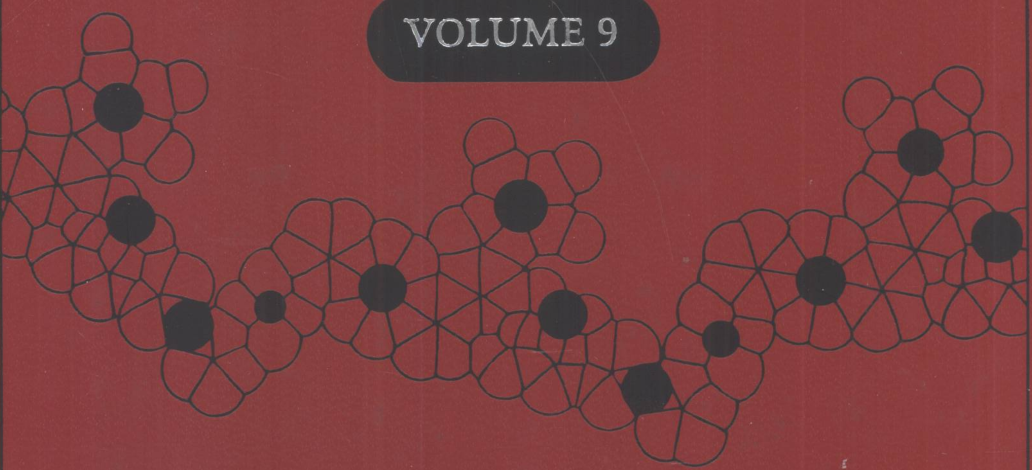
# MACROMOLECULES CONTAINING METAL and METAL-LIKE ELEMENTS

## VOLUME 9



## SUPRAMOLECULAR AND SELF-ASSEMBLED METAL-CONTAINING MATERIALS

Edited by

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# Macromolecules Containing Metal and Metal-Like Elements

## Volume 9

## Supramolecular and Self-Assembled Metal-Containing Materials

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## Volume 9

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# 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.

## I. REFERENCES

1. E.g., D. J. Cram and J. M. Cram, *Science*, **1974**, *183*, 803; C. J. Pedersen, *Science*, **1988**, *241*, 536; J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley, Hoboken, N. J., **1995.**
2. J.-M. Lehn, *Interdisciplinary Sci. Rev.*, **1985**, *10*, 72; J.-M. Lehn, *Science*, **1985**, *227*, 849; M. Ruben, J.-M. Lehn, and P. Mueller, *Chem. Soc. Rev.*, **2006**, *35* (11), 1056.

3. Three examples in 2008: B. Xu, Z. Yang, G. Liang, and Q. Wang, U.S. Patent 2007224273 (**2008**); M. Pouzot, C. J. E. Schmitt, and R. Mezzenga, Eur. Patent WO2008025784 (**2008**), K. Cho and D. H. Kim, U.S. Patent 20080041300 (**2008**).
4. F. Zhao and M. Zhao, *Recent Res. Devel. Physics*, **2005**, *6*(5), 1.
5. A. Y. Tsivadze, G. V. Ionova, V. K. Mikhalko, and Y. N. Kostrubov, *Rus. Chem. Rev.*, **2007**, *76*(3), 213; A. Harada and K. Kataoka, *Prog. Polym. Sci.*, **2006**, *31*(11), 949; M. D. Ward, *Coord. Chem. Rev.*, **2006**, *250*, 312; M. J. W. Ludden, D. N. Reinhoudt, and J. Huskens, *Chem. Soc. Rev.*, **2006**, *35*(11), 1122; A. Scarso and J. Rebek Jr., *Topics Current Chem.*, **2006**, *265*, 1; P. L. Barthelemy, J. Stephen, and M. Grinstaff, *Pure Appl. Chem.*, **2005**, *77*(12), 2133; M. Schmittel and V. Kalsani, *Topics Current Chem.*, **2005**, *245*, 1; F. J. M. Hoeben, P. Jonkheijm, E.W. Meijer, and A. P. H. J. Schenning, *Chem. Rev.*, **2005**, *105*(4), 1491; K. Bhattacharyya, *Acct. Chem. Res.*, **2003**, *36*(2), 95; J. T. Groves, *Proc. Nat. Acad. Sci.*, **2003**, *100*(7), 3569.
6. G. W. Gokel, *Advances in Supramolecular Chemistry*, vols. *1–9*, Cerberus Press, South Miami, FL (1990–2003).

# Series Preface

Most traditional macromolecules are composed of less than 10 elements (mainly C, H, N, O, S, P, Cl, 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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