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Structure and Bonding

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Topics addressed in the series now include the design and engineering of molecular solids such as molecular machines, surfaces, two dimensional materials, metal clusters and supramolecular species based either on complementary hydrogen bonding networks or metal coordination centers in metal-organic framework materials (MOFs). Also of interest is the study of reaction coordinates of organometallic transformations and catalytic processes, and the electronic properties of metal ions involved in important biochemical enzymatic reactions.

Volumes on physical and spectroscopic techniques used to provide insights into structural and bonding problems, as well as experimental studies associated with the development of bonding models, reactivity pathways and rates of chemical processes are also relevant for the series.

Structure and Bonding is able to contribute to the challenges of communicating the enormous amount of data now produced in contemporary research by producing volumes which summarize important developments in selected areas of current interest and provide the conceptual framework necessary to use and interpret mega-databases.

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Yu-Fei Song
Editor

Polyoxometalate-Based Assemblies and Functional Materials

With contributions by

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Preface

Metal oxides have attracted wide attention due to their unique structures, and recent focus has shifted from accidental discovery of intriguing molecular structures to rational design of sophisticated complex assemblies and the development of various functionalities. Polyoxometalates (POMs), as a large group of anionic metal oxides, have experienced a similar process during the past two centuries. POMs have expanded the research area to include a new range of multifunctional materials, aiming to find practical application in both academics and industries. Thanks to the rapid progress of crystallography and spectroscopic techniques, the advances in structural controllability and the elaboration of structure-property relationship have endowed POMs-based materials with outstanding performances in catalysis, photo-sensing, energy conversion, storage etc. In this volume of *Structure and Bonding*, we invite a few young and vibrant chemists in this field to contribute a comprehensive discussion on the recent development of novel polyoxometalate syntheses and functionality.

In the chapter ‘Building Block Libraries and Structural Considerations in the Self-assembly of Polyoxometalate and Polyoxothiometalate Systems’, Miras and coworkers give an overview of the development of polyoxometalates with a particular focus on the synthetic methodologies and reactivity. Even though a complete understanding of the self-assembly process during polyoxometalate cluster formation is a challenge, the template synthetic approach proposed by the authors’ group might throw light on the design and discovery of novel complex clusters. In the chapter ‘Structure and Bonding in Molecular Vanadium Oxides: From Templates via Host–Guest Chemistry to Applications’, the historic development and current trends in polyoxovanadate synthesis and applications in catalysis and magnetism are discussed by Streb et al., with specific considerations on the formation mechanisms of linking isolated vanadates into supramolecular architectures. In the chapter ‘Polyoxometalate-Based Photo-Sensitive Functional Hybrid Materials’, Song and colleagues concentrate on the photo-sensitive properties of polyoxometalate hybrids. The synthetic methods of covalently grafting organic functional molecules onto polyoxometalate clusters have been presented, and the

photo-responsive properties of such hybrids in both solid states and solutions have been investigated in detail. In the chapter ‘Porous Ionic Crystals Based on Polyoxometalates’, Uchida et al. summarizes the recent work of her group on polyoxometalate-containing porous ionic crystals, and the potential applications in heterogeneous catalysis, gas adsorption/separation, and ion-uptake/conduction are also featured. The kinetic control of the self-assembly process provides a great insight into the relation of ionic crystal structure and the relevant properties. In the chapter ‘Polyoxometalates Assemblies and Their Electrochemical Applications’, Lan and coworkers explore the redox activity of polyoxometalates and their applications for clean and renewable energy. Various strategies to prepare polyoxometalate-assisted composite materials are discussed and the reactivity towards hydrogen evolution reaction, oxygen evolution reaction, and water splitting are highlighted. In the chapter ‘Gel-Electrophoretic Chromatography of Polyoxometalate Clusters in Aqueous Solution’, a study of gel electrophoresis on the discovery and separation of polyoxometalate clusters is investigated by Tsunashima et al. The cluster size, charge density, and counteraction are suggested to be correlated to the mobility and separation mechanism of unknown cluster systems in solution. In the chapter ‘Alkoxido-Derivatised Lindqvist and Keggin-Type Polyoxometalates’, Errington describes the latest research achievements on the protolytic behaviors of Lindqvist- and Keggin-type polyoxometalates in organic solvents. The syntheses and subsequent reactivity of such clusters are explored and monitored by the powerful technique of NMR in non-aqueous solution.

As a volume editor, I would like to express my sincere appreciation to all the authors who have contributed to this book. Without their hard and excellent work this book might have not been completed. Such a collection of important research works in the field of polyoxometalate surely will be an essential reference to chemists, material scientists, and industrial researchers. We wish this book will be of great interest to young researchers who wish to get involved in this area, and inspire them to explore the beauty of polyoxometalates.

Beijing, China
November 2017

Yu-Fei Song

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