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Structure and Bonding

Aims and Scope

The series *Structure and Bonding* publishes critical reviews on topics of research concerned with chemical structure and bonding. The scope of the series spans the entire Periodic Table and addresses structure and bonding issues associated with all of the elements. It also focuses attention on new and developing areas of modern structural and theoretical chemistry such as nanostructures, molecular electronics, designed molecular solids, surfaces, metal clusters and supramolecular structures. Physical and spectroscopic techniques used to determine, examine and model structures fall within the purview of *Structure and Bonding* to the extent that the focus is on the scientific results obtained and not on specialist information concerning the techniques themselves. Issues associated with the development of bonding models and generalizations that illuminate the reactivity pathways and rates of chemical processes are also relevant

The individual volumes in the series are thematic. The goal of each volume is to give the reader, whether at a university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to a larger scientific audience. Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years should be presented using selected examples to illustrate the principles discussed. A description of the physical basis of the experimental techniques that have been used to provide the primary data may also be appropriate, if it has not been covered in detail elsewhere. The coverage need not be exhaustive in data, but should rather be conceptual, concentrating on the new principles being developed that will allow the reader, who is not a specialist in the area covered, to understand the data presented. Discussion of possible future research directions in the area is welcomed.

Review articles for the individual volumes are invited by the volume editors.

In references *Structure and Bonding* is abbreviated *Struct Bond* and is cited as a journal.

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Peng Cheng
Editor

Lanthanide Metal-Organic Frameworks

With contributions by

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Preface

The title of this volume consists of two keywords, "lanthanide" and "metal-organic frameworks", both of which are among the most active fields of research in chemistry and material science. In comparison with other types of metal ions, lanthanide ions exhibit a large atomic magnetic moment, strong spin-orbital coupling, high coordination number, and abundant coordination modes originating from their unique 4*f* electronic configurations, which endow lanthanide complexes with various structures and highly distinctive optical, electric, and magnetic properties as well as significant applications covering a vast range in daily living, laboratory research, industrial production, and high technology at present. Metal-organic frameworks, MOFs as the abbreviation, have been one of the most famous and active molecular materials in this century till now. MOFs are a kind of porous material and constructed from organic ligands and metal ions, which exhibit fascinating structural and chemical properties and attract considerable attention in vast areas including resource, environment, and materials. As a kind of organic–inorganic hybrid material, the structure of MOFs can be easily adjusted through altering the type of either organic ligand or metal ions, which subsequently leads to extensive properties meeting different application requests such as energy and pollution gas storage, luminescent detector, molecular magnets, catalysis, and so on.

As a constituent of the "Structure and Bonding" book series, this volume serves to provide the readers with some fundamentals of one specified family of MOFs, lanthanide metal-organic frameworks (Ln-MOFs), including the homo Ln-MOFs and hetero Ln-transition metal-organic frameworks. The volume comprises nine chapters covering general knowledge and the recent developments of Ln-MOFs, including synthetic strategies, the appropriate and representative functions, and potential applications.

The first chapter of this volume by Zhou illustrates a general picture of MOFs and then specifies Ln-MOFs out of MOF materials by the characteristic structures, properties, and applications attributing to the high coordination number, hard Lewis acidity, and strong magnetic anisotropy originating from the *f* block of lanthanides. Several well-known Ln-MOFs structures are presented to demonstrate the various synthetic strategies, interesting structural and chemical properties including

porosity, chirality, magnetism, and luminescence, as well as the overview of potential applications including gas storage, catalysis, and chemical sensing.

Chirality is one of the central elements for life on our earth and is important for most of the scientific areas. Chiral MOFs have drawn much attention as a kind of new low symmetric material based on their particular characters, such as high density of active catalytic centers, high level of porosity, regular and reliable crystalline nature, and relatively easy immobilization in comparison with other heterogeneous systems. In the second chapter by Liu, the synthetic approaches and structural features of chiral Ln-MOFs are summarized, and their applications in asymmetric catalysis, separation, and luminescence are revealed.

Gas storage and separation is one of the most widely studied and applied areas of MOFs. According to the unique electronic configuration, high coordination number, and flexible coordination environment of lanthanide ions, Ln-MOFs could exhibit high stability, high selectivity, and tunable pore sizes and shapes for the application of gas storage and separation. In the chapter by Chen, a comprehensive review is provided focusing on the synthesis and applications of Ln-MOFs in gas storage and separation including H_2 storage, selective CO_2 capture and separation as well as H_2 and CH_4 purification. Strategies for effectively enhancing gas storage capacities and selectivities of Ln-MOFs are presented as well.

Luminescence is one of the most representative features of lanthanide ions with sharp luminescent bands, large Stokes' shifts, and long luminescent lifetimes arising from the *f–f* transitions, leading to their diverse applications as chemical sensors, light-emitting devices, and biomedicine. The chapter by Zhang presents the luminescent Ln-MOFs containing the basic principles, recent research achievements and nanoscale Ln-MOFs as well as their applications in the field of cell imaging, drug delivery, and molecular sensing.

The assembly of the metal clusters into MOFs is another area of MOF-construction newly developed in recent years, which has led to series of unprecedented architectures and excellent properties by incorporating the particular characteristics of the clusters into the obtained frameworks. In comparison of the well-established research on transition metal clusters, construction of Ln-MOFs from lanthanide clusters is just at the beginning. Recent developments on the synthetic strategy and structures and properties of MOFs based on lanthanide clusters varying from di- to octatetraconta-nuclei are illustrated in the chapter by Hong, of which different fascinating topological networks and potential applications in a variety of fields are revealed.

Two chapters in this volume are about the hetero-MOFs (HMOFs), which are constructed by lanthanide ions together with transition metal ions. Since the chemical and physical properties originated from *d* and *f* electrons are totally different, it is difficult to synthesize HMOFs, while distinguishing characteristics with regard to structures and properties are endowed into HMOFs on the other hand by the combination of *d* and *f* electrons in a single framework. The chapter by myself presents an overview on HMOFs, covering the synthetic strategy and structures and properties of luminescence, magnetism, adsorption, etc. to help readers to have a general idea about HMOFs and to understand various aspects of

HMOFs. In the sixth chapter, Tanase reveals a specified branch of HMOFs, namely MOFs with *d–f* cyanide bridges, which are constituted from the unit of $Ln[M(CN)_n]$ (n =6, 8). Synthetic strategies and properties, especially the magnetic property, of this kind of HMOFs are reviewed in detail as well as the theoretical investigations.

As a complement, an individual series of MOFs from actinide elements with stepwise filled 5*f* orbitals are described in the chapter by Chen. The basic building units and the strategies to construct MOFs of uranium and other actinides are discussed. A comprehensive understanding of MOFs with actinide cations and valuable references for the development of novel MOF materials are provided.

Most of the chapters above are dealing with Ln-MOFs in single crystal or powder states, while in the last chapter by Zheng the scale of this volume is extended to the nanoscale. At first, a special series of Ln-MOFs, namely nanostructured Ln-MOFs, are thoroughly introduced, which are constructed from the subunits of nanosized lanthanide clusters or lanthanide–nonlanthanide metal clusters. Afterwards, Ln-MOFs in nano-crystal form are illustrated including synthetic methods, morphology, properties, and applications in imaging, luminescence, nanothermometry, sensing, and drug delivery.

Last but not least, I would like to extend my appreciation to the authors for their stupendous contributions to this book. I hope that the readers will get a satisfactory scene and find valuable information on the research and development of Ln-MOFs. I would also like to acknowledge Dr. J.G. Ma for the assistance in the preparation of this volume.

Tianjin, China Peng Cheng
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