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## Introduction

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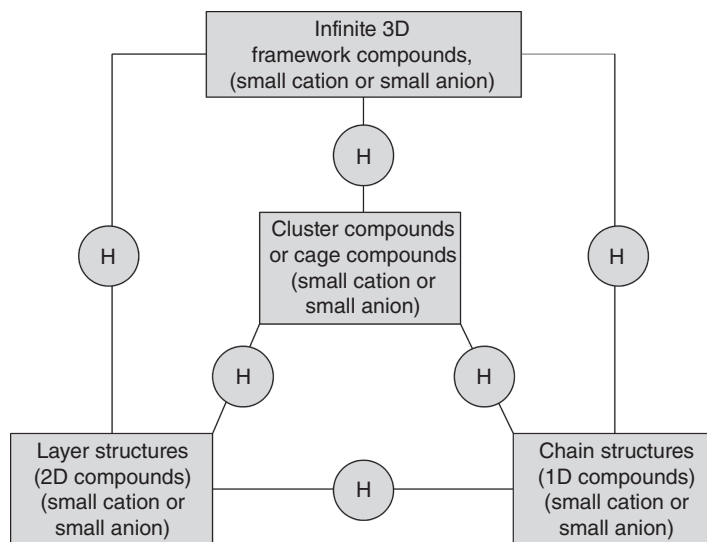
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The syntheses of new substances with specific functions are fundamental to the modern civilization, providing an inherent impetus for social, economic, scientific, and technological advancements. Worldwide governments and scientists are devoted to the discovery of new substances with specific functions and structures. The creation of new functional substances, which is the strategic highland for an innovative country, represents the core competency of this country. The creation of new substances belongs to major basic research. So far, there are still many important scientific issues unsolved at this stage, and we are far away from the key goal, that is, to develop the substances with desired properties. Structural chemistry fabricates this aim and leads the creation of new substances.

Structural chemistry is a discipline focusing on the bonding of atoms, molecules, and crystal packing as well as the correlations between the structure and the macroscopic chemical and physical properties. Therefore, structural chemistry serves as a source of the innovation of materials sciences. Although more than 23 million of substances have been synthesized or separated in the past century, only a small portion has found real-world applications. Currently, it remains a grand challenge for the scientific community to produce new substances with desired functions on a rational basis. One of the core tasks in the field of structural chemistry is to reveal the relationship between composition structure–function for creating new substances with expected properties through better molecular or structural design. In fact, the quantitative relationship between the structure and the property of a substance represents one of the challenges in chemistry in the twenty-first century. On the other hand, the synthetic processes must be economical, safe, resource-efficient, energy-saving, and environmentally benign. Chemists should strive for developing “perfect reaction chemistry,” i.e. synthesizing target compounds with a 100% yield and 100% selectivity without producing any waste. To create the new substances with desired functions, it is highly desirable to carry out function-directed structural design and structure-directed precise synthesis. That is the new developing direction of structural chemistry.

*Advanced Structural Chemistry: Tailoring Properties of Inorganic Materials and their Applications*, First Edition. Edited by Rong Cao.

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The classification of the ionic-covalent compounds

According to the bonding characteristics and structural dimensions, chemical substances may be divided into four categories. The first category includes the molecules, cluster compounds, or cage compounds with discrete structures, and such compounds can be assembled into chain structures (one-dimension = 1D, the second category), layer structures (2D, the third category), and framework structures (3D, the fourth category) through ionic or covalent bonding modes.

One of the main bottlenecks lies in the inadequacy of the original designing, methods, and theories for the creation of new functional substances with different structures. Therefore, by strengthening the research on the structure- and function-guided creation of new substances, this situation could be drastically changed. However, two key issues should be considered in the area of structural chemistry: (i) how to accomplish the oriented synthesis for the specific structure of matter? (ii) How to design the matter's structure with specific function? In this book, we intend to reveal the relationship between the structure and function of matter and develop efficient and precise synthetic methodologies and theoretical tools for new functional substances.

This book is written by the experts engaged in structural chemistry research of Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. It aims to reflect the recent research progress of structural chemistry in China and abroad. The book mainly includes two parts: synthesis and structure, and structure and property. It focuses on the structural design and properties of clusters, porous materials for gas sorption, separation and catalysis, and photoelectric or magnetic materials. This book clarifies the scientific connotation and subject development direction of structural chemistry.

In the first chapter, the metal–organic macrocycles containing regular/irregular polygons, including multilayered cyclic structures are discussed. In addition, helicates, tetrahedrons, triangular prisms, cubes, octahedrons, hendecahedrons, dodecahedrons, cuboctahedrons, hexadecahedrons, and barrel- and ball-shaped cages are reviewed. Discrete metal-organic metallasupramolecular structures have drawn increasing attention due to their special esthetic 2D or 3D structures and potential applications in molecular recognition, sensing, separation, and biomimetic catalysis. In general, metallasupramolecular structures can be defined as metallacycles and metallacages, while many borderline cases exist concerning the complexity of geometry of the ligands and shape of the internal cavity. To facilitate discussion, herein the metal centers are taken as vertices and the organic ligands as edges or faces in the polygons and polyhedra to define these metallasupramolecular structures as macrocycles and cages, respectively.

In Chapter 2, we summarize the development of synthetic strategies, analytical techniques, fundamental structure characteristics, and the typical applications of the metal-oxo clusters, which have been divided into three families of the transition metal-, main group metal-, and lanthanide-oxo clusters. The metal-oxo clusters with atomical precise structures are of importance in several disciplines relevant to synthetic chemistry, analytical chemistry, catalysis, biology, medicine, magnetism, and materials science. In the oxo clusters of transition metal part, structural fundamentals and novelties of the crystalline transition metal-oxo clusters, including Ti, V, Nb, Mo, Pd, W, and Ta, will be introduced. Besides, their tunable properties and potential applications related to the enormous structural diversities will also be briefly covered. In the oxo clusters of main group metal part, an overview on the main group borates, geminates, and aluminum elements will be presented. Both inorganic and organic ligand-supported oxo cluster structures will be introduced. Finally, in the oxo clusters of lanthanides part, we will present the recent advances in the high-nuclearity lanthanide clusters, which are classified by the protecting ligands including O-donor ligands, N-donor ligands, multiple N,O-donor ligands, calix[*n*]arenes, and other donor ligands such as Se- or C-donor ligands. Based upon these sufficient discussions, the dependence of the synthetic strategy of lanthanide-oxo clusters on the ligands, anions, and templating effects will also be summarized. We believe that these structurally well-defined metal-oxo clusters can provide models for decoding the mechanistic insight of the metal-based materials at the molecular level. In turn, the performance of these clusters could further feedback to the guidance of designing materials in a more controllable way.

Chapter 3 focuses on the synthetic and structural studies on the transition metal sulfide clusters, in particular, the heterometallic Mo–Fe–S and Mo(W)–Cu(Ag)–S clusters. Benefitting from the proposed structural models of FeMoco and inspired by the versatility of the unit construction concept, we synthesized a range of metal sulfide clusters exhibiting various structural types. Special attention has been paid to the designed synthesis of the molybdenum and tungsten heterometallic thioclusters with one or more cuboidal cluster units, as well as some novel mixed-metal sulfide coordination polymers. These results demonstrate how flexible the unit construction

method can be when it comes to making cluster compounds with desired structures based on the diverse coordination modes of the sulfur atom and the knowledge of structural chemistry. The ideas behind these syntheses are of significant value not only to the structural modeling of the biological catalytic active sites but also to the creation of novel molecular functional materials.

Chapter 4 summarizes the syntheses, crystal structures, and selected properties of a number of group 11–15 metal chalcogenides that are mainly obtained by Huang et al. Metal chalcogenides are a class of compounds characteristic of the covalent bonding between metal cations and chalcogen  $Q$  ( $Q = S, Se, Te$ ) anions. Metal chalcogenides are important materials showing excellent properties in ion exchange, semiconductor optoelectronics/thermoelectric, nonlinear optics, photocatalysis, etc. Neutral amine molecules have been successfully incorporated into the group 12 metal chalcogenides, say II–VI semiconductors, forming a novel class of organic–inorganic hybrid nanostructures with a general formula of  $[(MQ)_n(L)_x]$  ( $MQ = ZnS, ZnSe, ZnTe, CdS, CdSe$ , etc.;  $L =$  mono- or di-amines or hydrazine;  $n = 1, 2$ ;  $x = 0.5, 1, 2$ ). The hybrid materials exhibit strong quantum confinement effects and outstanding properties such as largely modified optic absorptions, white light emission, and nearly zero/negative thermal expansion. Some of the obtained chalcogenidometalates demonstrate superior ion-exchange properties of selectively capturing hazardous metal ions such as radioactive  $Cs^+$ ,  $Sr^{2+}$ ,  $UO_2^{2+}$ , and  $Ln^{3+}$  ions from complex solutions.

In Chapter 5, various metal–organic frameworks (MOFs) are categorically highlighted on the basis of their dimensions, with a focus on the construction and structural analysis, which provides an introduction of recent achievements in MOFs not only for novices but also for experienced researchers. It is expected to guide the design and preparation of more novel and advanced functional MOF materials. MOFs possess the unique features over traditional inorganic or organic materials, including structural tunability, ultrahigh porosity, large surface areas, etc., which make them being widely applied in various areas such as storage and separation, energy transfer, catalysis, enzyme inhibitor, sensing, drug delivery, and so on. MOFs have received great attention in the last two decades, and in a short time, they have matured and grown to a huge system. According to the extended manner, the structures of MOFs can be described as one-, two-, or three-dimensional infinite networks.

In Chapter 6, we give a brief survey of recent advances in the rational assembly of polyoxometalate (POM)/chalcogenidometalate-based clusters and superlattices, polyhedral coordination supermolecules, and MOFs to show the knowledge on their synthesis mechanism and procedures. First, we present the synthetic and design approaches to the many POM types encompassing iso-POMs, hetero-POMs, organically derived POMs by alkylation or coordination, and POM–MOF hybrids. Next, we summarize the design and synthesis of crystallographically defined chalcogenidometalate clusters, including supertetrahedral series of  $Tn$ ,  $Pn$ ,  $Cn$ ,  $Tm,n$ , and oxychalcogenide types, most of which are allowed to be fabricated by the mixed-metal and cationic-template strategies to deal with the local and the global charge issues. Then, we outline the recent developments of coordination-driven

self-assembly, with a focus on discrete architectures, viz metallacages of polyhedral shapes through well-defined directional-bonding assembly strategies (e.g. edge-directed, face-directed, and symmetry-adapted approaches) including diverse linking modes. Finally, we provide an overview of secondary building units (SBUs) mainly of metal carboxylates (classified by their geometry and the number of metal atoms), and the linkers bearing other binding groups, such as pyridyls, azoles, phenols, and their representative network examples, also highlight some synthetic strategies, including modulated synthesis, isorecticular expansion, topology-guided design, and multivariate chemistry.

In Chapter 7, we summarize the typical topological networks of MOFs with some prominent examples. Over the past decade, great progress of coordination polymers including MOFs has been made and tens of thousands of new compounds have been synthesized. Topological analysis supplies a convenient tool to understand and simplify a large number of complicated compounds at the early stage. With the development of new concept “reticular synthesis,” the design and synthesis MOFs have gradually tended to be practical and theoretical. The so-called “reticular synthesis” refers to the process of assembling well-designed rigid molecular building units into predetermined regular structures (or networks) through strong bonding. “Reticular synthesis” provides a reasonable way to synthesize solid materials with high stability, extended structure, predesigned molecular building units, and special properties. Two important aspects of “reticular synthesis” are the rational design of SBUs and framework topologies. Numerous MOFs constructed by various SBUs and organic ligands but with same underlying topological networks can be designed and synthesized. Therefore, topological analysis has become a powerful tool to design and predict new MOFs.

In Chapter 8, about 60 classical examples selected from the literature on a wide range of inorganic chalcogenide classes are presented, including centrosymmetric (CS) and non-centrosymmetric (NCS) crystal structures. These chalcogenides display a rich structure diversity based on the BBUs and can be divided into five classes according to the dimensional features: (i) the zero-dimensional (0D) discrete clusters; (ii) one-dimensional (1D) chains; (iii) two-dimensional (2D) layers; (iv) three-dimensional (3D) frameworks; and (v) mixed-dimensional (MD) structures. In this chapter, we focus on the unit cell, space group, and dimensional change as well as the structural assembly of selected chalcogenides. This work gives some exploring strategies for novel chalcogenides with diverse dimensions.

In Chapter 9, we wish to present advances in the past 10 years for three kinds of optical materials: electroluminescent materials, photochromic materials, and second-order nonlinear optical (NLO) materials. Optical materials refer to materials that may modify parameters of input light (such as phase, intensity, and frequency) or switch reciprocally optical and nonoptical signals (such as electric, heat, and sound). Electroluminescent materials are materials that can be excited to excited states and then return to ground state with the release of light. They have been widely applied to LEDs or OLEDs, which have brought revolution of both lighting and display fields. Photochromic materials are bistable materials that may be switched between two ground states with at least one direction being excited

by light. They have been used for glassware (such as sun glasses, automobile rearview mirror, building window, etc.) and chromic ink (for anti-fake, cloth decorating, etc.) in the market. Other applications, such as switching, memory, bioimaging, and radiation monitoring, have also been demonstrated in laboratory. Second-order NLO materials are usually crystals without inversion symmetry that are capable of generating a second harmonic. They play a significant role in the field of laser-related science and technology, such as semiconductor manufacturing, photolithography, optical storage, and high-capacity communication networks. This chapter emphasizes the description of relations between structures and electroluminescent properties for  $d^8/d^{10}$  heteronuclear metal complexes, photochromic properties for viologen compounds and their analogs, and second-order NLO properties for the KBBF, SBBO,  $AB_4O_6$ , apatite-like borates,  $ABCO_3$ ,  $A_3VO(O_2)_2CO_3$ , and  $AX^{II}_4X^{III}_5Se_{12}$  families' derivatives.

Chapter 10 will discuss the relationship between the symmetry-breaking crystal structures and ferroelectric properties, and the recent advances of molecular ferroelectrics are also systematically summarized. As an important family of electroactive materials, ferroelectrics with the polar structures are characterized by spontaneous polarization, of which the direction can be reversibly switched under external electric field. Ferroelectrics demonstrate diverse physical attributes including piezoelectricity, pyroelectricity, NLO effect, mechanical functions, and dielectric properties, occupying an indispensable position in the field of condensed matter physics. All these fascinating properties and wide applications of ferroelectric materials are closely related to their unique structural characteristics. Essentially, spontaneous polarization of ferroelectrics can only exist below the Curie temperature point ( $T_c$ ), coupling with the remarkable symmetry breaking during the paraelectric-to-ferroelectric transitions. Various physical properties for ferroelectric materials exhibit giant anomalies in the vicinity of  $T_c$ , stemming from their structural changes. Compared with traditional inorganic ferroelectrics, the counterpart of molecular ferroelectrics displays many distinct characteristics, such as light weight, easy processing, mechanical flexibility, tunable structure, biocompatibility, etc. Therefore, molecular ferroelectrics are currently becoming one of the research hotspots.

In Chapter 11, three series of inorganic, organic, and inorganic-organic hybrid conductive materials were selected from the literature. An overview of some representative fantastic advancement in terms of crystal growth methods, inorganic/organic crystalline conductors, and semiconductors is presented along with current challenges and future research directions provided finally. Crystalline conductive materials have been receiving increasing attention in recent years, not only for their unique physical properties and their potential applications in future electronics. They can be divided into inorganic conductive materials, organic conductive materials, and inorganic-organic hybrid conductive materials. Inorganic conductive materials are the earliest emerging conductive materials and now becoming one of the most crucial functional materials. Organic conductive material is an interdisciplinary research field concerning the design, synthesis,

characterization, and application of organic small molecules or polymers that show desirable electronic properties such as conductivity, semiconductivity, and even superconductivity. Organic–inorganic hybrid conductive material is a crystalline hybrid material composed of organic linker bridged metal ions or inorganic clusters. The deepened study of structure–property relationships is necessary to help guide the design and synthesis of novel functional conductive materials.

In Chapter 12, we will give a comprehensive overview of magnetostructural correlations that have been illustrated in the field of molecular magnets, in particular those reported by our institute. We will examine the environments of spin carriers, low-dimensional magnets, the magnetic exchanges between nearest-neighbor spin carriers, and the diversity of topologies of magnetic frameworks. The correlations between these structural features and the seemingly complex magnetic behaviors including spin crossover, magnetic slow relaxation, magnetic ordering, and spin frustration will be discussed.

In Chapter 13, we present a comprehensive and detailed introduction of gas uptake properties of MOFs. First, we provide the basic concepts of gas adsorption, such as physical adsorption, chemical adsorption, Langmuir monolayer adsorption, and BET multilayer adsorption, and expound the correlation between the type of adsorption isotherms and MOF structures. Second, we classify the pore sizes of MOFs into three kinds based on IUPAC definition and discuss the relationship between pore size and sorption isotherms. Third, we describe the defects in MOFs and their measuring technologies and further expatiate on the connection between defects and adsorption capacities. Fourth, we summarize some representative MOFs with high surface area and discuss four universal factors and their influence on the surface area of MOFs. Finally, we introduce the concept of adsorption enthalpy and elaborate three methods to calculate adsorption enthalpy based on the experiments. Besides, we distinguish the difference between adsorption amount and usable adsorption amount and discuss the factors influencing adsorption enthalpy of materials and the influence of adsorption enthalpy on adsorption capacities and work capacities in practical application. We expect this chapter can deliver significant guidance for researchers to design/discover novel MOFs with excellent properties of gas storage and separation and therefore expand their practical application.

In Chapter 14, we introduce the CO<sub>2</sub> capture and separation, separation of hydrocarbons, noble gases, hydrogen isotopes, and the enantioselective separation based on MOFs. Meanwhile, the relationship between structure and separation during these processes will be discussed in details.

In Chapter 15, we review and summarize the typical strategies and examples in MOF catalysis to give a brief but broad scope overview of the MOF catalysis area. We will first discuss catalysis with different active sites: (i) open metal nodes (SBUs) and modified SBUs for Lewis acid catalysis, oxidation reaction, Suzuki–Miyaura coupling reaction, and so on; (ii) linkers functionalized by Brønsted acids, unsaturated metal complexes, or organic bases; and (iii) pore-encapsulated guest species such as metal nanoparticles, POMs, metal complexes, and enzymes. Three major approaches are discussed next to show the unique advantage of MOFs compared

to traditional heterogeneous and homogeneous catalytic systems: heterogeneous asymmetric catalysis based on privileged ligands or chiral pore structure; cooperative or sequential catalysis that involves more than one active sites; and synergistic photocatalysis for CO<sub>2</sub> reduction, water splitting, and organic reactions.

This book is dedicated to the 60th anniversary of Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, and its founder director, Professor Jiaxi Lu, on the memory of his 105th birthday.