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Book Review

Zouhair Asfari, Volker Böhmer, Jack Harrowfield and Jacques Vicens (eds.), *Calixarenes 2001*, Kluwer Academic Publishers, Dordrecht. 2001 x + 683 pages, EURO 209, USD 182, GBP 127. ISBN 0-7923-6960-2.

The book *Calixarenes 2001* is written by a number of well-known calixarene chemists who have been working in this field for the past decades. They are specialists in their own field describing various striking features of calixarenes. The book is divided into 36 chapters which review the literature mostly up to 2000. They are not in order so that one can read each chapter independently. Nevertheless, the content can be roughly categorized into 5 parts: synthesis, physical properties, receptor properties, coordination chemistry and applications.

Synthesis of calixarenes and their modifications

There are many chapters concerning synthesis of calixarenes and modifications of their functional groups. Gutsche has provided a fascinating review on the synthesis of calixarenes and resorcarenes in Chapter 1. The details of a single-step and fragmentation synthesis have been described, and mechanistic studies are carefully mentioned. The author also briefly covers the synthesis of thiacalixarenes. However, the detail of thiacalix[4]arenes is summarized in Chapter 6 by Hosseini. Chapter 2 describes thoroughly chemical modification of calix[4]arenes both at the upper and lower rims and also modification at the methylene bridges. The modifications of resorcarenes at the hydroxy groups and at the aromatic rings are also summarized. In Chapter 3, the author describes the preparation of calix[5]arenes by one-step synthesis and fragment condensation. Lower rim and upper rim manipulations are also discussed. The host-guest chemistry of calix[5]arenes with neutral molecules such as fullerenes and amines and with charged guests like metal ions, ammonium, and amino acid are briefly stated. The modification of calix[6]arene is treated in Chapter 4. The author has summarized the ways to functionalize calix[6]arene regioselectively. The synthesis of bridged calix[6]arene as well as capped calix[6]arene is included in this chapter. Although the chemistry of larger calix[n]arenes (n = 7, 8, 9) is much less explored, one can find their chemistry in Chapter 5. Chiral calix[8]arenes and the complexing properties of calix[8]arenes are also mentioned briefly. Chapter 6 written by Hosseini gives details of the synthesis of thiacalix[4]arenes, the functionalization of thiacalix[4]arenes at both the lower and upper rims, and the oxidation at the sulfur-bridge to form tetrasulfinyl- and tetrasulfonylcalix[4]arenes. The author also describes thoroughly the synthesis of mercaptocalix[4]arenes and briefly mentions the coordination chemistry of both thia- and mercaptocalix[4]arene. Another type of calixarenes, double- and multi-calixarenes, synthesized by connecting two units of calixarenes employing either single or double bridges and multiple bridges are summarized in Chapter 7. Cyclic oligomers, annelated calixarene and calixarene dendrimers are described extensively in this chapter. Chapter 9 focuses on the synthesis and functionalization of the resorcarene-based cavitands (bridging resorcarene) including the deep-cavity cavitands and water-soluble cavitands. The author also reviews the complexation between neutral molecules, cations and anions concisely as well as the use of cavitands as molecular building blocks for construction of larger molecules. In Chapter 10, the author discusses the chemistry of carcerands, the globular closed-surface molecules with an empty internal cavity, including complexation with neutral molecules and cations. The remarkable uses of these molecules as reaction vessels are concisely stated. In Chapter 11, the synthesis, structure, conformational behavior and ionophoric properties of calixarene analogues, homocalixarenes, are described thoroughly. Chapter 12 provides the detail of the synthesis and properties of homooxa- and homoazacalixarenes including functionalization at the lower and upper rims. The conformational and complexation studies are reviewed briefly. In Chapter 13, the author describes the synthesis of calixarenes from heterocyclic compounds namely calixpyrroles, calixfurans, calixthiophenes, calixpyridines, calixindoles, calixbenzofurans, calixureas and mixed heterocycle calixarenes. After the extensive chapters on the synthesis of various kinds of calixarenes, Chapter 14 covers a different area *viz* oxidation and reduction directly at the phenol units. The author discusses extensively the oxidation of calix[4]arene to calix[4]quinone or to spirodienone derivatives and also mentions briefly the reactions of the derivatives. Hydrogenation of the aromatic rings to yield saturated calix[4]arenes and their interesting isomerisms is also included. Last but not least in calixarene synthesis, Chapter 24 describes the synthesis of charged and neutral water-soluble calixarenes. Complexation of water-soluble calixarenes with cations, anions and neutral molecules is also treated in this chapter.

Physical properties of calixarenes

The physical properties of calixarenes, such as conformations and stereodynamics, are also reviewed by well known chemists specializing in this field of study (mostly by com-

putational methods). Chapter 15 provides information on conformational studies of calix[4]arenes by various molecular modeling techniques. Chapter 16 summarizes the information on the dynamic structure of host-guest calixarene systems analyzed by both solid and solution NMR spectroscopy. In Chapter 17, the author gives good information on molecular modeling of metal ion-calixarenes complexation and extraction. Chapter 18 provides information on computer modeling of calixarenes complexing with alkali metal ions. Chapter 19 is different from the other chapters in this section. It gives information on thermodynamic parameters (obtained from experiments) of many calixarene derivatives in different media before and after complexation with metal ions including extraction processes.

Calixarene derivatives as receptors for cations, anions and neutral molecules

The most remarkable feature of calixarenes is the capability to be used as receptors for cations, anions and neutral molecules. Starting with Chapter 8, this chapter gives details of calixarenes as receptors for neutral molecules using assembly through hydrogen bonding or solvophobic forces. Self-assembly of other cavitands as molecular capsules and self-assembly mediated by metal ions are also briefly reviewed. Later, Chapter 20 provides a thorough synthetic approach to mono-crown ether, bis-crown ether and hetero crown ether calixarenes for cation receptors. Allosteric properties of azobenzene crown calix[4]arene are also briefly mentioned. A concise treatment of calixcryptands is also included. The use of crown ether derivatives as transacylase mimics and molecular machines is summarized briefly. Chapter 21 concerns stability and association constant measurements of calixarene esters, ketones, amides, thioamides and carboxylic acids towards various metal ions. Beer and Matthews give an extensive review of calixarene-based anion receptors in Chapter 23. Inorganic-based systems such as cobaltocenium-based receptors and ferrocene-based receptors and organic-based receptors such as urea are summarized extensively. The charged species anion receptor and calix[4]pyrroles have been concisely mentioned. In addition, simultaneous cation-anion binding is also included in the chapter. Chapter 25 describes the physical studies of the recognition of various calixarenes towards small neutral molecules such as CH_3CN, CH_3NO_2, etc. Inclusion studies in the solid state are briefly reviewed. Shinkai and coworkers give a good review of calixarenes, homooxacalixarenes and cyclotriveratrylene as receptors for fullerenes in Chapter 26. Applications of calixarenes, such as separation of fullerenes or use of the fullerene-complex for DNA cleavage, are also briefly described.

Applications of calixarenes

In this part of the book (Chapters 22, 27, 31–36) authors carefully describe a plethora of fascinating applications of calixarenes ranging from extractants or stationary phases in liquid and gas chromatography to sensors and molecular devices. Chapter 22 gives information on many calixarene derivatives containing oxygen, nitrogen, sulfur and phosphorus as extractant for heavy metal ions. In Chapter 27, Ungaro and colleagues describe the attachment of peptide chain or amino acids or saccharide units to calix[4]arenes and resorc[4]arenes to produce receptors for peptides and carbohydrates respectively in order to mimic the natural proteins. Vancomycin mimics by various calixarenes bearing peptide bridges and applications in pharmacology and biomimetic catalysts are concisely reviewed. In Chapter 31, the authors discuss two types of luminescent molecular devices: (i) encapsulation complexes of luminescent lanthanide ions and (ii) molecular receptors acting as sensors via luminescent properties. The authors provide an extensive review on the first type of molecular devices while briefly mention the second type. Chapter 32 gives details of calixarene-based ligands for optical signaling in chemical analysis by colorimetry and fluorimetry. Their applications as sensors are summarized in Chapter 34. Chapter 33 discusses thin films made from calix[4]arenes by both the self-assembly and Langmuir-Blodgett methods. Some physical properties of these films such as adsorption and permeability are mentioned. Examples of applications of films such as nonlinear optical, pyroelectric and luminescence are also given in the chapter. Chapter 34 written by Diamond and coworkers focuses on the use of calixarenes for the development of chemical sensors. Calixarenes have been used in electrochemical sensors as ion selective agents such as in ion selective electrodes (ISE), ion-selective field effect transistors (ISFETs), electrolyte-insulator-semiconductor (EIS) and quartz-crystal microbalance (QCM). Optical sensors made from calixarenes containing chromoionophores have been briefly reviewed. Applications of calixarenes in nuclear waste extractions are summarized in Chapter 35. This chapter provides details on crown ether or ester derived calixarenes used in extraction of metal ions in nuclear waste. Chapter 36 gives a conclusive review on calixarene-based and resorcarene-based stationary phases for gas chromatography, liquid chromatography and electrophoretic separations.

Coordination chemistry of calixarenes

The following three chapters may be of interest to inorganic chemists. Chapter 28 gives an overview of the coordination chemistry of calixarenes. Metal centers bound to phenolic units and donor atoms of pendent functional groups have been reviewed extensively. Metal centers bonded to π-donor calixarenes and special uses of calixarenes in catalysis are discussed briefly. Chapter 29 by Floriani and colleagues focuses on the metallation of calix[4]arenes and their O-alkylated derivatives using phenolic oxygen as ligands. Particular emphasis is placed on modeling studies of heterogeneous metal-oxo surfaces using metalla-calix[4]arenes. The coordination chemistry of lanthanides and actinides which are well-known to have high and variable coordination numbers is reviewed in Chapter 30. The author describes the

use of phenolic units of calixarenes as ligands for coordinating f-block metal ions. The author also reveals interesting coordination and geometry of the f-block metal complexes obtained from X-ray crystallography.

This book gives an excellent summary of progress in the field of calixarene chemistry in the last three decades so that readers can foresee its future. It is, therefore, suitable for both starters who would like to explore further interesting features of calixarenes and researchers who are already in the field. This book should also be of interest to students and researchers in analytical-, bio-, inorganic-, organic-, physical- and supramolecular chemistry, including those who are dealing with nanochemistry research.

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