

Design and Construction of Coordination Polymers.

Edited by Mao-Chun Hong and Ling Chen (both at Chinese Academy of Sciences, Fuzhou, Fujian, People's Republic of China). John Wiley & Sons, Inc.: Hoboken, NJ. 2009. xvi + 420 pp. \$110. ISBN 978-0-470-29450-5.

Coordination polymers (CPs) are compounds that consist of metals or metal clusters coordinated to multifunctional organic ligands, and they have been studied for several decades, perhaps even since the early 1700s if you regard Prussian blue as a prototype. However, it was not until the early 1990s that systematic crystal-engineering approaches were adopted for the design of CPs. Shortly thereafter it was realized that porous coordination polymers (PCPs), also commonly known as metal-organic frameworks (MOFs), offer unprecedented levels of permanent porosity in the context of crystalline materials. Today, PCPs deservedly lie at the forefront of contemporary materials research because their modular nature combines nanoscale porosity with enormous diversity of structure/property. Indeed, PCPs are perhaps uniquely suited to serve as platforms for a wide range of applications including gas storage, gas separations, chemical/biological sensors, chemical/biological threat remediation, catalysis, light harvesting, and drug delivery. It should therefore not be surprising that CPs are very well recognized internationally, and there has been a resulting explosion in primary literature publications on CPs; currently there are 2000+ publications per year that address design and/or function of CPs. There has also been a plethora of review articles and monographs devoted to CPs in recent years, of particular note being a themed issue of *Chemical Society Reviews* (2009, 38, Issue 5) and the monograph *Coordination Polymers: Design, Analysis and Application* by Batten, Neville, and Turner (Royal Society of Chemistry, Cambridge, 2008). One might therefore question whether a new book is needed on the subject. Given the sheer volume of current literature on PCPs, the answer is yes, but only if new material is presented or different perspectives are addressed.

This book was published in recognition of the 50th anniversary of the founding of the Fujian Institute on the Structure of Matter, Chinese Academy of Sciences. This is somewhat fitting given the Fujian Institute's historically important leading role in materials science in China and China's current leadership role in CPs; ca. 80% of the current literature on CPs originates from China. The book is a compendium of chapters from different authors. Some are quite narrowly focused upon structure or composition of a particular subset of CPs, whereas others address broader issues or properties.

The chapters that are more narrowly focused tend to complement each other well, although Chapters 1 and 5 both address Ag(I) compounds. Chapter 1 covers Ag-N coordination modes with various ligands and also competition with other ligands, counterions, and argentophilic interactions. Chapter 5 presents a broad analysis of Ag(I) CPs, in which the range of coordination numbers and how such networks are designed using the "node" and "spacer" approach are described. A broad range of ligands including S and P donor ligands are also addressed, and structure/function is discussed. Chapter 2 focuses upon In(III) coordination polymers formed from multicarboxylate ligands and presents details about synthesis, structure, and properties that are discussed in the context

of the better known M(II) carboxylate CPs. Chapter 4 addresses CPs based upon polyoxometallates and focuses upon structural diversity rather than properties. A detailed overview of heavy main group iodometallates is given in Chapter 9, and both discrete complexes and CPs are addressed. The subject of function is covered through optical and thermal properties. Chapter 10 focuses upon the use of mixed metal sulfide clusters based upon $M = Mo$ or W and $M' = Cu$ as precursors to CPs. Luminescent and nonlinear optical properties are given. Chapter 13 focuses upon synthetic models of biomimetic metal complexes and their use as therapeutic agents. This chapter is well presented but seems out of place in the context of the other chapters and title of the book.

The remaining chapters are more generally relevant to CPs or emphasize a particular function. Chapter 3 reviews the use of solvothermal reactions with emphasis upon *in situ* synthesis of ligands, e.g., carboxylate ligands prepared from cyano compounds. Because the ligands are generated *in situ*, their concentrations may be controlled by reaction temperature, thus maintaining control of ligand concentration during the reaction in a manner that is otherwise hard to achieve. Chapter 6 provides an overview of how CP structure can be controlled by noncovalent interactions such as H-bonds, π - π interactions, etc. and steric forces. The use of bulky substituents to prevent interpenetration in CPs is highlighted. Chapter 7 is an introduction to ferroelectric materials with emphasis upon the crystallographic conditions required to facilitate the effect. The use of homochiral ligands to enforce crystallization in an acentric space group is emphasized. Chapter 8 focuses upon magnetic molecular solids using three-atom ligands as bridges. Azido, formato, cyanato, thiocyanato, selenocyanato, nitrito, and other ligands are used to link metals such as Mn(III), Co(II), and Ni(II) to form 0D to 3D structures that exhibit magnetic behavior at low temperatures. PCPs are investigated to evaluate the effect of guest molecules on T_c . Chapters 11 and 12 focus upon PCPs for gas storage and separation, perhaps the most widely studied property of PCPs. Chapter 11 addresses the synthesis and structures of a limited series of PCPs and looks at TGA, pore size, hydrogen binding energies, and selective sorption of organic molecules. Chapter 12 focuses upon broader issues related to hydrogen storage by detailing technological goals for such storage and how various parameters such as surface area, pore volume, pore size, catenation, ligand functionalization, and open metal sites are relevant for practical hydrogen storage. This chapter directly addresses the challenge facing PCPs in the context of hydrogen storage, i.e., low binding energy toward H_2 , and also highlights tools for investigating hydrogen adsorption, such as INS and neutron powder diffraction.

In summary, the strength of the book is that it is timely, given the increasingly large volume of primary literature that is being generated on CPs. Furthermore, the chapters addressing specialized topics, which are not found elsewhere, are covered in detail, and although the general chapters tend to overlap with other recent reviews, they cover the important topics and do it well. Overall, the sum of the individual components makes the whole a useful reference to complement other recent contributions on the subject of CPs. The weaknesses of the book are that the references seem to date to 2007 and several broadly relevant topics such as topology,

interpenetration, computational modeling of PCPs, catalytic PCPs, and pillared PCPs are not covered well or at all.

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Advances in Friedel–Crafts Acylation Reactions: Catalytic and Green Processes. By Giovanni Sartori and Raimondo Maggi (both at University of Parma, Italy). CRC Press (an imprint of the Taylor & Francis Group): Boca Raton, FL. 2009. xii + 209 pp. \$149.95. ISBN 978-1-4200-6792-7.

Friedel–Crafts (FC) acylation reactions constitute a well-established synthetic protocol for the chemical functionalization of aromatic compounds. Since its discovery in the late 1870s, the methodology has experienced continuous growth in popularity within both academic and industrial chemical communities. The demand for the design and development of eco-sustainable chemical manufactures drove the application of FC acylation in a new direction that featured sustainability and efficiency as the main goals. Here, the combination of innovative techniques, such as homogeneous and heterogeneous catalysis, continuous-flow processes, and alternative reaction media, became essential for pursuing these objectives. Although FC acylation reactions have been the subject of several reviews and monographs, an up-to-date overview of *green* and catalytic methodologies was still lacking. The aim of *Advances in Friedel–Crafts Acylation Reactions: Catalytic and Green Processes* is to fill this vacancy by collecting in six chapters the most efficient and fascinating synthetic methodologies for the preparation of aromatic ketones.

After an introductory chapter focusing mainly on the history of FC acylation reactions, the book is organized into four parts

that address stoichiometric reactions, homogeneous catalytic approaches, heterogeneous catalytic protocols, and Fries rearrangement. In-depth mechanistic details of the presented chemistries and their limitations can be found throughout the chapters.

The book is well structured and provides the reader with up-to-date references, especially in Chapters 3–5. The authors also present a number of stoichiometric procedures for FC acylation that feature an extraordinary level of selectivity or environmentally benign reaction media as dominant aspects. Nearly two-thirds of the book is devoted to the fascinating realm of heterogeneously catalyzed acylation of aromatic compounds, with a section dedicated to the direct chemical reactions of phenol, e.g., Fries rearrangement, on laboratory as well as industrial scales. Such an interest is justified by the facile removal/recovery via filtration or centrifugation of the solid Brønsted/Lewis acids employed, thus leading to a net increase in the amount of product formed from a given amount of catalyst.

In summary, this reference book covers a rather broad range of synthetic methodologies for the preparation of aromatic ketones. New researchers in the field as well as expert industrial practitioners will find valuable insights and up-to-date references here. I would personally recommend this book to all colleagues and graduate-level students who are pursuing research in the field of synthetic manipulation of aromatic compounds. A perfect balance between historical background and new trends toward low-impact environmental strategies can be found throughout the book.

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