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Flavin-Based Catalysis - Preface

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Preface

Participation in catalytic processes is one of the main roles of flavins. Nature has been using this concept for millions of years. The discovery, description of the structure and function of flavins in the late nineteenth and first half of the twentieth century has triggered exploitation of the catalytic capabilities of flavins in man-made synthetic transformations, either using enzymatic or artificial systems. Nowadays, flavins and flavoproteins are enjoying an increased interest from a broad audience, which includes researchers active in synthetic chemistry, enzymology, biocatalysis, and spectroscopy. With new natural flavins still being discovered in recent years, new flavoenzyme structures and mechanisms elucidated, new flavin derivatives synthesized, and new photocatalytic and biomimetic approaches developed, it is a very dynamic field of research. Even if the most common flavin cofactors were discovered about one century ago, the field is alive and kicking. There are more than 1000 new scientific literature contributions on flavin-related research per year. Many of them are relevant to catalysis. Considering the increasing frequency of new discoveries, one may ask: Are there any limits to flavin catalysis?

Our idea was to prepare a book covering various aspects of flavin catalysis (organo-, bio-, and photocatalysis), which is done in eight chapters. These are accompanied by four introductory chapters overviewing important natural and artificial flavin derivatives, including recently discovered flavin cofactors, their role, and noncanonical chemistry. There, also flavin properties are described with a special attention to those related to catalysis like acid–base and redox properties, reactivity and noncovalent interactions (Chapters 1 and 2). Chapter 3 summarizes spectral properties of flavin derivatives as this has implications for light-dependent processes. Also, a comprehensive chapter on catalytic modes of flavins is included; it provides an overview on ways in which members of the flavin family are involved in catalysis, regardless of whether the reactions take place in enzymes or in artificial catalytic systems (Chapter 4).

The next chapters focus on different fields of catalysis in which flavins are the core catalysts. Each chapter has an introduction with the information necessary to read the main part and a conclusion section sketching main developments and future outlook. While the chapters are ordered in a logical way, they can also be used as standalone papers that inform the reader on specific aspects of flavins and flavin-related chemistry. Organocatalytic transformations are summarized in two

chapters. In the first one (Chapter 5), organocatalytic processes using both hydrogen peroxide and oxygen in oxygenation processes (“artificial monooxygenases”) are reviewed. In the second chapter (Chapter 6), cooperative and supramolecular systems involving artificial flavin derivatives are presented and discussed. Three chapters are devoted to biocatalytic systems providing an overview of different flavoenzyme classes and their respective reaction mechanisms. The chapters discuss the flavoenzymes in the context of biocatalytic applications. The individual chapters are focused on (i) reactions catalyzed by flavoprotein monooxygenases and halogenases (Chapter 7), (ii) biocatalytic hydrogenations catalyzed by reductases (Chapter 8), and (iii) oxidations mediated by flavoprotein reductases and oxidases (Chapter 9). The last three chapters covers aspects of flavin-based photocatalysis. Chapter 10 is focused on early-stage investigations and benzylic oxidations, which are typical for flavin photocatalysis. Recently, new applications appeared, namely cycloadditions, sulfoxidations, decarboxylations or C–C couplings, which are summarized in Chapter 11. Finally, a chapter has been dedicated to recently developed light-dependent biocatalytic processes (“photobiocatalysis”) and their applications (Chapter 12).

The editors are very grateful to the individual contributors for their effort and enthusiasm to prepare their chapters. We also wish to thank Milos Trajkovic for careful proofreading and Eva Svobodová for helping with manuscript preparation in their final form. Thanks to our joint effort, we created a work that not only captures the current state of knowledge concerning flavin-based catalysis but also illustrates the forever-valid basic principles and points to the still-unresolved issues of flavin catalysis. We hope that the book can be of help for the reader to be informed on the current knowledge of flavins and their catalytic potential, and possibly get captivated by the fascinating world of flavins.

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