

Handbook of Porphyrin Science

with Applications to Chemistry, Physics,
Materials Science, Engineering, Biology
and Medicine



Volume 5 **Heme Proteins**

Karl M. Kadish • Kevin M. Smith • Roger Gullard

Editors

Handbook of Porphyrin Science

with Applications to Chemistry, Physics,
Materials Science, Engineering, Biology
and Medicine



Volume 5
Heme Proteins

Editors

Karl M. Kadish

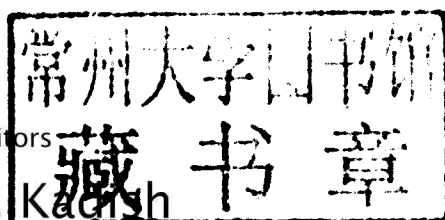
University of Houston, USA

Kevin M. Smith

Louisiana State University, USA

Roger Guilard

Université de Bourgogne, France



 **World Scientific**

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI

Published by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

HANDBOOK OF PORPHYRIN SCIENCE

with Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine
(Volumes 1–5)

Copyright © 2010 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN-13 978-981-4280-16-7 (Set)

ISBN-10 981-4280-16-X (Set)

Typeset by Stallion Press

Email: enquiries@stallionpress.com

Printed in Singapore by Mainland Press Pte Ltd.

Handbook of Porphyrin Science

with Applications to Chemistry, Physics,
Materials Science, Engineering, Biology
and Medicine

HANDBOOK OF PORPHYRIN SCIENCE
with Applications to Chemistry, Physics, Materials Science,
Engineering, Biology and Medicine
(Volumes 1–5)

ISSN: 1793-9518

Editors: Karl M. Kadish (*University of Houston, USA*),
Kevin M. Smith (*Louisiana State University, USA*) and
Roger Guillard (*Université de Bourgogne, France*)

- Vol. 1 Supramolecular Chemistry
- Vol. 2 Synthesis and Coordination Chemistry
- Vol. 3 Synthetic Methodology
- Vol. 4 Phototherapy, Radioimmunotherapy and Imaging
- Vol. 5 Heme Proteins

Preface

Although the porphyrin and tetrapyrrole research area was regarded as “fully matured” during the 20th century, as evidenced for example by the awarding of numerous Nobel Prizes to its principal researchers, new advances and accomplishments in the field still amaze us as editors. The area continues to blossom and to expand into new areas of science and applications that would probably never have occurred to our 20th century heroes. An earlier *Porphyrin Handbook* assembled the large amount of factual data that had been accumulated during the 20th century. Our new venture, the *Handbook of Porphyrin Science* takes a completely new look at our research area and comprehensively details the contemporary science now appearing in the scientific literature that would indeed have been hard to predict even 10 years ago. In particular, fundamentally new methodologies and potential commercial applications of the beautiful compounds that we all love are exemplified, fully recognizing the subtitle of the series — “with applications to chemistry, physics, materials science, engineering, biology and medicine”.

The three of us have complementary expertise in physical chemistry, synthetic and bioorganic chemistry, and in synthetic and mechanistic organometallic chemistry; this has enabled us to cover the whole field of porphyrin science and applications, and to devise comprehensive volume and author content. As of the date of writing, between the three of us, we have published more than 1600 tetrapyrrole research articles, and hold 31 patents related to commercial applications of porphyrin science. So we do know our field, and this has enabled us to assemble a first-rate group of experts who have written comprehensive up-to-date chapters with accuracy and authority; we thank our authors for their cooperation and willingness to go along with our highly ambitious schedule for production of these volumes.

We look forward to comments from our readers, and to suggestions that might enable us to expand our basic interests and scientific coverage even further. Meanwhile, we hope that porphyrin researchers, old, new and of the future, will enjoy reading these volumes just as much as we enjoyed planning and, with the help of World Scientific Publishing Company, producing them from manuscript to published article, in a timely manner.

Karl M. Kadish (Houston, Texas, USA)
Kevin M. Smith (Baton Rouge, Louisiana, USA)
Roger Guillard (Dijon, Bourgogne, France)
January, 2010

Contributing Authors*

Hasrat Ali

Université de Sherbrooke
Sherbrooke, Québec, Canada
Chapter 16

Cristina Alonso

University of Hull
HU6 7RX, Kingston-upon-Hull, UK
Chapter 17

Naoki Aratani

Kyoto University
Kyoto 606-8502, Japan
aratani@kuchem.kyoto-u.ac.jp
Chapter 1

Teodor Silviu Balaban

Karlsruhe Institute of Technology
D-76021 Karlsruhe, Germany
Silviu.Balaban@int.fzk.de
Chapter 3

David P. Ballou

University of Michigan
Ann Arbor, MI 48109-5606, USA
Chapter 28

Ross W. Boyle

University of Hull
r.w.boyle@hull.ac.uk
Chapter 17

Ozguncem Bozkulak

Childrens Hospital Los Angeles
Los Angeles, CA 90027, USA
Chapter 22

José A.S. Cavaleiro,

University of Aveiro
3810-193 Aveiro, Portugal
jcavaleiro@ua.pt
Chapter 9

Sung Cho

Yonsei University
Seoul, 120-747, Korea
Chapter 5

Daniel P. Collins

University of South Carolina
Columbia, SC 29208, USA
Chapter 28

John H. Dawson

University of South Carolina, USA
Columbia, SC 29208, USA
dawson@mail.chem.sc.edu
Chapter 28

Ilia G. Denisov

The University of Illinois
Urbana, IL 61801, USA
Denisov@illinois.edu
Chapter 26

*Full contact information for authors can be found on the title page of each chapter.

Charles Michael Drain

Hunter College of The City University
of New York

New York, NY 10065, USA

cdrain@hunter.cuny.edu

Chapter 15

Francis D'Souza

Wichita State University

Wichita, KS 67260-0051, USA

Francis.DSouza@wichita.edu

Chapter 4

Manivannan Ethirajan

Roswell Park Cancer Institute

Buffalo, NY 14263, USA

Chapter 19

Angela Ferrario

Childrens Hospital Los Angeles
Los Angeles, CA 90027, USA

Chapter 22

Kimberly B. Fields

University of South Florida
Tampa, FL 33620, USA

Chapter 13

Hiroyuki Furuta

Kyushu University

Fukuoka 819-0395, Japan

hfuruta@cstf.kyushu-u.ac.jp

Chapter 10

Jean-Paul Gisselbrecht

Université de Strasbourg
67000 Strasbourg, France
gissel@unistra.fr

Chapter 14

Charles J. Gomer

University of Southern California
Los Angeles, CA 90027, USA

Chapter 22

Bruno Grimm

Friedrich-Alexander-University
Erlangen-Nuremberg

91058 Erlangen, Germany

Chapter 2

Dirk M. Guldi

Friedrich-Alexander-University
Erlangen-Nuremberg

91058 Erlangen, Germany

dirk.guldi@chemie.uni-erlangen.de

Chapter 2

Anita Hausmann

Friedrich-Alexander-University
Erlangen-Nuremberg

91058 Erlangen, Germany

Chapter 2

Takashi Hayashi

Osaka University

Suita 565-0871, Japan

thayashi@chem.eng.osaka-u.ac.jp

Chapter 23

Osamu Ito

Tohoku University

Sendai, 981-3215, Japan

Chapter 4

Christophe Jeandon

Université de Strasbourg
67000 Strasbourg, France
cjeandon@unistra.fr

Chapter 14

Norbert Jux

Universität Erlangen-Nürnberg
91054 Erlangen, Germany
norbert.jux@chemie.uni-erlangen.de
Chapter 20

Axel Kahnt

Friedrich-Alexander-University
Erlangen-Nuremberg
91058 Erlangen, Germany
Chapter 2

David Kessel

Wayne State University School of
Medicine
Detroit, MI 48201, USA
dhkessel@med.wayne.edu
Chapter 21

Dongho Kim

Yonsei University
Seoul, 120-747, Korea
dongho@yonsei.ac.kr
Chapters 5, 6

Kil Suk Kim

Yonsei University
Seoul, 120-747, Korea
Chapter 6

Lechosław Latos-Grażyński

University of Wrocław
Wrocław 50 383, Poland
llg@wchuwr.pl
Chapter 8

Genxi Li

Nanjing University
Nanjing 210093, PR China
genxili@nju.edu.cn
Chapter 27

Jong Min Lim

Yonsei University
Seoul, 120-747, Korea
Chapter 6

Evgeny A. Lukyanets

Organic Intermediates and Dyes Institute
Moscow, 123995, Russia
rmeluk@niopik.ru
Chapter 11

Marian Luna

Childrens Hospital Los Angeles
Los Angeles, CA 90027, USA
Chapter 22

Shingo Nagano

Tottori University
Tottori 680-8552, Japan
Chapter 25

Victor N. Nemykin

University of Minnesota Duluth
Duluth, MN 55812, USA
vnemykin@d.umn.edu
Chapter 11

Maria G.P.M.S. Neves

University of Aveiro
3810-193 Aveiro, Portugal
Chapter 9

Tetsuo Okujima

Ehime University
Matsuyama 790-8577, Japan
Chapter 7

Noboru Ono

Ehime University
Matsuyama 790-8577, Japan
ononbr@dpc.ehime-u.ac.jp
Chapter 7

Atsuhiko Osuka

Kyoto University
Kyoto 606-8502, Japan
osuka@kuchem.kyoto-u.ac.jp
Chapter 1

Ravindra K. Pandey

Roswell Park Cancer Institute
Buffalo, NY 14263, USA
ravindra.pandey@roswellpark.org
Chapter 19

Nayan J. Patel

Roswell Park Cancer Institute
Buffalo, NY 14263, USA
Chapter 19

Mikoř Pawlicki

University of Wrocław
Wrocław 50 383, Poland
Chapter 8

Sébastien Richeter

Université Montpellier 2
34095 Montpellier Cedex 5, France
sebastien.richeter@univ-montp2.fr
Chapter 14

Beate Röder

Humboldt-Universität zu Berlin
12489 Berlin, Germany
roeder@physik.hu-berlin.de
Chapter 20

Natalie Rucker

Childrens Hospital Los Angeles
Los Angeles, CA 90027, USA
Chapter 22

Joshua V. Ruppel

University of South Florida
Tampa, FL 33620, USA
Chapter 13

Romain Ruppert

Université de Strasbourg
67000 Strasbourg, France
rruppert@unistra.fr
Chapter 14

Aoife Ryan

Trinity College Dublin
Dublin 2, Ireland
Chapter 12

Wolfgang Seitz

Friedrich-Alexander-University
Erlangen-Nuremberg
91058 Erlangen, Germany
Chapter 2

Mathias O. Senge

Trinity College Dublin
Dublin 2, Ireland
sengem@tcd.ie
Chapter 12

Natalia N. Sergeeva

Trinity College Dublin
Dublin 2, Ireland
Chapter 12

Jae-Yoon Shin

Yonsei University
Seoul, 120-747, Korea
Chapter 6

Yoshitsugu Shiro

Harima Institute
Hyogo 679-5148, Japan
yshiro@riken.jp
Chapters 24, 25

Martha Sibrian-Vazquez

Portland State University
Portland, OR 97201, USA
Chapter 18

Sunaina Singh

Hunter College of The City University
of New York
New York, NY 10065, USA
Chapter 15

Stephen G. Sligar

The University of Illinois
Urbana, IL 61801, USA
s-sligar@uiuc.edu
Chapter 26

Nicole L. Snyder

Hamilton College
Clinton, NY 13323, USA
Chapter 13

Fabian Spänig

Friedrich-Alexander-University
Erlangen-Nuremberg
91058 Erlangen, Germany
Chapter 2

Tatyana Spolitak

University of Michigan
Ann Arbor, MI 48109-5606, USA
Chapter 28

Hiroshi Sugimoto

Harima Institute
Hyogo 679-5148, Japan
Chapter 24

Osamu Takikawa

National Center for Geriatrics and
Gerontology
Obu, Aichi 474-8522, Japan
Chapter 24

Motoki Toganoh

Kyushu University
Fukuoka 819-0395, Japan
Chapter 10

Augusto C. Tomé

University of Aveiro
3810-193 Aveiro, Portugal
Chapter 9

Johan E. van Lier

Université de Sherbrooke
Sherbrooke, Québec, Canada
Johannes.Van.Lier@USherbrooke.ca
Chapter 16

Maria da Graça H. Vicente

Louisiana State University
Baton Rouge, LA 70803, USA
vicente@lsu.edu
Chapter 18

Sam Wong

Childrens Hospital Los Angeles
Los Angeles, CA 90027, USA
Chapter 22

Frank Xu

Childrens Hospital Los Angeles
Los Angeles, CA 90027, USA
Chapter 22

Hiroko Yamada

Ehime University
Matsuyama 790-8577, Japan
Chapter 7

Jaesung Yang

Yonsei University
Seoul, 120-747, Korea
Chapter 5

Hyejin Yoo

Yonsei University
Seoul, 120-747, Korea
Chapter 5

Min-Chul Yoon

Yonsei University
Seoul, 120-747, Korea
Chapter 6

Zin Seok Yoon

Yonsei University
Seoul, 120-747, Korea
Chapter 5

X. Peter Zhang

University of South Florida
Tampa, FL 33620, USA
pzhang@cas.usf.edu
Chapter 13

Contents of Volumes 1–5

Volume 1 Supramolecular Chemistry

1. Synthetic Strategies Toward Multiporphyrinic Architectures
Naoki Aratani and Atsuhiko Osuka
2. Charge Transfer Between Porphyrins/Phthalocyanines and Carbon Nanostructures
Bruno Grimm, Anita Hausmann, Axel Kahnt, Wolfgang Seitz, Fabian Spänig and Dirk M. Guldi
3. Self-Assembling Porphyrins and Chlorins as Synthetic Mimics of the Chlorosomal Bacteriochlorophylls
Teodor Silviu Balaban
4. Tetrapyrrole–Nanocarbon Hybrids: Self-Assembly and Photoinduced Electron Transfer
Francis D'Souza and Osamu Ito
5. Photophysical Properties of Various Directly Linked Porphyrin Arrays
Zin Seok Yoon, Jaesung Yang, Hyejin Yoo, Sung Cho and Dongho Kim
6. Photophysics and Photochemistry of Various Expanded Porphyrins
Jong Min Lim, Min-Chul Yoon, Kil Suk Kim, Jae-Yoon Shin and Dongho Kim

Volume 2 Synthesis and Coordination Chemistry

7. Synthesis of Porphyrins Fused with Aromatic Rings
Noboru Ono, Hiroko Yamada and Tetsuo Okujima
8. Carbaporphyrinoids — Synthesis and Coordination Properties
Miłosz Pawlicki and Lechosław Latos-Grażyński
9. *meso*-Tetraarylporphyrin Derivatives: New Synthetic Methodologies
José A.S. Cavaleiro, Augusto C. Tomé and Maria G.P.M.S. Neves
10. Synthesis and Metal Coordination of N-Confused and N-Fused Porphyrinoids
Motoki Toganoh and Hiroyuki Furuta

Volume 3 Synthetic Methodology

11. The Key Role of Peripheral Substituents in the Chemistry of Phthalocyanines
Victor N. Nemykin and Evgeny A. Lukyanets
12. Organometallic C–C Coupling Reactions for Porphyrins
Natalia N. Sergeeva, Mathias O. Senge and Aoife Ryan
13. Porphyrin Functionalization via Palladium-Catalyzed Carbon–Heteroatom Cross-Coupling Reactions
Kimberly B. Fields, Joshua V. Ruppel, Nicole L. Snyder and X. Peter Zhang
14. Peripherally Metalated Porphyrin Derivatives: Synthetic Approaches and Properties
Sébastien Richeter, Christophe Jeandon, Jean-Paul Gisselbrecht and Romain Ruppert
15. Combinatorial Libraries of Porphyrins: Chemistry and Applications
Charles Michael Drain and Sunaina Singh

Volume 4 Phototherapy, Radioimmunotherapy and Imaging

16. Porphyrins and Phthalocyanines as Photosensitizers and Radiosensitizers
Hasrat Ali and Johan E. van Lier
17. Bioconjugates of Porphyrins and Related Molecules for Photodynamic Therapy
Cristina Alonso and Ross W. Boyle
18. Syntheses of Boronated Porphyrins and Their Application in BNCT
Maria da Graça H. Vicente and Martha Sibrian-Vazquez
19. Porphyrin-Based Multifunctional Agents for Tumor-Imaging and Photodynamic Therapy (PDT)
Manivannan Ethirajan, Nayan J. Patel and Ravindra K. Pandey
20. Targeting Strategies for Tetrapyrrole-Based Photodynamic Therapy of Tumors
Norbert Jux and Beate Röder
21. Mechanisms of Cell Death in Photodynamic Therapy
David Kessel
22. Photodynamic Therapy and the Tumor Microenvironment
Charles J. Gomer, Angela Ferrario, Marian Luna, Natalie Rucker, Sam Wong, Ozguncem Bozkulak and Frank Xu

Volume 5 Heme Proteins

23. Hemoproteins Reconstituted with Artificially Created Hemes
Takashi Hayashi
24. Tryptophan Catabolism by Heme Dioxygenases
Hiroshi Sugimoto, Osamu Takikawa and Yoshitsugu Shiro
25. NO Chemistry by Heme-Enzymes
Yoshitsugu Shiro and Shingo Nagano
26. Cytochrome P450 Enzymes
Iliia G. Denisov and Stephen G. Sligar
27. Heme Protein-Based Electrochemical Biosensors
Genxi Li
28. The Generation and Characterization of the Compounds I and ES States of Cytochrome P450 Using Rapid Mixing Methods
Daniel P. Collins, Tatyana Spolidak, David P. Ballou and John H. Dawson

Contents

Preface	xi
Contributing Authors	xiii
Contents of Volumes 1–5	xix

23 / Hemoproteins Reconstituted with Artificially Created Hemes **1**

Takashi Hayashi

I. Introduction	2
II. Molecular Design of Artificial Hemes	5
III. Preparation of Apo- and Reconstituted Proteins	6
IV. Structure–Function Relationship of Reconstituted Hemoproteins	7
A. Modification of Peripheral Substituents	7
1. The Role of 2- and 4-Substituents in the Heme Framework	7
2. The Role of 6- and 7-Propionate Side Chains in the Heme Framework	12
3. Heme Disorder	17
4. Fluorinated Peripheral Substituents	19
5. The Positions of Propionates	19
6. Nonpropionated Hemes	21
7. Other Peripheral Substituents	22
B. Metal Substitution of Hemes	24
1. General	24
2. Cobalt Hemoproteins	24
3. Manganese Hemoproteins	25
4. Zinc Hemoproteins	26
5. Mixed-Metal Hybrid Hemoglobins	27
6. Other Metal Substitutions	27
C. Incorporation of Porphyrin Analogs	28
1. Chlorins	28
2. Chlorophyll Derivatives	30
3. Phthalocyanine Derivatives	30
4. Azaporphyrins	31
5. Other Porphyrin Analogs	32

V. Functionalization of Hemoproteins by Substitution with Artificial Prosthetic Groups	32
A. Modulation of Hemoprotein Activity by Artificial Porphyrinoids	32
1. Regulation of Myoglobin Function	32
a. Porphycene	32
b. Corrphycene	33
c. Hemiporphycene	33
2. Regulation of Peroxidase Function	34
a. Porphycene	34
b. Corrole	35
B. Functionalization by Modification of Heme-Propionate Side Chains	35
1. Construction of Electron Transfer Systems	35
a. Electron Transfer Model using a Single Protein	37
b. Electron Transfer Model using a Protein-Protein Complex ..	40
2. Construction of Interfaces on the Protein Surface	41
3. Construction of Substrate Binding Sites	44
C. New Nanobiomaterials	48
1. Design and Preparation of Biocatalysts	48
2. Immobilization of Hemoproteins on Membranes or Electrodes	49
3. Hemoprotein Assembly	53
VI. Conclusions	57
VII. References	58

24 / Tryptophan Catabolism by Heme Dioxygenases 71

Hiroshi Sugimoto, Osamu Takikawa and Yoshitsugu Shiro

List of Abbreviations	72
I. Biology and Biochemistry of Heme Dioxygenases	73
A. Introduction	73
B. IDO and TDO	73
C. Primary Structures of IDO and TDO	74
D. Properties of IDO2	75
E. Catalytic Properties of IDO and TDO	75
F. Endogenous Reducing System for IDO and TDO	76
G. Physiological Roles of IDO	77
H. Physiological Roles of TDO	78
I. Pathological Roles of IDO	78
J. Conclusions	80