Chlorophylls and Bacteriochlorophylls

Advances in Photosynthesis and Respiration

VOLUME 25

The scope of our series, beginning with volume 11, reflects the concept that photosynthesis and respiration are intertwined with respect to both the protein complexes involved and to the entire bioenergetic machinery of all life. *Advances in Photosynthesis and Respiration* is a book series that provides a comprehensive and state-of-the-art account of research in photosynthesis and respiration. Photosynthesis is the process by which higher plants, algae, and certain species of bacteria transform and store solar energy in the form of energy-rich organic molecules. These compounds are in turn used as the energy source for all growth and reproduction in these and almost all other organisms. As such, virtually all life on the planet ultimately depends on photosynthetic energy conversion. Respiration, which occurs in mitochondrial and bacterial membranes, utilizes energy present in organic molecules to fuel a wide range of metabolic reactions critical for cell growth and development. In addition, many photosynthetic organisms engage in energetically wasteful photorespiration that begins in the chloroplast with an oxygenation reaction catalyzed by the same enzyme responsible for capturing carbon dioxide in photosynthesis. This series of books spans topics from physics to agronomy and medicine, from femtosecond processes to season long production, from the photophysics of reaction centers, through the electrochemistry of intermediate electron transfer, to the physiology of whole orgamisms, and from X-ray crystallography of proteins to the morphology or organelles and intact organisms. The goal of the series is to offer beginning researchers, advanced undergraduate students, graduate students, and even research specialists, a comprehensive, up-to-date picture of the remarkable advances across the full scope of research on photosynthesis, respiration and related processes.

The titles published in the Series are listed at on p. v/vi, those forthcoming volumes on p. 8. A complete list is also provided at the end of book following p. 603.

Chlorophylls and Bacteriochlorophylls

Biochemistry, Biophysics, Functions and Applications

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Cover illustration: Molecular structure that is characteristic of chlorophylls, with the central Mg (green), to which an extra ligand (orange) is bound from the α- or back side, together with an image of the Earth from outer space showing the chlorophyll distribution on the continents and in the oceans. The background shows maize tissue with the chloroplasts in green, where photosynthesis takes place. The structure is bacteriochlorophyll BChl3 from the reaction center of *Rhodobacter sphaeroides* (H. Komiya, T.O. Yeates, A.J. Chirino, D.C. Rees, J.P. Allen, G. Feher, Proc. Natl. Acad. Sci. USA 85, 7993, 1988, pdb entry 4RCR, structure prepared with DS ViewerPro V. 4.0, Accelrys). We thank Compton Tucker and Norman Kuring from NASA, USA, for granting the use of the SeaWiFS image of the Earth (July 1999, Hammer projection), and Gerhard Wanner (University of München, Germany) for granting the use of the maize micrograph. The color-coding for the SeaWIFS image can be found in the supplementary material at http://epub.ub.uni-muenchen.de/archive/00000776/

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From the Series Editor

Advances in Photosynthesis and Respiration

Volume 25: Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications

I am delighted to announce the publication, in the *Advances in Photosynthesis and Respiration* (AIPH) Series, of ***Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications,*** a book covering the key pigments that play many crucial roles at the heart of both oxygenic and anoxygenic photosynthesis. This volume was edited by four distinguished authorities: Bernhard Grimm (Berlin, Germany), Robert (Bob) Porra, (Canberra, Australia), Wolfhart Rüdiger (Munich, Germany) and Hugo Scheer (Munich, Germany). Several earlier AIPH volumes did include, by necessity, functions of chlorophylls and the bacteriochlorophylls acting as antenna and as key reaction center components, but none of the volumes focused on all the aspects of the properties and of the roles played by these key pigments not only in the natural process of photosynthesis but also in such applications as photodynamic treatment of cancerous tumors and the detection and measurement of chlorophyll-bearing phytoplankton from satellites in outer space. This book integrates all the knowledge on these pigments essential for life on earth. The current volume follows the 24 volumes listed below.

Published Volumes

- *Volume 1*: ***Molecular Biology of Cyanobacteria*** (28 Chapters; 881 pages; 1994; edited by Donald A. Bryant, from USA);
- *Volume 2:* ***Anoxygenic Photosynthetic Bacteria*** (62 Chapters; 1331 pages; 1995; edited by Robert E. Blankenship, Michael T. Madigan and Carl E. Bauer, from USA);
- *Volume 3:* ***Biophysical Techniques in Photosynthesis*** (24 Chapters; 411 pages; 1996; edited by the late Jan Amesz and the late Arnold J. Hoff, from The Netherlands);
- *Volume 4:* ***Oxygenic Photosynthesis: The Light Reactions*** (34 Chapters; 682 pages; 1996; edited by Donald R. Ort and Charles F. Yocum, from USA);
- *Volume 5:* ***Photosynthesis and the Environment*** (20 Chapters; 491 pages; 1996; edited by Neil R. Baker, from UK);
- *Volume 6:* ***Lipids in Photosynthesis: Structure, Function and Genetics*** (15 Chapters; 321 pages; 1998; edited by Paul-André Siegenthaler and Norio Murata, from Switzerland and Japan);
- *Volume 7:* ***The Molecular Biology of Chloroplasts and Mitochondria in Chlamydomonas*** (36 Chapters; 733 pages; 1998; edited by Jean David Rochaix, Michel Goldschmidt-Clermont and Sabeeha Merchant, from Switzerland and USA);
- *Volume 8:* ***The Photochemistry of Carotenoids*** (20 Chapters; 399 pages; 1999; edited by Harry A. Frank, Andrew J. Young, George Britton and Richard J. Cogdell, from USA and UK);
- *Volume 9:* ***Photosynthesis: Physiology and Metabolism*** (24 Chapters; 624 pages; 2000; edited by Richard C. Leegood, Thomas D. Sharkey and Susanne von Caemmerer, from UK, USA and Australia);
- *Volume 10:* ***Photosynthesis: Photobiochemistry and Photobiophysics*** (36 Chapters; 763 pages; 2001; authored by Bacon Ke, from USA);
- *Volume 11:* ***Regulation of Photosynthesis*** (32 Chapters; 613 pages; 2001; edited by Eva-Mari Aro and Bertil Andersson, from Finland and Sweden);
- *Volume 12:* ***Photosynthetic Nitrogen Assimilation and Associated Carbon and Respiratory Metabolism*** (16 Chapters; 284 pages; 2002; edited by Christine Foyer and Graham Noctor, from UK and France);
- *Volume 13:* ***Light Harvesting Antennas*** (17

Chapters; 513 pages; 2003; edited by Beverley Green and William Parson, from Canada and USA);

- *Volume 14:* ***Photosynthesis in Algae*** (19 Chapters; 479 pages; 2003; edited by Anthony Larkum, Susan Douglas and John Raven, from Australia, Canada and UK);
- *Volume 15:* ***Respiration in Archaea and Bacteria: Diversity of Prokaryotic Electron Transport Carriers*** (13 Chapters; 326 pages; 2004; edited by Davide Zannoni, from Italy);
- *Volume 16:* ***Respiration in Archaea and Bacteria: Diversity of Prokaryotic Respiratory Systems*** (13 chapters; 310 pages; 2004; edited by Davide Zannoni, from Italy);
- *Volume 17:* ***Plant Mitochondria: From Genome to Function*** (14 Chapters; 325 pages; 2004; edited by David A. Day, A. Harvey Millar and James Whelan, from Australia);
- *Volume 18:* ***Plant Respiration: From Cell to Ecosystem*** (13 Chapters; 250 pages; 2005; edited by Hans Lambers and Miquel Ribas-Carbo, from Australia and Spain).
- *Volume 19:* ***Chlorophyll a Fluorescence: A Signature of Photosynthesis*** (31 Chapters; 817 pages; 2004; edited by George C. Papageorgiou and Govindjee, from Greece and USA);
- *Volume 20:* ***Discoveries in Photosynthesis*** (111 Chapters, 1262 pages; 2005; edited by Govindjee, J. Thomas Beatty, Howard Gest and John F. Allen, from USA, Canada and Sweden (& UK));
- *Volume 21:* ***Photoprotection, Photoinhibition, Gene Regulation and Environment*** (21 Chapters, 378 pages; 2006; edited by Barbara Demmig-Adams, William Adams III and Autar K. Mattoo, all from USA);
- *Volume 22:* ***Photosystem II: The Light-Induced Water:Plastoquinone Oxidoreductase*** (34 Chapters; 826 pages; 2005; edited by Thomas J. Wydrzynski and Kimiyuki Satoh, from Australia and Japan);
- *Volume 23:* ***Structure and Function of the Plastids*** (27 Chapters; 2006; edited by Robert Wise and J. Kenneth Hoober, both from USA);
- *Volume 24:* ***Photosystem I: The Light-Induced Plastocyanin:Ferredoxin Oxidoreductase*** (40 Chapters; 2006; edited by John H. Golbeck from USA).

Further information on these books and ordering instructions can be found at <www.springeronline.com> under the Book Series 'Advances in Photosynthesis and Respiration.' Tables of Contents of volumes 1–24 can be found at <www.life.uiuc.edu/govindjee/photosynSeries/ttocs.html>. Special discounts are available for members of the International Society of Photosynthesis Research, ISPR (<http://www.photosynthesisresearch.org>).

About Volume 25: Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications

Chlorophylls are the most obvious natural pigments on Earth being observable, as they are, from outer-space; they also sustain all life on Earth via their involvement in photosynthesis. With 37 concise chapters, this book reviews recent progress and current status of studies of the chemistry, metabolism and spectroscopy of chlorophylls and chlorophyll-protein complexes. Also discussed is progress on the applications of the chlorophylls as photosensitizers in photodynamic therapy of cancerous tumors, as molecular probes, and as reporters on the physiological status of whole plants and ecosystems. The last book, dedicated to chlorophylls, was published in 1991, and has been out of print since 1995; thus, this book fills a gap by summarizing the chemical, physical, biological and medical aspects of chlorophyll research and development with a focus on the tremendous progress achieved over the past 15 years. The book is aimed equally at advanced students and both novice and experienced researchers: each of the five sections has an up-to-date introductory overview which is followed by a series of concise well-focused and fully-referenced chapters written by chemists, biochemists, biophysicists, photobiologists and pharmacologists.

This book has 37 authoritative Chapters written by 70 international authorities from 18 countries (Australia, Austria, Belarus, Czech Republic, Denmark, France, Germany, Indonesia, Israel, Japan, Malaysia, Mexico, The Netherlands, Russia, Spain, Switzerland, United Kingdom and the United States of America). It is, therefore, a truly international book and the editors deserve our thanks and our congratulations for giving this gift for our future. It was a Herculean task that Hugo Scheer and his co-editors, Bernhard Grimm, Bob Porra and Wolfhart Rüdiger, have accomplished. I remain in awe at the encyclopedic knowledge provided in this Bible of chlorophylls and bacteriochlorophylls (their structures; chemistry and analysis (9 chapters); their metabolism (9 chapters); their native environment (9 chapters); their functions (4 chapters); and finally their applications (6 chapters). The readers can easily find the titles and the authors of the individual chapters in the Table of Contents of this book. Instead of repeating this information here, I prefer to thank each and every author by name (listed in alphabetical order) that reads like a 'Who's Who in Chlorophyll and Bacteriochlorophyll research':

> Thijs J. Aartsma; Machiko Akiyama; James P. Allen; Idan Ashur; Samuel I.Beale; Christoph F. Beck; Robert E. Blankenship; Alexander S. Brandis; Paula Braun; Donald A. Bryant; Aline G. M. Chew; Ido de Boer; Huub J.M. de Groot; P. Leslie Dutton; Patrick W. Fowler; Niels-Ulrik Frigaard; Ritsuko Fujii; Adela Garcia-Martin; José L. Garrido; Bernhard Grimm; Dirk W. Heinz; Stefan Hörtensteiner; C. Neil Hunter; Dieter Jahn; Shirley W. Jeffrey; Yoshinori Kakitani; Hiromi Kano; Brendan J. Keely; Hideo Kise; Masami Kobayashi; Michal Koblizek; Jürgen Köhler; Yasushi Koyama; Bernhard Kräutler; Frithjof C. Küpper; Hendrik Küpper; Lee-Gyan Kwa; Anthony W.D. Larkum; Dieter Leupold; Leenawaty Limantara; Heiko Lokstein; Julia A. Maresca; Alexander N. Melkozernov; André Morel; Christopher C. Moser; Jürgen Moser; Mamuro Nango; Ladislav Nedbal; Dror Noy; Harald Paulsen; Robert (Bob) J. Porra; Wolfhart Rüdiger; Claudia Ryppa; Yoram Salomon; Hugo Scheer; Avidgor Scherz; Wolf-Dieter Schubert; Mathias O. Senge; Yuzo Shioi; Martin Spiller; Erich Steiner; Matthias von Jan; Josef Wachtveitl; Tadashi Watanabe; Arno Wiehe; JoAnn C. Williams, Elena Yaronskaya; Roie Yerushalmi; Manuel Zapata, and Wolfgang Zinth.

The Web Site for the Book

A unique innovation introduced by the editors for this book has been the construction of a web site that hosts the supplementary material including several colored figures. It is located at <http://epub.ub.uni-muenchen.de/archive/00000776/>. Our readers will really appreciate this contribution by the editors.

A Brief History—From Then till Now

Discoveries

- In 1818, two French scientists Pierre Joseph Pelletier (1788–1842) and Joseph Bienaimé Caventou (1795–1877) named the green plant pigment chlorophyll ('green of leaf ').
- In 1877, the Russian physiologist Climent A. Timiriazeff (1843–1920) established the red maximum of the absorption spectrum of chlorophyll and showed that red light absorbed by chlorophyll is the most efficient for photosynthesis. On the basis of this experiment, he claimed that chlorophyll is an optical and chemical photosensitizer of photosynthesis. He proposed that light absorption by chlorophyll causes its chemical transformation, which induces further reactions leading to photosynthesis.
- In 1906, the Russian botanist Mikhail Semenovich Tswett (1872–1919) separated the plant pigments (chlorophylls and carotenoids) by passing a solution containing the natural pigment mixture through glass columns packed with finely-divided calcium carbonate, thereby inventing a new technique termed appropriately chromatography ('color representation' or 'color writing').
- In 1915, Richard Martin Willstätter (1872–1942), of Munich, Germany, received the Nobel Prize in Chemistry for his detailed chemical investigations on chlorophyll, including its chemical nature; he suggested that chlorophylls play an active role in photosynthesis. Willstätter's close collaborator in these studies was Arthur Stoll (1887–1971) of Switzerland.
- In 1930, Hans Fischer (1881–1945), also of Munich, Germany, received the Nobel Prize in Chemistry: he had made new inroads in the chemistry of chlorophyll, whose structure he elucidated in the subsequent 12 years. The award recognized his researches into the constitution of porphyrins, hemins and chlorophylls.
- In 1965, Robert Burns Woodward (1917-1979), of Harvard, USA, received the Nobel Prize in Chemistry for the synthesis of many organic compounds including chlorophyll, the topic of this book.
- Shortly after, in 1966, the terpenoid specialist Basil C.C. Weedon of Imperial College, London,

published a full record of the synthesis of phytol, the esterifying alcohol of most chlorophylls that comprises about 1/3 of their mass.

The Books

The appearance over the past 100 years of several books dedicated to chlorophylls, emphasizes the importance of and continuing interest in the subject.

- In 1913, a first concise account of chlorophyll research was published in a 423 page book *Untersuchungen über Chlorophyll* by Richard Willstätter and Arthur Stoll (Verlag von Julius Springer, Berlin).
- Between 1934 and 1940, Hans Fischer and Hans Orth published a monumental work *Die Chemie des Pyrrols* (Akademische Verlagsgesellschaft, Leipzig). The 2nd half of volume 2, by Hans Fischer and Adolf Stern, published in 1940, was entirely dedicated to chlorophylls. The relevance of this book is witnessed by its repeated reprinting, first in 1943 (Edwards Brothers, Ann Arbor, Michigan) and again in 1968 (Johnson Reprint Corporation, New York and London).
- In 1966, Leo P. Vernon and Gilbert R. Seely, both from USA, edited a 679 page book *The Chlorophylls* (Academic Press, New York); they had 22 authors, but none are in the current Grimm et al. book.
- In 1991, one of the editors of the current book, Hugo Scheer from Munich, Germany, edited a 1,257 page detailed and beautiful *opus* (*Chlorophylls*, CRC Press, Boca Raton). This book had 72 authors and 42 chapters. I am delighted to see that among these 72 authors, Sam Beale; Masami Kobayashi; Tony Larkum; Bob Porra; Wolfhart Rüdiger; Hugo Scheer; Avigdor Scherz; Yuzo Shioi; and Tadashi Watanabe are also authors in the current book.

For a time-line on oxygenic photosynthesis, see Govindjee and David Krogmann (2004) *Photosynthesis Research* 80: 15–57, and on anoxygenic photosynthesis, see H. Gest and R. E. Blankenship (2004) *Photosynthesis Research* 80: 59–70. Jack Fajer (2004) has provided a personal perspective on chlorophyll chemistry in *Photosynthesis Research* 80: 165–172.

Future AIPH Books

The readers of the current series are encouraged to watch for the publication of the forthcoming books (not necessarily arranged in the order of future appearance):

- ***Biophysical Techniques in Photosynthesis II*** **(**Editors: Thijs J. Aartsma and Jörg Matisyk**);**
- ***Photosynthesis: A Comprehensive Treatise; Biochemistry, Biophysics, Physiology and Molecular Biology*, *Part 1*** (Editors: Julian Eaton-Rye and Baishnab Tripathy); and
- ***Photosynthesis: A Comprehensive Treatise; Biochemistry, Biophysics, Physiology and Molecular Biology, Part 2*** (Editors: Baishnab Tripathy and Julian Eaton-Rye).

In addition to these contracted books, we are in touch with prospective Editors for the following books:

- Chloroplast Bioengineering
- Molecular Biology of Cyanobacteria II.
- ATP Synthase
- Genomics and Proteomics
- Anoxygenic Photosynthetic Bacteria II
- Hydrogen Evolution
- Sulfur Metabolism in Photosynthetic Systems
- Global Aspects, Parts 1 and 2
- Artificial Photosynthesis

Readers are encouraged to send their suggestions for future volumes (topics, names of future editors, and of future authors) to me by E-mail (gov@uiuc.edu) or fax (+1-217-244-7246).

In view of the interdisciplinary character of research in photosynthesis and respiration, it is my earnest hope that this series of books will be used in educating students and researchers not only in Plant Sciences, Molecular and Cell Biology, Integrative Biology, Biotechnology, Agricultural Sciences, Microbiology, Biochemistry, and Biophysics, but also in Bioengineering, Chemistry, and Physics.

I take this opportunity to thank and congratulate Hugo Scheer (corresponding editor), Robert Porra, Bernhard Grimm and Wolfhart Rüdiger for their outstanding and painstaking editorial work. I thank all the 70 authors (listed above) of volume 25 of the AIPH Series: without their authoritative chapters, there would be no such volume. I especially thank Larry Orr for typesetting this book: his expertise has been crucial in bringing this book to completion. We are grateful to Jacco Flipsen and Noeline

Gibson (both of Springer) for their friendly working relationship with us during the production of this book. I also thank Jeff Haas (Director of Information Technology, Life Sciences, University of Illinois at Urbana-Champaign, UIUC), Evan DeLucia (Head, Department of Plant Biology, UIUC) and my dear wife Rajni Govindjee for constant support.

February 15, 2006

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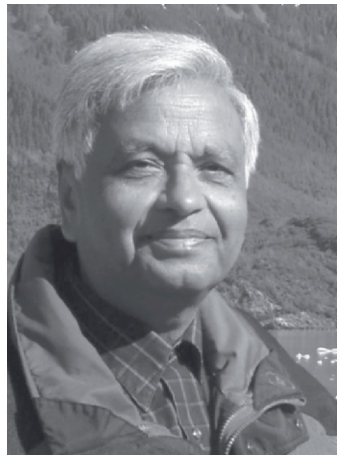

Govindjee

Govindjee, born in 1932, obtained his BSc (Chemistry, Biology) and MSc (Botany) in 1952 and 1954, from the University of Allahabad, India. He was a student of Robert Emerson and of Eugene Rabinowitch, receiving his PhD (Biophysics), in 1960, from the University of Illinois at Urbana-Champaign (UIUC), IL. He has focused mainly on "*Photosystem II*" (PS II, water:plastoquinone oxidoreductase) throughout his career. His early research included the discovery of a short-wavelength form of chlorophyll (Chl) *a* functioning in the Chl *b*-containing system, now called PS II (in 1960, with Eugene Rabinowitch); of the two-light effect in Chl *a* fluorescence (1960); and of the two-light effect (Emerson Enhancement) in NADP-reduction in chloroplasts (1962–1964, with Rajni Govindjee and George Hoch). In collaboration with his ~25 graduate students and postdoctoral associates, he has worked on the origins of the different spectral fluorescing forms of Chl *a* and the temperature dependence of excitation energy transfer down to 4 K (1963–1970); established basic relationships between Chl *a* fluorescence and photosynthetic reactions (1968–1988); discovered a unique role of bicarbonate on the acceptor side of PS II, particularly in protonation events involving the Q_B binding region (1970–1998); formulated the theory of thermoluminescence in plants (1983, with Don DeVault); made the first picosecond measurement on the primary photochemistry of PS II (1989–1997, with Michael Seibert and Michael Wasielewski); and pioneered the use of the lifetime of Chl *a* fluorescence in understanding photoprotection against excess light (with Adam Gilmore). His current focus, however, is on the "*History of Photosynthesis Research*" and in '*Photosynthesis Education.*' He has served the UIUC as an Assistant Professor, Associate Professor and Professor (1961–1999). Since 1999, he has been Professor Emeritus of Biochemistry, Biophysics and Plant Biology at the UIUC. His honors include: Fellow of the American Association of Advancement of Science (1976); Distinguished Lecturer of the School of Life Sciences, UIUC (1978); Fellow and Life Member of the National Academy of Sciences, India (Allahabad, 1978); President of the American Society of Photobiology (1980-1981); Fulbright Senior Lecturer (1996–1997); and Honorary President of the 13th International Photosynthesis Congress (Montréal, 2004).

Contents

Metabolism

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Functions

Applications

Preface

Chlorophylls (from the Greek: *chloros*-green and *phyllon*-leaf) are, beyond any doubt, the most visible and most abundant organic pigments on Earth. Indeed, as beautifully illustrated on the cover of the book, they are clearly visible from outer-space. It has been estimated that between 10^9 and 10^{12} tons of chlorophylls are produced annually on Earth. Much of this synthesis, if not most, occurs in the oceans where marine algae and photosynthetic bacteria of lakes and tidal flats, with their shorter life cycles than terrestrial plants, abound. But it is not only because of their abundance that chlorophylls are important. Chlorophylls derive their ultimate importance from their role as the key pigments which capture radiant energy from the sun for plant, algal and bacterial photosynthesis, a process which supports life on Earth, even non-photosynthesizing life forms such as animals, including ourselves. This knowledge seems inherent to man after the invention of agriculture as it is expressed widely in our general and religious literature alike: in the great Aton-Hymn we hear the Egyptians praise the sun: 'your rays nourish every garden…'; in the biblical quote we are informed 'all flesh is grass'; and, in Ingeborg Bachmann's poem 'To the Sun' we read 'more beautiful…. than other celestial bodies, as your and my life depend on it day by day…'

While the importance of light for plant growth has been realized since the beginning of agriculture, a role for the chlorophylls in this process was proposed less than 130 years ago in 1877 by the Russian plant physiologist, Climent Timiriazoff. It was 1913, however, before the first concise chemists' account of chlorophyll research was published by Richard Willstätter and Arthur Stoll in their book *Untersuchungen über Chlorophyll* (Investigations on Chlorophylls). Since then three more books on chlorophylls have appeared testifying not only to their importance in photosynthesis, but increasingly to the useful applications being discovered for them. The second book devoted entirely to chlorophylls is Part 2 of Volume 2 of *Die Chemie des Pyrrols* (The Chemistry of Pyrroles) published by Hans Fischer and Adolf Stern in 1940: this book highlighted the research of the Fischer school, and of other chlorophyll researchers like Henry Conant, which culminated in the elucidation of the structures of chlorophylls *a* and *b*, and suggested the structure of bacteriochlorophyll *a*. This book was reproduced in the USA in both 1943 and 1968 and is still cited today because of the wealth of information it provided. The next book, *The Chlorophylls*, edited by Leo P. Vernon and Gilbert R. Seely appeared in 1966 by which time many more chlorophylls were known and the emphasis changed from the chemistry to the biochemical and physiological roles of these pigments in photosynthesis. The fourth book, *Chlorophylls*, edited by one of the current authors (H.S.) and published in 1991, described the tremendous broadening of the subject which occurred in the intervening years. It described the rapid progress in the biosynthesis of chlorophylls and its regulation, the development and applications of new analytical and spectroscopic techniques, the progress in structure elucidation of new chlorophylls, their chemistry, and their evolution over geological timescales; also, the isolation of several chlorophyll-protein complexes, the crystallization of two of them, and the emerging molecular details of their native protein environments were described, and the applications of chlorophylls in medicine were summarized.

The now completed fifth book on chlorophylls is aimed at summarizing our current knowledge on plant, bacterial and algal chlorophylls, with a focus on the many advances made over the past 15 years. Many new chlorophylls have been isolated following, mainly, the development of new chromatographic techniques, and their novel structures have been determined. New bacteriochlorophylls have been isolated from phototrophic bacteria and, from marine algae, new chlorophylls have been found with increasingly complex structures: one is esterified to a glycolipid. Probably many more await discovery. Besides the obvious plant chlorophylls, bacteriochlorophylls are increasingly cited in the modern photosynthesis literature. In attempting to understand photosynthesis in molecular detail, not only plants but also photosynthetic bacteria have been exploited by photosynthesis researchers for the obvious advantages of their rapid growth in defined media and controlled environments, and also for the relative simplicity of their photosynthetic apparatus. Most chlorophylls found in living organisms occur in chlorophyll-protein complexes, containing up to 100 chlorophylls; their structures, therefore, hold the key to the safe and efficient harvesting of light but their elucidation also presented a formidable challenge. However, the organization of chlorosomes, the light-harvesting complexes of green bacteria, relies mainly on chlorophyll-chlorophyll interactions, thereby reviving older concepts of, for example, Joseph J. Katz and coworkers.

Since the first high-resolution crystal structure of a membrane protein, the reaction center of photosynthetic purple bacteria, was published in 1984, examples of the crystal structures of most of the relevant classes of chlorophyll-protein complexes have become available. These advances were complemented by methods to selectively modify the pigments and the proteins. By using increasingly sophisticated spectroscopic techniques, such studies served as a base for advancing our understanding, on the molecular level, of the function of these pigment-protein complexes. As the first multi-chromophore complexes of known atomic structure were examined by advanced steady-state and kinetic spectroscopy, the results have challenged experimental and theoretical physicists to critically test existing theories of electron and energy transfer. These studies of the complexes have equally challenged the chemists: since the true understanding of structures always implies the capacity to rebuild functional structures *de novo,* and several groups have successfully pursued the fabrication of synthetic chlorophyll-binding proteins. Eventually, this combined knowledge may help to harvest the sun on a technical scale.

Already, the intimate knowledge of chlorophyll functions has led to diagnostic and therapeutic applications. The possibility now exists to use chlorophyll spectroscopy for remote, non-invasive monitoring of the physiological status of individual plants, of ecosystems or of the whole Earth, or to use chlorophyll derivatives to detect and treat cancer, monitor oxygen tension, or measure partial electron flow from ligands to coordinating metals. An important aspect in modern research is the stress which can be imposed on the plant system by excess or changing light and by low temperatures: chlorophyll proteins, almost always, contain carotenoids which function as protectants against photodynamic (i.e., light- and- oxygen-induced) damage by chlorophylls. These potentially deleterious effects on chlorophylls are associated with their intense absorption and long excited-state lifetimes, which have been selected during the evolution of photosynthesis. Since animals lack such efficient photoprotection, the phototoxicity of chlorophylls has also attracted the medical interest and they have shown particular promise in the selective damage of tumors at the cellular or vascular level.

This book is aimed at a broad audience from advanced students to experienced scientists in basic and applied research, in chemistry, physics, physiology, medicine and geosciences. It has five sections, covering structures, properties and the analysis of chlorophylls (part 1), their metabolism (part 2), their native environment (part 3), their functions (part 4) and their applications (part 5). In each section, an overview is followed by a series of chapters focused on the basic concepts and including recent developments. We are grateful to the 70 authors who contributed to this group effort extending over several years: we hope that the result proves worthy of these efforts.

December 24, 2005

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Bernhard Grimm

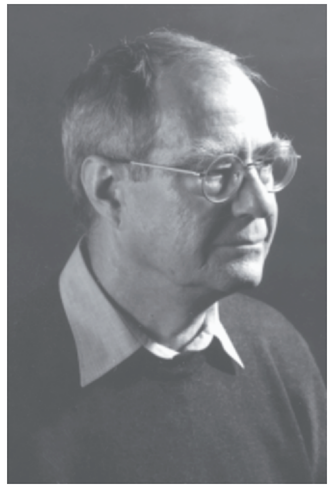
Bernhard Grimm is Professor of Plant Physiology in the Institute of Biology at the Humboldt University in Berlin, Germany. He studied Biology at the University of Hannover from 1978 to 1984 and received his PhD for his thesis on 'Early light inducible proteins' under the supervision of Klaus Kloppstech at the Institute of Botany in 1987. He continued as a postdoctoral fellow at the Carlsberg Laboratory, Copenhagen, Denmark, in the department of Diter von Wettstein and studied 5-aminolevulinate and chlorophyll biosyntheses with Gamini Kannangara and Simon Gough. During his PhD and postdoctoral studies, visits to the laboratories of Itzhak Ohad, Jersualem and Hans Jansonius, Basel, proved most rewarding. Bernhard accepted a position as research group leader at the re-formed Institute of Plant Genetics and Crop Plant Research (IPK), Gatersleben, in the Eastern part of Germany. While he previously used biochemical techniques for analysis of various enzymatic steps in chlorophyll biosynthesis at the Carlsberg Laboratory, he continued to explore the regulation mechanisms of this pathway by introducing transgenic and mutant plants with deregulated expression of many enzymes in the tetrapyrrole pathway. In 1993, he completed his Habilitation in Plant Physiology at the University of Hannover before accepting, in 2001, his present Professorial position at the Humboldt University. The expertise of his group includes methods in molecular genetics and biology, tissue culture work, biochemical analysis of proteins, porphyrin intermediates and photosynthesis. Current research in tetrapyrrole biosynthesis includes studies on the control of Mg porphyrin biosynthesis and on the rate limiting step, 5-aminolevulinate formation, as well as the cellular response to photoreactive porphyrins. His studies were facilitated by the enthusiastic collaboration of students and postdoctoral fellows in his group and with many research groups. The latter include productive studies: on oxidative stress with Heinrich Sandermann (Munich); on X-ray crystallography of glutamate-semialdehyde amino transferase structure with Hans Jansonius (Basel) and of uroporphyrinogen decarboxylase structure with Robert Huber (Munich); on porphyrin mutants of *Chlamydomonas* with Christoph Beck (Freiburg); on geranyl-geraniol reductase with Wolfhart Rüdiger (Munich); on photoprotection with Paul Hoffmann (Berlin); and, on circadian rhythm with Klaus Kloppstech (Hannover), on control of chlorophyll synthesis with Nicolai Shalygo and Elena Yaronskaja (Minsk), on tocopherol biosynthesis with Michel Havaux (Cadarache), on tetrapyrrole synthesis in *Physcomitrella* with Ralf Reski (Freiburg), on plastid derived signaling with Thomas Börner (Berlin), on nucleotide transporters with Ekkehard Neuhaus (Kaiserslautern), and on peroxidizing herbicide resistant mutants with Tatjana Ezhova (Moscow) and Kyoungwhan Back (Gwangju, Korea). Bernhard acknowledges the contributions of his own research team and of all his colleagues: these studies have contributed to the better understanding of the regulation and physiology of tetrapyrrole metabolism.

Robert J. Porra

Robert (Bob) Porra has been 45-years in Canberra (Australia) with Plant Industry-Commonwealth Scientific and Industrial Research Organization (PI-CSIRO) where, following retirement in 1993, he remains an Honorary Research Fellow. Born in 1931 in Adelaide (Australia), he graduated with a BSc (Honors) in Biochemistry at the University of Adelaide in 1958 and PhD at the Australian National University, Canberra, in 1963, for research on heme biosynthesis at PI-CSIRO with John Falk. Post-doctoral research in 1964 with the late June Lascelles (1924–2004) at the University of Oxford (UK) extended studies of Fe^{2+}-ion incorporation into hemes by mammalian-mitochondrial ferrochelatases to the ferrochelatases of photosynthetic bacteria. Later, at PI-CSIRO, ferrochelatases were studied in higher-plant mitochondria, proplastids and chloroplasts. In 1969–1971, with David Griffiths (University of Warwick, UK) and Owen Jones (University of Bristol, UK), research switched to the regulation of 5-aminolevulinate (ALA) and heme biosynthesis. Later at PI-CSIRO, with Horst Grimme from Bremen University (Germany), regulation of ALA and chlorophyll (Chl) biosynthesis was studied in regreening, nitrogen-starved *Chlorella fusca*: the difficulty of pigment extraction from these cells kindled an enduring fascination with the extraction and determination of Chl *a* and Chl *b* in plant and algal cells. Studies of ALA biosynthesis, by the succinate-glycine (Shemin) pathway in *Rhodobacter sphaeroides* and the glutamyl-tRNA-mediated (C_5) pathway in greening maize, started in 1979 with Horst Senger (University of Marburg, Germany) and culminated in 1981 with ^{13}C-NMR experiments at PI-CSIRO, with Peter Wright (Sydney University, Australia) and Otto Klein (Marburg), which unequivocally demonstrated that Chls formed in greening maize were derived entirely from ALA generated by the C_5 pathway. Bob has enjoyed many visits to the University of Munich (Germany), during a 17-year (1989–2006) association with Hugo Scheer. Together, they conducted experiments on greening maize and various photosynthetic bacteria, using ^{18}O-labelling coupled to mass spectrometry and unequivocally established the origin of all oxygen-bearing side chains of Chls *a* and *b*, and of bacteriochlorophyll *a,* by determining which arose from O_2 or from H_2O by oxygenase- or hydratase-mechanisms, respectively. These Munich studies were supported by the Deutcher Akademischer Austauschdienst and Deutsche Forschungsgemeinschaft.

Wolfhart Rüdiger

Wolfhart Rüdiger was Professor of Phytochemistry at the 'Botanisches Institut' of the University of Munich for 32 years. After his retirement in 2001, he became Professor Emeritus at the same institute. Born in 1933 in Stolp (Germany), he graduated in Chemistry (Dipl.-Chem. in 1958, and doctorate in 1961) for research on chlorophyll (Chl) biosynthesis at the University of Würzburg (Germany) with Franz-Gottwalt Fischer. His post-doctoral research was with Hans-Joachim Bielig (Max-Planck-Institut, Heidelberg, and Marine Biological Station, Naples, Italy); he worked on vanadium metabolism in tunicates. In 1963, he moved to the University of Saarbrücken (Germany) and started research on bile pigments in animals and plants; it led to the elucidation of the chromophore structures of phycobiliproteins in 1967 (with Pádraig Ó Carra, Galway, Ireland) and of the photoreceptor phytochrome in 1969 (with David Correll, Washington). In 1971, he was appointed professor in Munich where he continued this research that culminated, in 1983, in the detection of *cis-trans*-isomerization as the primary reaction of the phytochrome chromophore. Other research interests included the plant photoreceptor for phototropism, phototropin; the photoreaction of the latter was established in 2001 as photo-addition of cysteine to the flavin chromophore. However, his major research, throughout the years in Munich, was concerned with Chl biosynthesis. Continuing research included: in 1980, the detection and study of Chl synthase activity which catalyses the phytylation of Chl; in 1994, the demonstration with John Mullet (Texas Agricultural and Mechanical University, College Station, USA) of its role in stabilizing Chl a-binding proteins; and, in 1977, with Carl Bauer (Indiana University, Bloomington, USA) a substrate specificity study of the recombinant enzyme. Later, the substrate specificity of protochlorophyllide oxidoreductase was studied by Wolfhart in cooperation with Margareta Ryberg and Christer Sundqvist (Gotenburg, Sweden). Studies with Christoph Beck (Freiburg, Germany) revealed, in 1997, that the Chl precursor, magnesium-protoporphyrin, is a plastid signal for the regulation of the expression of nuclear genes. In 2000, cooperation with Ayumi Tanaka (Sapporo, Japan) resulted in the first in vitro synthesis of Chl *b*, mediated by recombinant chlorophyllide a oxygenase. In 1994, Wolfhart Rüdiger received an Honorary Doctorate (Dr.h.c.) from the University of Gotenburg (Sweden).



Hugo Scheer

Hugo Scheer is Professor of Plant Biochemistry and Biophysics at the University of Munich, Germany. Born in 1942 in Berlin, Germany, he received his diploma (1968) and doctorate (1970) in chemistry at the Technical University of Braunschweig, Germany, for studies on the stereochemistry and spectroscopy of tetrapyrrole pigments. He became interested in photosynthesis during his post-doctoral research (1973–1975) with Joseph J. Katz and James R. Norris at Argonne National Laboratory, Chicago, USA, while researching the redox and aggregation chemistry of chlorophylls. In 1975, Hugo joined the Botanisches Institut, University of Munich, where he completed his Habilitation in 1978, and was appointed Professor in 1980. Initially, in Munich, he worked on linear tetrapyrroles, and their adaptation to diverse functions by static and dynamic interactions with the apoproteins and other chromophores. He extended this work to chlorophyll and carotenoid proteins, where there are, in addition, pronounced pigment-pigment interactions. In bili- and chlorophyll-protein complexes, absorption energies, excited state lifetimes or redox potentials of chromophores were changed by directed chemical modification, and the effects on energy- and electron transfer studied. Recently, these studies have involved transmetallated bacteriochlorophylls, and their medical applications in photodynamic therapy of tumors. This work, and related studies by other Munich research groups, has led to a DFG-funded Collaborative Research Center (Sonderforschungsbereich 533) 'Light-induced dynamics of biopolymers,' chaired by Hugo Scheer since 1997. During his career, Hugo has visited: Avigdor Scherz (Weizmann Institute, Rehovot, Israel) studying chlorophyll aggregation and chlorophylls in photodynamic therapy; Robert Porra (CSIRO-Division of Plant Industry, Canberra, Australia) working on the reduction of chlorophyll protein complexes by borohydrides; Tomas Gillbro (University of Umea, Sweden) where he studied the bleaching of biliproteins; and, Ken Sauer (University of California, Berkeley, USA) investigating energy transfer in biliproteins. More recently, he was introduced to genetic engineering by Nicole Tandeau de Marsac (Institut Pasteur, Paris, France) and Jean Houmard (École National Superieur, Paris, France). In China, he worked with Kai-Hong Zhao (Huazhong University, Wuhan, China) on enzymatic chromophore ligation in biliproteins and also with Gen-Xi Li (University of Nanjing, China) where Hugo received an Honorary Professorship. Hugo is grateful for the friendship and for all the scientific contributions of his students and colleagues, both in Germany and overseas, and also for the very generous funding of his research by the Alexander von Humboldt Foundation (Bonn), Deutsche Akademischer Austauschdienst (DAAD, Bonn), Deutsche Forschungsgemeinschaft (DFG, Bonn), German Ministry of Science and Technology (Bonn and Berlin), German-Israel Foundation (GIF, Jerusalem), European Community (Brussels), Hans Fischer Gesellschaft (München), INTAS (New York), NEDO (Tokyo) and the VW Foundation (Hannover).

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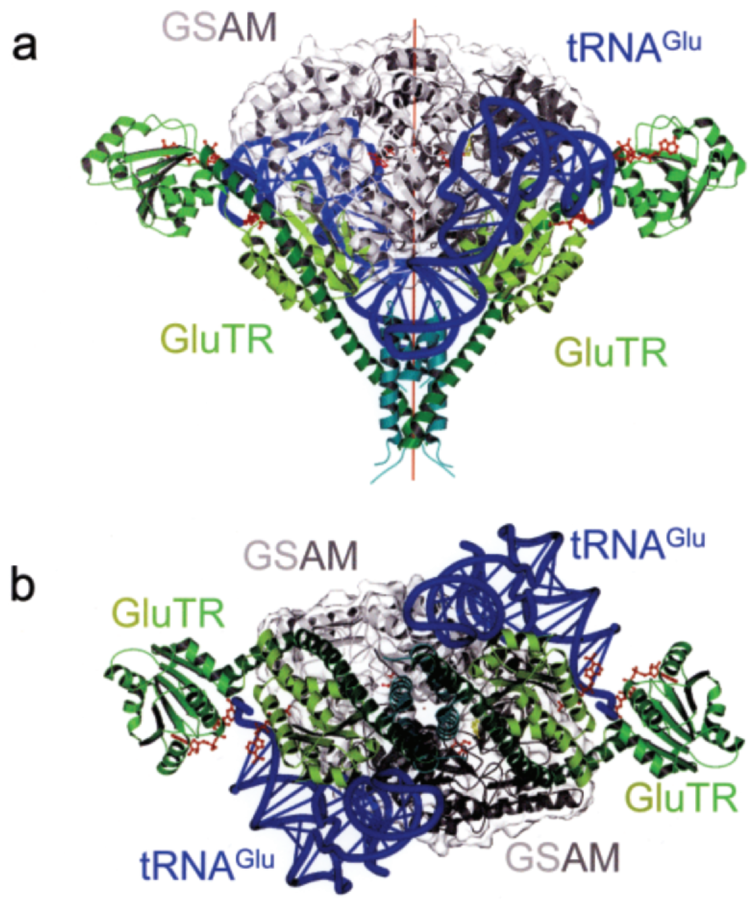
Color Plates



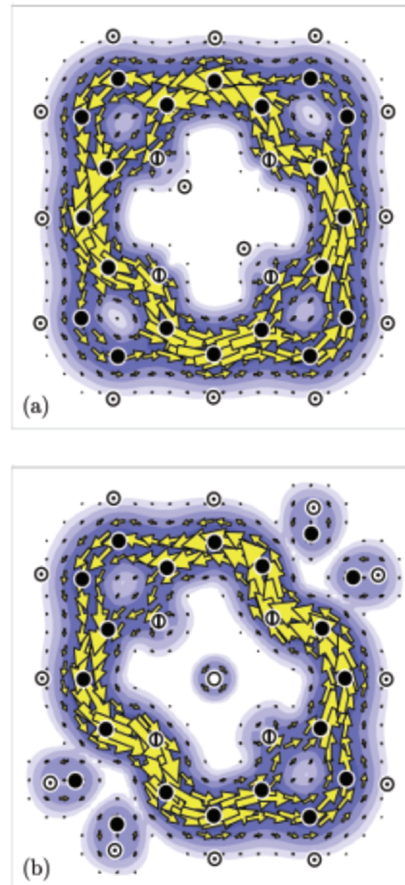


Fig. 1. The proposed ternary complex of glutamyl-tRNA-reductase (GluTR)/glutamyl transfer RNA (tRNA^{Glu})/glutamate-1-semialdehyde-aminomutase (GSAM) viewed (a) perpendicular to the common two-fold axis and (b) along this axis from the dimerization domain of GluTR (opposite direction to Fig. 3a shown in Chapter 12, p. 165). The ribbon depiction of GluTR is rendered in shades of green. tRNA^{Glu} is represented as a backbone model (purple), while GSAM is shown by a transparent surface covering a gray and white ribbon diagram. (Produced as Fig. 1 in Chapter 12, p. 161.) See Chapter 12, p. 168.

Fig. 2. Global ring currents, induced by a perpendicular magnetic field, in the π–electron distributions of (a) free-base porphin and (b) magnesium bacteriochlorin are rationalized, as are the electronic spectra, by a four-orbital model. Plotting conventions are given in the legend to Fig. 5 shown in Chapter 23, p. 343. See Chapter 23, p. 344.

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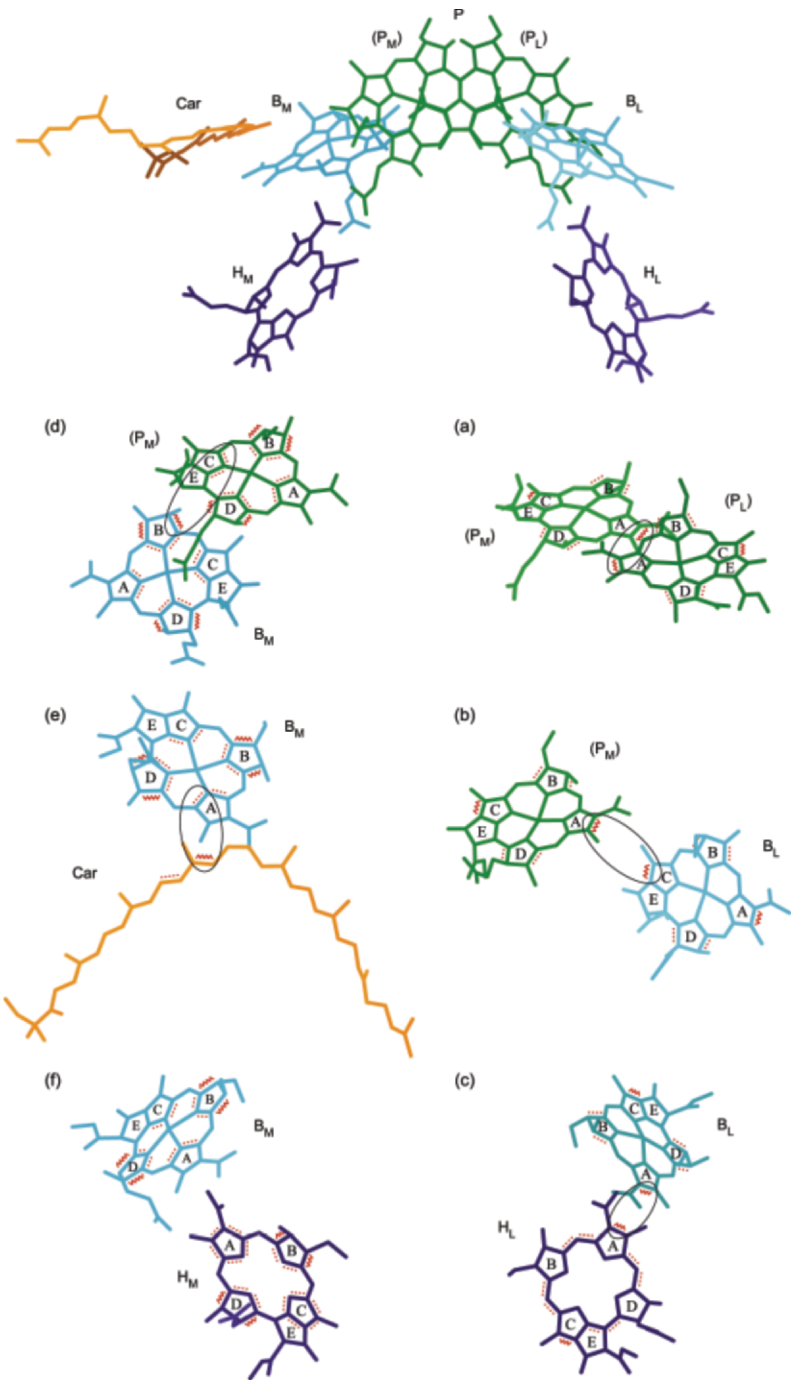

Fig. 1. Spatial arrangement of the special pair bacteriochlophylls (P, tentatively named 'P_L' and 'P_M'), the accessory bacteriochlophylls (B_L and B_M), the bacteriopheophytins (H_L and H_M) and the carotenoid (Car) molecules in the RC from *Rhodobacter sphaeroides* strain AM260W (Richard J. Cogdell, personal communication). The regions where the largest and the second-largest changes in bond order take place (where the highest occupied molecular orbital (HOMO) and/or the lowest unoccupied molecular orbital (LUMO) are/is expected to be most or second-most localized) are indicated by wavy and dotted red lines in each pigment molecule (see Fig. 4, Chapter 22, p. 330); further, overlap of those regions is indicated by a black circle for each pigment pair. See Chapter 22, p. 332.