

# Photosynthetic Protein Complexes

A Structural Approach

*Edited by*

*Petra Fromme*



**WILEY-  
BLACKWELL**

WILEY-VCH Verlag GmbH & Co. KGaA



**Photosynthetic  
Protein Complexes**

*Edited by  
Petra Fromme*

## ***Related Titles***

Collings, A. F., Critchley, C. (eds.)

### **Artificial Photosynthesis From Basic Biology to Industrial Application**

2005

ISBN: 978-3-527-31090-6

Kahl, G., Meksem, K. (eds.)

### **The Handbook of Plant Functional Genomics Concepts and Protocols**

2008

ISBN: 978-3-527-31885-8

Meksem, K., Kahl, G. (eds.)

### **The Handbook of Plant Genome Mapping Genetic and Physical Mapping**

2005

ISBN: 978-3-527-31116-3

Roberts, K. (ed.)

### **Handbook of Plant Science 2 Volume Set**

2007

ISBN: 978-0-470-05723-0

Buchner, J., Kiefhaber, T. (eds.)

### **Protein Folding Handbook**

2005

ISBN: 978-3-527-30784-5

Tamm, L. K. (ed.)

### **Protein-Lipid Interactions From Membrane Domains to Cellular Networks**

2005

ISBN: 978-3-527-31151-4

# Photosynthetic Protein Complexes

A Structural Approach

*Edited by*

*Petra Fromme*



**WILEY-  
BLACKWELL**

WILEY-VCH Verlag GmbH & Co. KGaA

## The Editor

### **Prof. Dr. Petra Fromme**

Department of Chemistry and Biochemistry  
Arizona State University  
PO Box 871604  
Tempe, Arizona 85287-1604  
USA

■ All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

**Library of Congress Card No.:** applied for

### **British Library Cataloguing-in-Publication Data**

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

### **Bibliographic information published by the Deutsche Nationalbibliothek**

Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

**Composition** SNP Best-set Typesetter Ltd., Hong Kong

**Printing** betz-druck GmbH, Darmstadt

**Bookbinding** Litges & Dopf GmbH, Heppenheim

Printed in the Federal Republic of Germany  
Printed on acid-free paper

**ISBN:** 978-3-527-31730-1

## Dedication



*Horst Tobias Witt*  
1922–2007

This book is dedicated to Horst Tobias Witt, whose heart beat for Photosynthesis, until his last breath. He was one of the leading figures of Photosynthesis and he is greatly missed by all of us.

Horst Tobias Witt devoted his entire scientific career to unraveling the secrets of Photosynthesis. Early on in his scientific career, he was fascinated by energy conversion, and by the ability of plants to split water. He once even told me the story of how it had very nearly barred him from getting his Ph.D.! While he was

Photo of Horst Tobias Witt published in *Photosynthesis Research*, 96, 5–8. With kind permission from Springer.

working in the physics department at the Georg-August-University of Göttingen, he secretly grew algae in his drawer to study the process of photosynthesis and water splitting. One weekend, there was a leak in the system—which led to a spill of green algae solution flowing out under the doorway of the lab. This was discovered by his Ph.D. advisor Professor Dr. Robert Pohl. He confronted Horst with two options: either concentrate his efforts on his assigned Ph.D. topic, in solid state physics or change his focus to Photosynthesis—but with the requirement of solving the mechanism of water splitting in his Ph.D. thesis. Witt, however, was very smart—and, knowing that the latter would be a lifetime project, decided to graduate as soon as possible by placing his effort on the given topic. He would then focus the rest of his life on the goal of unraveling the secrets of photosynthesis.

After finishing his Dissertation in the field of solid state physics, he joined the Max Planck Institute of Physical Chemistry in Göttingen, Germany, in 1950. There, he worked with Manfred Eigen and Theodor Förster and started to study the kinetics of the photoreactions in Photosynthesis using flash photometry to identify the major redox cofactors of the electron transport chain by their spectral properties. He moved to the University of Marburg in 1955, where he and his coworkers were key players in the discovery of two separate light reactions—a major breakthrough in the understanding of Photosynthesis—which were discovered at the same time and independently by three groups: Witt's group, the group of Bessel Kok and the group of Lou Dysens.

In 1962, he accepted the position of Director at the Max Volmer Institute, at the Technical University Berlin, where he changed its image and research focus from a physical-chemical one to one centered on the field of Biophysical Chemistry. This research institute subsequently became one of the major research institutions in the field of photosynthesis.

He accepted the position in Berlin one year after the wall was built and the transition from Marburg to Berlin was difficult for his wife Dr. Ingrid Witt and their three children, Roland, Carola and Ingrid. His family had to make many sacrifices over the years to his devotion to Photosynthesis, but this did not hinder Dr. Ingrid Witt in making the major discovery, along-side her husband, of the first crystals of Photosystem I in the late 1980s. Over the years, Witt had many offers to join other universities in Germany and around the globe, including offers to become Director of the Max Planck Institute, but he turned them all down. He did not want to leave the very productive research environment in Berlin, where he stayed and was active in research until his heart stopped beating on the 14th of May 2007.

The discoveries of Horst Tobias Witt and his coworkers are too numerous to list them all in this short dedication, but I want to highlight at least a few examples. It is to Witt and his coworkers that we can attribute identification of the reaction center pigment in Photosystem II as a chlorophyll *a*, with an absorption maximum of 680nm (P680). It was also they who identified a phylloquinone ( $Q_A$ ) as the stable electron acceptor in Photosystem II—and discovered the role of the plastoquinone pool and the electrochromic effect as a consequence of the electrochromic poten-



tial—thereby providing strong experimental evidence for the chemiosmotic hypothesis of ATP synthesis by Mitchell.

HT Witt was a strong personality, and always worked with young, enthusiastic and creative people. Many of them became major key players in the field of Photosynthesis in their own right. Gernot Renger, Ulrich Siggel, Wolfgang Junge, Berd Rumberg, Wolfgang Haehnel, Peter Gräber, Eberhard Schlodder, Klaus Brettel, Matthias Rögner and Jan Dekker, just to name a few, have worked at the Max Volmer Institute and collaborated with HT Witt. They have all made major discoveries and are leading experts in the field.

By the beginning of the 1980's, most of the cofactors of the electron transport chain had been discovered; many of them by through the efforts of HT Witt and his group of collaborators. However, interpretation of the spectroscopic results was difficult without structural information on the spatial arrangement of the proteins and cofactors of the electron transport chain. HT Witt was very excited when the structure of the first membrane protein, the purple bacterial reaction center, was discovered in 1985 by the pioneering work of Hartmut Michel and Johann Deisenhofer, who crystallized the protein complex and received the Nobel award for their work together with Robert Huber. Now, Witt's dream became to crystallize both Photosystem I and II—a task which many people considered impossible, taking the much greater complexity and instability of the Photosystems into account. He first tried to crystallize Photosystem II, as this protein was his “heartblood”. But his wife, Dr. Ingrid Witt, who worked with him on the crystallization project, convinced him to change gears and try isolating and crystallizing Photosystem I. They acquired the first crystals of Photosystem I in 1988. When I joined the group in 1990, I had the great pleasure of working with Ingrid Witt for three month, before she finally retired and I continued her work. The projects on structure determination of Photosystem I and II were a collaboration of our group at the Max Volmer Institute at the TU-Berlin and the group of Norbert Krauß and Wolfram Saenger at the FU-Berlin. In 1993, the first crystal structure of Photosystem I was determined at a resolution of 6 Å—and the atomic structure was finally solved at 2.5 Å in 2001. This is still the largest membrane protein that has ever been crystallized, consisting of 36 individual proteins and 381 cofactors.

At the end of the 1990, Athina Zouni joined our group as post-Doctoral fellow, to work with us on the crystallization of Photosystem II. I still remember that we packed a print-out of the diffraction pattern of the first PSII crystals in a gift box, which we gave HT Witt as a gift for his birthday on March 1, 1998. He was very excited. Taking all the experience with Photosystem I crystallization into account, it took only three years to improve the crystals and solve the first structure of water oxidizing complex of Photosystem II at a resolution of 3.8 Å, in 2001. For the first time, the location and shape of the water-oxidizing Mn cluster was discovered—and Witt's dream of so many years finally came true at the age of 79. He was now able to see, for the first time, the site of water splitting. All further structures that have been published at improved resolution are based on the same crystals from the thermophilic cyanobacterium, *TS. elongatus*, that had been discovered by HT Witt and his coworkers.

HT Witt was an elected member of the Berlin-Brandenburgische Akademie der Wissenschaften, Deutsche Akademie der Naturforscher Leopoldina Halle, Akademie der Wissenschaften zu Göttingen and Österreichischen Akademie der Wissenschaften. He has received numerous scientific awards and honors for his work including the Otto-Warburg Medal, the Peter-Mitchell Medal, the Feldberg-Prize and the Charles-F. Ketterling Prize. In 2001 he became honorary doctorate (Dr. h.c.) of the University of Göttingen and at the 4th of December 2006 he received one of the most prestigious honors of Germany: the “Bundesverdienstkreuz 1. Klasse” (Federal Cross of Merit 1st class).

HT Witt will be always remembered as a legend, and his life shows that keeping dreams and curiosity alive will allow scientists to finally unravel the secrets of one the great mysteries of Nature: Photosynthesis.

We will all keep HT Witt in our best memories. He is greatly missed by his colleagues, friends and his family.

## Contents

	<b>Preface</b>	XVII
	<b>List of Contributors</b>	XIX
	<b>Abbreviations</b>	XXV
<b>1</b>	<b>Overview of Photosynthesis</b>	<b>1</b>
	<i>Petra Fromme and Ingo Grotjohann</i>	
1.1	Introduction to Photosynthesis: The Main Energy Source for Our Planet	1
1.2	The Protein Complexes of Oxygenic Photosynthesis	3
1.2.1	Photosystem II	3
1.2.2	The Cytochrome <i>b<sub>6</sub>f</i> Complex	4
1.2.3	The Soluble Electron Transfer Proteins: Plastocyanin and Cytochrome <i>c<sub>6</sub></i>	7
1.2.4	Photosystem I	7
1.2.5	Ferredoxin, Flavodoxin, and FNR	8
1.3	From Water to NADPH: Overview of the Electron Transfer Chain in Oxygenic Photosynthesis	9
1.4	Coupling of Electrochemical Potential to ATP Synthesis	11
1.5	Anoxygenic Photosynthesis	13
1.6	The Antenna Systems	14
1.6.1	The Core Antenna Systems of the Photosystems	14
1.6.2	LHC-I and LHC-II, the Antenna Systems of Higher Plants	15
1.6.3	The Phycobilisomes	16
1.6.4	Chlorosomes	18
1.6.5	LH1 and LH2	18
<b>2</b>	<b>Structure and Function of Cyanobacterial Photosystem I</b>	<b>23</b>
	<i>Norbert Krauß</i>	
2.1	Introduction	23
2.2	Structural Overview	25
2.3	The Protein Subunits	27
2.3.1	The Core Subunits PsaA and PsaB	27

2.3.2	The Stromal Ridge: PsaC, PsaD and PsaE	30
2.3.2.1	Subunit PsaC	31
2.3.2.2	Subunit PsaD	32
2.3.2.3	Subunit PsaE	32
2.3.3	The Small Membrane-Integral Subunits	33
2.3.3.1	Subunits PsaL, PsaI, PsaM	34
2.3.3.2	Subunits PsaF, PsaJ, PsaX	35
2.4	The Electron Transfer Chain	37
2.4.1	The First Pair of Chlorophylls	39
2.4.2	The Second and Third Pairs of Chlorophylls	41
2.4.3	The Pair of Phylloquinones	43
2.4.4	The First [4Fe4S] Cluster, F <sub>X</sub>	46
2.4.5	The Terminal [4Fe4S] Clusters, F <sub>A</sub> and F <sub>B</sub>	46
2.5	The Core Antenna System	47
2.5.1	The Antenna Chlorophylls	48
2.5.2	The Carotenoids	51
<b>3</b>	<b>A Glimpse into the Atomic Structure of Plant Photosystem I</b>	<b>65</b>
	<i>Alexey Amunts, Omri Drory, and Nathan Nelson</i>	
3.1	Introduction	65
3.2	The General Architecture of Plant PSI	66
3.3	The Core Complex	68
3.4	Light-Harvesting Complex of Higher Plants	70
3.5	Interaction with Electron Donors and Acceptors	71
3.6	The Modality of PSI	75
<b>4</b>	<b>Structure and Function of Photosystem II</b>	<b>83</b>
	<i>Jian-Ren Shen, Takahiro Henmi, and Nobuo Kamiya</i>	
4.1	Introduction	83
4.2	The Structure of Protein Subunits	85
4.2.1	Overall Structure	85
4.2.2	Structure of the D1 and D2 Reaction Center Subunits	85
4.2.3	Structure of the CP47 and CP43 Subunits	87
4.2.4	Structure of the LMM Subunits	89
4.2.5	Structure of the Extrinsic Proteins	90
4.3	The Electron Transfer Chain (ETC)	91
4.3.1	Overview	91
4.3.2	The Photosystem II Reaction Center Chlorophylls (P680)	93
4.3.3	The Quinone Acceptors and Non-Haem Iron	94
4.3.4	The Mn <sub>4</sub> Ca Cluster	95
4.3.5	Carotenoids and the Secondary Electron Transfer Pathway	97
4.3.6	Location and Possible Functions of Lipids	98
4.4	The Energy Transfer Pathways	99
4.4.1	The Location of Chlorophylls and the Energy Transfer Pathways within CP47 and CP43	99

4.4.2	The Energy Transfer from CP47 and CP43 to PSII-RC	101
4.5	Concluding Remarks and Perspectives	101
<b>5</b>	<b>Current Models and Mechanism of Water Splitting</b>	<b>107</b>
	<i>Robert M. McCarrick and R. David Britt</i>	
5.1	Introduction	107
5.1.1	Photosystem II	107
5.2.1	The Oxygen-Evolving Complex	108
5.2	The Structure of the OEC	109
5.2.1	Early Spectroscopic Results from Chloroplast Membranes	109
5.2.2	Spectroscopic Studies of Isolated PSII	111
5.2.3	The Dimer of Dimers Structure	112
5.2.4	The Monomer Trimer or “Dangler” Structure	114
5.2.5	X-Ray Diffraction and XAS of PSII Crystals	115
5.2.6	Quantum Mechanical Structural Models	117
5.3	Mechanisms of Water Oxidation	118
5.3.1	Energetic Considerations	118
5.3.2	S State Advancement	119
5.3.3	Water Binding and Proton Release	121
5.3.4	Hydrogen Atom Abstraction Model (Babcock Model)	123
5.3.5	Brudvig/Pecoraro Mechanisms for Water Oxidation	125
5.3.6	Messinger Mechanism	127
5.3.7	Agreement between Proposed Mechanisms and Spectroscopic Data	129
<b>6</b>	<b>Supercomplexes of Photosystems I and II with External Antenna Complexes in Cyanobacteria and Plants</b>	<b>137</b>
	<i>Jan P. Dekker and Egbert J. Boekema</i>	
6.1	Introduction	137
6.2	Supercomplexes with Proteins from the LHC Superfamily	138
6.2.1	PSII-LHC-II Supercomplexes	139
6.2.2	PSI-LHC-I Supercomplexes	142
6.2.3	PSI-LHC-I-LHC-II Supercomplexes	145
6.3	Supercomplexes with Proteins from the Core Complex Family	147
6.3.1	PSI-IsiA and PSI-Pcb Supercomplexes	148
6.3.2	PSII-Pcb Supercomplexes	150
<b>7</b>	<b>Cytochrome <math>b_6f</math> Complex, Core Structure, Spectroscopy, and Function of Heme <math>c_n</math> and <math>n</math>-Side Electron and Proton Transfer Reactions</b>	<b>155</b>
	<i>William A. Cramer, Danas Baniulis, Eiki Yamashita, Huamin Zhang, Anna I. Zatsman, and Mike P. Hendrich</i>	
7.1	Structure of the Cytochrome $b_6f$ Complex; Comparison with the Cytochrome $bc_1$ Complex	155

- 7.1.1 Principle Features of the Structure 155
- 7.1.2 Difference in Prosthetic Group Content of  $bc_1$  and  $b_6f$  Complexes 157
- 7.1.3 Symmetry and Asymmetry 158
- 7.1.4 Questions about Structure–Function at the Outset 159
- 7.1.5 Evolution:  $cyt\ b_6f$  vs  $bc_1$  160
- 7.2 Electron and Proton Transfer Pathways 161
- 7.2.1 The Q-Cycle and Modifications 161
- 7.2.2 Question of Obligatory Application of the Q-Cycle Model to the  $b_6f$  Complex 162
- 7.2.3 Production of Superoxide and Other ROS 163
- 7.3 Stromal  $n$ -Side Electron Transfer: Properties and Function of Heme  $c_n$  164
- 7.3.1 Application of Novel EPR Analysis 164
- 7.3.2 EPR Spectra of  $b_6f$  Complex 164
- 7.3.3 Low-Field Spectra 164
- 7.3.4 Novel Properties of Heme  $c_n$  167
- 7.3.5 Plastoquinone as a Ligand of Heme  $c_n$  168
- 7.3.6 Functions and Unwanted Functions of Heme  $c_n$  169
- 7.4 Stromal  $n$ -Side Proton Uptake Pathway 169

## 8 Plastocyanin and Cytochrome $c_6$ : the Soluble Electron Carriers between the Cytochrome $b_6f$ Complex and Photosystem I 181

*Antonio Díaz-Quintana, Manuel Hervás, José A. Navarro, and Miguel A. De la Rosa*

- 8.1 Introduction 181
- 8.2 An Evolutionary Proposal 182
- 8.3 General Features of Pc and Cyt  $c_6$  Structures 184
- 8.4 Reaction Mechanisms 187
- 8.4.1 Kinetic Models 187
- 8.4.2 Nature of the Interaction Forces 188
- 8.5 Evolution of Pc and Cyt  $c_6$  191
- 8.5.1 Evolution of the Reaction Mechanisms 191
- 8.5.2 Increase in Specificity and Efficiency 191
- 8.5.3 Role of the Soluble Proteins in Driving the Interactions 192
- 8.6 Structural Analysis of the Transient Complexes 192
- 8.7 Concluding Remarks 196

## 9 The Structure of the $H^+$ -ATP Synthase from Chloroplasts 201

*Bettina Böttcher and Peter Gräber*

- 9.1 Introduction 201
- 9.2 The Structure of  $CF_1$  204
- 9.3 The Structure of  $CF_0$  206
- 9.4 The Structure of  $CF_0F_1$  208
- 9.5 Structure and Function of  $CF_0F_1$  209

<b>10</b>	<b>Structure of the Light-Harvesting Complex II</b>	<b>217</b>
	<i>Zhenfeng Liu and Wenrui Chang</i>	
10.1	Introduction	217
10.2	Crystal Packing: A Novel Type of Membrane Protein Crystal	218
10.3	LHC-II Trimer and Monomer	220
10.3.1	LHC-II Trimer	220
10.3.2	LHC-II Monomer	223
10.4	Chlorophylls: Identity, Binding and Interactions	225
10.4.1	Identification of Chlorophylls	225
10.4.2	Chlorophyll Binding Sites	225
10.4.3	Interactions between Chlorophylls	227
10.5	Carotenoids	229
10.6	Mechanism of Excitation Energy Transfer and the Role of <i>LHC-II</i> in Non-photochemical Quenching	231
10.6.1	Mechanism of Excitation Energy Transfer	231
10.6.2	The Role of <i>LHC-II</i> in Non-photochemical Quenching	234
10.7	Summary	238
<b>11</b>	<b>Structure of the Phycobilisome Antennae in Cyanobacteria and Red Algae</b>	<b>243</b>
	<i>Noam Adir</i>	
11.1	Introduction	243
11.1.1	Photosynthetic Antennas	243
11.1.2	Photosynthetic Organisms that Utilize the Phycobilisome	244
11.2	Basic Structural Characteristics of the Phycobilisome Component Proteins	244
11.2.1	Isolation of Phycobilisomes and Phycobiliproteins	247
11.2.2	Crystallization of Phycobilisomes	248
11.2.3	X-Ray Structures of PBP	248
11.2.3.1	Allophycocyanin	249
11.2.3.2	Phycocyanin	251
11.2.3.3	Phycoerythrocyanin	253
11.2.3.4	Phycoerythrin	254
11.2.3.5	Cryptophyte Phycoerythrin	255
11.2.3.6	Linker Proteins	255
11.2.4	Phycobiliprotein Post-translational Modifications	257
11.2.4.1	Bilin Lyases	257
11.2.4.2	Methylation of $\beta$ Asn <sup>72</sup>	258
11.2.4.3	Phosphorylation and Glycosylation of Linker Proteins	258
11.3	Self Assembly and Disassembly of the Phycobilisome	259
11.3.1	Phycobilisome Assembly	259
11.3.2	Phycobilisome Disassembly	262
11.4	Phycobilisome Function	263
11.4.1	Phycobilisome Binding to PSII and PSI	263

11.4.2	Energy Transfer within the Phycobilisome	265
11.5	Final Remarks	266
<b>12</b>	<b>Reaction Centers from Purple Bacteria</b>	<b>275</b>
	<i>James P. Allen and JoAnn C. Williams</i>	
12.1	Introduction	275
12.2	The Overall Structure	276
12.3	Bacteriochlorophyll Dimer	278
12.4	Bacteriochlorophyll and Bacteriopheophytin Monomers	281
12.5	Primary Quinone, Secondary Quinone, and Non-heme Iron	282
12.6	Carotenoid	283
12.7	Electron Transfer	283
12.8	Evolution from Anoxygenic to Oxygenic Photosynthesis	285
12.9	Biotechnological Applications	286
<b>13</b>	<b>Anoxygenic Type-I Photosystems and Evolution of Photosynthetic Reaction Centers</b>	<b>295</b>
	<i>Martin F. Hohmann-Marriott and Robert E. Blankenship</i>	
13.1	Introduction	295
13.2	The Photosynthetic Way of Life	296
13.3	The Photosystem of Heliobacteria	299
13.3.1	Reaction Center Core	300
13.3.2	External Subunit	301
13.3.3	Pigments	301
13.3.4	Electron Donor	302
13.3.5	Charge Separation	302
13.3.6	Charge Stabilization	302
13.4	The Photosystem of Green Sulfur Bacteria	302
13.4.1	Photosystem Center Core	303
13.4.2	External Subunits	303
13.4.3	Pigments	304
13.4.4	Charge Separation	304
13.4.5	Charge Stabilization	304
13.5	Photosystem I of Cyanobacteria and Plastids	305
13.5.1	Reaction Center Core	305
13.5.2	External Subunits	306
13.5.3	Light-Harvesting Systems	307
13.5.4	Interfacing with the Light-Harvesting System	308
13.5.5	Pigments	309
13.5.6	Electron Donors	310
13.5.7	Electron Acceptors	310
13.5.8	Charge Stabilization	311
13.6	The Ur-Reaction Center	312
13.7	Conclusions	317



<b>14</b>	<b>The Structure of Purple Bacterial Antenna Complexes</b>	<b>325</b>
	<i>Richard J. Cogdell, Alastair T. Gardiner, Mads Gabrielsen, June Southall, Aleksander W. Roszak, Neil W. Isaacs, Ritsuko Fujii, and Hideki Hashimoto</i>	
14.1	Introduction	325
14.2	Knowledge of the Structural Arrangements before the Determination of the Crystal Structure	326
14.3	The X-Ray Crystal Structure of the LH2 Complex from <i>Rps. acidophila</i> strain 10050	327
14.4	The Structure of RC–LH1 Core Complexes	332
14.5	Energy Transfer	335
<b>15</b>	<b>Ferredoxin and Flavodoxin Mediated Electron Transfer in Photosystem I</b>	<b>341</b>
	<i>Raimund Fromme</i>	
15.1	Introduction	341
15.2	The Structure of Ferredoxin in Plants, Red Algae and Cyanobacteria	342
15.3	Ferredoxin in Different Organisms	342
15.4	Electron Transfer between Ferredoxin and Ferredoxin NADP <sup>+</sup> Reductase	344
15.5	Flavodoxin	345
15.6	Docking to Photosystem I	345
15.6.1	Subunit PsaC	346
15.6.2	Subunit PsaD	346
15.6.3	Subunit PsaE	347
	<b>Index</b>	<b>353</b>



## Preface

Photosynthesis is the most important biological processes on earth. It converts light energy from the sun into chemical energy, and provides a food source for all higher life on earth. All fossil fuels have been produced by the photosynthetic process. Oxygenic Photosynthesis changed the atmosphere from anoxic to oxygen-rich 2.5 billion years ago, by using water as the electron donor for the photosynthetic process. All of the oxygen in the atmosphere, which is essential for all respiratory processes, is produced by this route. The appearance and rise of abundant atmospheric oxygen has also resulted in huge changes in the geology of our planet and allowed formation of the ozone layer, which protects life on the surface of the earth from highly damaging UV radiation.

Interest in Photosynthesis goes far beyond the academic, since understanding of the structures and molecular details of the processes has huge implications for the future of mankind. Discovery of the molecular mechanisms of Photosynthesis holds the clue for solving the energy crisis, forming the basis for development of new routes towards biological energy sources.

Nature has been developing and optimizing Photosynthesis for the past 2.5 billion years. Light is captured by huge antenna systems and transferred to the photosynthetic reaction centers, which are large, nanoscale, biosolar energy converters consisting of more than 100 000 atoms each. The electrons for these events are extracted from water, which is split into oxygen and protons. Nature uses a fundamental electrical concept for the primary energy conversion process. First, the membrane is “charged”, like a battery, during the event of electron and proton transfer. Then, the energy is stored in the form of chemical bonds, in the high-energy molecule ATP, as well as in the form of reduced hydrogen, as NADPH. These molecules are later used in the “dark” reactions of Photosynthesis, to build up carbohydrates and all other biomolecules in the biosphere. The primary processes in Photosynthesis drive all higher life on our planet Earth. Once we are able to understand how nature has accomplished this remarkable task, we will be better-equipped to secure the energy needs of humans through the conversion and utilization of solar energy.

The major structures of the photosynthetic complexes have only been revealed relatively recently. This is the first book to describe the structure and function of all major photosynthetic complexes on the basis of high-resolution structures. This

book is also unique in that all 15 chapters are written by experts in the field, who are key players in the discovery of the structure and function of the protein complexes of Photosynthesis. The structures and functions of all of the major protein complexes that catalyze the primary events in Photosynthesis, from light capturing to electron transfer and ATP and NADPH production, are described in this book.

This book is an essential tool for comprehensive understanding of Photosynthesis, and is aimed at a very broad audience. Readers from high-school level to engineers working on bioenergy conversion, as well as experts in Photosynthesis, will enjoy reading it, with the beautiful and fascinating structures of the protein complexes shown in full color, and all color figures directly included in the text. Another very important feature is that it is designed as a teaching tool. It is accompanied by a website, at [www.wiley-vch.de/publish/en/books/ISBN978-3-527-31730-1](http://www.wiley-vch.de/publish/en/books/ISBN978-3-527-31730-1), where all figures from the book are freely accessible and can be downloaded without any password protection. The figures can be directly used for lectures and teaching in the classroom. The website is constantly updated with new animations and figures. In addition, abstracts of all the chapters are freely accessible, and individual chapters can be downloaded, using a pay-per-view option, from the publisher's website at [www.interscience.wiley.com](http://www.interscience.wiley.com).

I want to thank all of the authors who have contributed to this book. They are very busy researchers from all over the world, on the verge of making new discoveries every day, and I am very happy that they so kindly agreed to devote so much of their busy time to write the chapters. These authors have brought to life a dream of publishing this unique and exciting book about one of the major discoveries in science – the unraveling of the secrets of Photosynthesis, which were invented by Nature 2.5 Billion years ago.

I am sure that you, as a reader, will love this book and find it a powerful tool for research and teaching.

Read it and enjoy!!

Tempe, July 2008

*Petra Fromme*

## List of Contributors

**Noam Adir**

Technion – Israel Institute of  
Technology  
Schulich Faculty of Chemistry  
Technion City  
Haifa 32000  
Israel

**James P. Allen**

Arizona State University  
Department of Chemistry and  
Biochemistry  
PO Box 871604  
Tempe, AZ 85287-1604  
USA

**Alexey Amunts**

Tel Aviv University  
Department Biochemistry  
Sherman Building  
Tel Aviv 69978  
Israel

**Danas Baniulis**

Purdue University  
Department of Biological  
Sciences  
915 West State St.  
West Lafayette, IN 47907  
USA

**Robert E. Blankenship**

Washington University  
Departments of Chemistry  
Laboratory Sciences 401B  
St. Louis, MO 63130-4899  
USA

**Egbert J. Boekema**

University of Groningen  
Groningen Biomolecular Sciences and  
Biotechnology Institute  
Department of Biophysical Chemistry  
Nijenborgh 4  
9747 A.G. Groningen  
The Netherlands

**Bettina Böttcher**

European Molecular Biology  
Laboratory  
Meyerhofstraße 1  
69126 Heidelberg  
Germany

**R. David Britt**

University of California  
Chemistry Department  
One Shields Avenue  
Davis, CA 95616  
USA

**Wenrui Chang**

Chinese Academy of Sciences  
National Laboratory of  
Biomacromolecules  
Institute of Biophysics  
15 Datun Road  
Chaoyang District  
Beijing 100101  
People's Republic of China

**Richard J. Cogdell**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and  
Molecular Biology  
Glasgow G12 8QQ  
Scotland  
UK

**William A. Cramer**

Purdue University  
Department of Biological  
Sciences  
915 West State St.  
West Lafayette, IN 47907  
USA

**Miguel A. De la Rosa**

Universidad de Sevilla & CSIC  
Instituto de Bioquímica Vegetal y  
Fotosíntesis  
Américo Vespucio 49  
41092 Sevilla  
Spain

**Jan P. Dekker**

V.U. University Amsterdam  
Faculty of Sciences  
Division of Physics and  
Astronomy  
De Boelelaan 1081  
1081 H.V. Amsterdam  
The Netherlands

**Antonio Díaz-Quintana**

Universidad de Sevilla & CSIC  
Instituto de Bioquímica Vegetal y  
Fotosíntesis  
Américo Vespucio 49  
41092 Sevilla  
Spain

**Omri Drory**

Tel Aviv University  
Department of Biochemistry  
Sherman Building  
Tel Aviv 69978  
Israel

**Petra Fromme**

Arizona State University  
Department of Chemistry and  
Biochemistry  
Main Campus Room PSC-307  
PO Box 871604  
Tempe, AZ 85287-1604  
USA

**Raimund Fromme**

Arizona State University  
Department of Chemistry and  
Biochemistry  
PO Box 871604  
Tempe, AZ 85287-1604  
USA

**Ritsuko Fujii**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and Molecu-  
lar Biology  
Glasgow G12 8QQ  
Scotland  
UK

**Mads Gabrielsen**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and  
Molecular Biology  
Glasgow G12 8QQ  
Scotland  
UK

**Alastair T. Gardiner**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and  
Molecular Biology  
Glasgow G12 8QQ  
Scotland  
UK

**Peter Gräber**

Albert Ludwigs Universität  
Freiburg  
Institut für Physikalische Chemie  
Albertstraße 23a  
79104 Freiburg  
Germany

**Hideki Hashimoto**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and  
Molecular Biology  
Glasgow G12 8QQ  
Scotland  
UK

**Michael P. Hendrich**

Carnegie Mellon University  
Department of Chemistry  
Pittsburgh, PA 15213  
USA

**Takahiro Henmi**

Osaka City University  
The Graduate School of Science  
Sugimoto 3-3-138, Sumiyoshi  
Osaka 558-8585  
Japan

**Manuel Hervás**

Universidad de Sevilla & CSIC  
Instituto de Bioquímica Vegetal y  
Fotosíntesis  
Américo Vespucio 49  
41092 Sevilla  
Spain

**Martin F. Hohmann-Marriott**

National Institutes of Health  
National Institute of Biomedical  
Imaging and Bioengineering  
9000 Rockville Pike  
Bethesda, MD 20892  
USA

**Ingo Grotjohann**

Arizona State University  
Department of Chemistry and  
Biochemistry  
PO Box 871604  
Tempe, AZ 85287-1604  
USA

**Neil W. Isaacs**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and Molecu-  
lar Biology  
Glasgow G12 8QQ  
Scotland  
UK

**Nobuo Kamiya**

Osaka City University  
Graduate School of Science  
Sugimoto 3-3-138  
Sumiyoshi  
Osaka 558-8585  
Japan

**Norbert Krauß**

Queen Mary University of  
London  
School of Biological and  
Chemical Sciences  
Mile End Campus  
London E1 4NS  
UK

**Zhenfeng Liu**

California Institute of Technology  
Howard Hughes Medical  
Institute  
Pasadena, CA 91125  
USA

**Robert M. McCarrick**

University of California  
Chemistry Department  
One Shields Avenue  
Davis, CA 95616  
USA

**José A. Navarro**

Universidad de Sevilla & CSIC  
Instituto de Bioquímica Vegetal y  
Fotosíntesis  
Américo Vespucio 49  
41092 Sevilla  
Spain

**Nathan Nelson**

Tel Aviv University  
Department of Biochemistry  
Sherman Building  
Tel Aviv 69978  
Israel

**Aleksander W. Roszak**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and Molecu-  
lar Biology  
Glasgow G12 8QQ  
Scotland  
UK

**Jian-Ren Shen**

Okayama University  
The Graduate School of Natural  
Science and Technology  
Division of Bio-sciences  
Naka-Tsushima 3-1-1  
Okayama 700-8530  
Japan

**June Southall**

University of Glasgow  
Institute of Biomedical and Life  
Sciences  
Division of Biochemistry and Molecu-  
lar Biology  
Glasgow G12 8QQ  
Scotland  
UK

**JoAnn C. Williams**

Arizona State University  
Department of Chemistry and  
Biochemistry  
Tempe, AZ 85287-1604  
USA

**Eiki Yamashita**

Osaka University  
Institute of Protein Research  
Toyonaka  
Osaka  
560-0043  
Japan



**Anna I. Zatsman**

Carnegie Mellon University  
Department of Chemistry  
Pittsburgh, PA 15213  
USA

**Huamin Zhang**

SSCI-Abtuit Inc.  
West Lafayette, IN 47907  
USA



## Abbreviations

$\Delta\tilde{\mu}_H^+$	trans-membrane proton electrochemical potential gradient
accChl	accessory chlorophyll
AFM	atomic force microscopy
Ant	antheraxanthin
APC	allophycocyanin
BChl	bacteriochlorophyll
BIF	banded iron formation
C	carbon
Car	carotenoid
CCA	complimentary chromatic adaptation
Chl	chlorophyll
Chl <sub>D1</sub> and Chl <sub>D2</sub>	two accessory chlorophyll <i>a</i> molecules bound to D1 and D2 subunits, respectively
ChlZ <sub>D1</sub> and ChlZ <sub>D2</sub>	two peripheral chlorophyll <i>a</i> molecules bound to D1 and D2 subunits, respectively
CL	cardiolipid
CP	chlorophyll binding protein
CP43	chlorophyll <i>a</i> -containing protein with apparent molecular mass of 43-kDa
CP47	chlorophyll <i>a</i> -containing protein with apparent molecular mass of 47-kDa
cyt	cytochrome
D1	reaction center subunits of PSII
D2	reaction center subunits of PSII
DBMIB	2,5-dibromo, 3-methyl, 6-isopropyl-benzoquinone
DG DG	digalactosyl diacylglycerol
ELIP	early light-induced protein
EM	electron microscopy
$E_m$	midpoint oxidation–reduction potential
EPR	electron paramagnetic resonance
ETC	electron transport (or transfer) chain
EXAFS	extended x-ray absorption fine structure
FAD	flavin adenine dinucleotide

FAP	filamentous anoxygenic phototroph
Fd	ferredoxin
FeS-type	RCs that have FeS as final electron acceptors, also known as Type I RC
FMN	flavin mononucleotide
FMO	Fenna-Matthews-Olson protein
FNR	ferredoxin-NADP <sup>+</sup> reductase
GSB	green sulfur bacteria
H-, L-, M-	the 3 major integral polypeptide subunits of the <i>Rb. sphaeroides</i> purple bacterial reaction center
IsiA	iron-stress-induced protein A
$k_2$	second-order rate constant
$K_A$	equilibrium constant for complex association
$k_{et}$	electron transfer rate constant
$K_R$	equilibrium constant for complex reorganization
LHC-I	light-harvesting complex I in plants and algae
LHC-II	light-harvesting complex II in plants and algae
LH1	light-harvesting complex 1 in purple bacteria
LH2	light-harvesting complex 2 in purple bacteria
LMM	low-molecular mass
LPC	lysophosphatidylcholine
LP	linker protein
MGDG	monogalactosyldiacylglycerol
NADP <sup>+</sup>	nicotinamide adenine dinucleotide phosphate
NASA	National Aeronautics and Space Administration
Neo	neoxanthin
NG	nonyl- $\alpha$ -D-glucoside
NMA	N-methyl asparagine
NMR	nuclear magnetic resonance
NPQ	non-photochemical quenching
NQNO	2-n-nonyl-4-hydroxyquinoline N-oxide
NRD	non-radiative dissipation
OEC	oxygen-evolving complex
PBP	phycobiliprotein
PBS	phycobilisome
Pc	plastocyanin
PC	phycocyanin
PCB	phycocyanobilin
P <sub>D1</sub> and P <sub>D2</sub>	PS II reaction center chlorophylls bound to D1 and D2 subunits, respectively
PDB	Protein Data Bank
PE	phycoerythrin
PEB	phycoerythrobilin
PEC	phycoerythrocyanin
PG	phosphatidyldiacylglycerol

pheo	pheophytin
PQ	plastoquinone
PQH <sub>2</sub>	plastoquinol
pseudo-C2	pseudo-twofold
PS	photosystem (consisting of the RC fused or associated with the core antenna domain)
PSI	photosystem I
PSII	photosystem II
PUB	phycoeuobilin
PVB	phycoviolobilin
Q <sub>A</sub>	tightly bound quinone in photosystem II and the purple bacterial reaction center
Q <sub>B</sub>	mobile quinone in photosystem II and the purple bacterial reaction center
qE	high-energy quenching
qI	photoinhibition
QM/MM	quantum mechanical/molecular mechanical modeling
Q-type	RCs that have a mobile quinone as final electron acceptor, also known as Type II RC
RC	reaction center
rf	radio frequency
r.m.s.d.	root mean squared deviation
ROS	reactive oxygen species
SH3	Src homology 3
SQ	semiquinone
SQDG	sulfoquinovosyldiacylglycerol
suIV	subunit IV
TDS	tridecyl-stigmatellin
TMH	transmembrane helix
Tyr <sub>Z</sub>	redox-active tyrosines, D1-Tyr161 in photosystem II
Tyr <sub>D</sub>	redox-active tyrosines, D2-Tyr160 in photosystem II
UQ	ubiquinone
UQH <sub>2</sub>	ubiquinol
UV	ultraviolet
VDE	violaxanthin de-epoxidase
Xanc	xanthophyll-cycle
XANES	x-ray absorption near edge structure
XAS	x-ray absorption spectroscopy
Zea	zeaxanthin

