Photosynthetic Protein Complexes

A Structural Approach

Edited by
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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>.

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 wanted 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 potential – 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 "Bundesverdienst-kreuz 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

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, 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.

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*

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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_{D1} and Chl_{D2}	two accessory chlorophyll *a* molecules bound to D1 and D2 subunits, respectively
$ChlZ_{D1}$ and $ChlZ_{D2}$	two peripheral chlorophyll *a* molecules bound to D1 and D2 subunits, respectively
CL	cardiolipid
CP	chlorophyll binding protein
CP43	chlorophyll *a*-containing protein with apparent molecular mass of 43-kDa
CP47	chlorophyll *a*-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
DGDG	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-$NADP^+$ reductase
GSB	green sulfur bacteria
H-, L-, M-	the 3 major integral polypeptide subunits of the *Rb. sphaeroides* 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
$NADP^+$	nicotinamide adenine dinucleotide phosphate
NASA	National Aeronautics and Space Administration
Neo	neoxanthin
NG	nonyl-+-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_{D1} and P_{D2}	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_2	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	phycoeurobilin
PVB	phycoviolobilin
Q_A	tightly bound quinone in photosystem II and the purple bacterial reaction center
Q_B	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_Z	redox-active tyrosines, D1-Tyr161 in photosystem II
Tyr_D	redox-active tyrosines, D2-Tyr160 in photosystem II
UQ	ubiquinone
UQH_2	ubiquinol
UV	ultraviolet
VDE	violaxanthin de-epoxidase
Xanc	xanthophyll-cycle
XANES	x-ray absorption near edge structure
XAS	x-ray absorption spectroscopy
Zea	zeaxanthin