

Photosystem II

The Light-Driven Water:Plastoquinone Oxidoreductase

Edited by

Thomas J. Wydrzynski
*The Australian National University,
Canberra, Australia*

and

Kimiyuki Satoh
*Okayama University,
Okayama, Japan*

Assistant Editor

Joel A. Freeman

 Springer

Contents

Editorial	v
Contents	xi
Preface	xxi
Author Index	xxvii
Color Plates	CP1–CP16
Dedication/Perspective: A tribute to Jerry Babcock	1–10

Part I: Perspective of Photosystem II Research

1	Introduction to Photosystem II	11–22
	<i>Kimiyuki Satoh, Thomas J. Wydrzynski and Govindjee</i>	
	Summary	11
	I. Discovery of Oxygen and O ₂ Production by Plants	12
	II. Conceptual Development of Photosystem II	12
	III. O ₂ Production — Phenomenology	13
	IV. Isolation of the Chemical Entity—Structural Organization of Photosystem II	14
	V. Functional Sites — Catalytic Role of Photosystem II	16
	VI. Future Perspectives	18
	Acknowledgments	19
	References	19

Part II: Protein Constituents of Photosystem II

2	Distal and Extrinsic Photosystem II Antennas	23–44
	<i>Beverley R. Green and Elisabeth Gantt</i>	
	Summary	23
	I. Introduction	24
	II. Phycobiliproteins and Phycobilisomes	24
	III. Prochlorophyte Antennas and the IsiA Proteins	30
	IV. The LHC Superfamily of Chloroplasts	31
	Acknowledgments	39
	References	39
3	The CP47 and CP43 Core Antenna Components	45–70
	<i>Julian J. Eaton-Rye and Cindy Putnam-Evans</i>	
	Summary	45
	I. Introduction	46

II.	The <i>psbB</i> and <i>psbC</i> Genes	49
III.	Overview of Energy Transfer and Chlorophyll Binding	50
IV.	The Hydrophilic Domains of CP47 and CP43	54
V.	Conclusions	64
	Acknowledgments	65
	References	65
4	The D1 and D2 Core Proteins	71–94
	<i>Peter J. Nixon, Mary Sarcina and Bruce A. Diner</i>	
	Summary	72
I.	Introduction	72
II.	Identification of the D1 and D2 Proteins	72
III.	The Primary Structures of D1 and D2	73
IV.	Identification of the D1 and D2 Proteins as the Photosystem II Reaction Center Subunits	74
V.	Mutagenesis of the D1 and D2 Proteins	76
VI.	Concluding Remarks	86
	Acknowledgments	86
	References	87
5	The Extrinsic Proteins of Photosystem II	95–120
	<i>Terry M. Bricker and Robert L. Burnap</i>	
	Summary	95
I.	Introduction	96
II.	The 33 kDa Manganese-Stabilizing Protein (PsbO)	96
III.	The 24 kDa and 16 kDa Proteins (PsbP and PsbQ) in Higher Plants	103
IV.	Multiple Expressed Genes of the Extrinsic Proteins in Higher Plants	107
V.	Cytochrome c_{550} (PsbV) in Cyanobacteria	108
VI.	The PsbU Protein in Cyanobacteria	112
VII.	Conclusions	113
	Acknowledgments	114
	References	114
6	The Low Molecular Weight Proteins of Photosystem II	121–138
	<i>Leeann E. Thornton, Johnna L. Roose, Himadri B. Pakrasi and Masahiko Ikeuchi</i>	
	Summary	121
I.	Introduction	122
II.	Membrane Spanning Subunits	123
III.	Extrinsic Subunits	132
IV.	Conclusion	133
	Acknowledgments	133
	References	133

Part III: Organization of Functional Sites in Photosystem II

7	Primary Electron Transfer	139–175
	<i>Gernot Renger and Alfred R. Holzwarth</i>	
	Summary	140
	I. Introduction	140
	II. Cofactors of Stable Charge Separation in Photosystem II	140
	III. Photophysical Properties of Pigment Protein Complexes	142
	IV. Nature and Properties of P680 and Pheo	150
	V. Kinetics and Energetics of Charge Separation	158
	VI. Forward, Back and Side Reactions of Radical Ion Pair P680 ^{•+} Q _A ^{•-}	166
	VII. Concluding Remarks and Future Perspectives	167
	Acknowledgments	168
	References	168
8	The Iron-Quinone Acceptor Complex	177–206
	<i>Vassili Petrouleas and Antony R. Crofts</i>	
	Summary	178
	I. Introduction	178
	II. Probing the Iron-Quinone Complex Through the Iron Site	178
	III. Organization of the Quinone Binding Sites: The Two-Electron Gate	185
	IV. Conclusions	199
	Acknowledgments	199
	References	200
9	The Redox-Active Tyrosines Y_Z and Y_D	207–233
	<i>Bruce A. Diner and R. David Britt</i>	
	Summary	207
	I. Introduction	208
	II. Chemical Nature of Signal II	209
	III. Protonation States of the Oxidized and Reduced Forms of Tyrosine	214
	IV. Localization of Y _Z and Y _D	216
	V. The Proton Acceptor and Hydrogen-Bonding	216
	VI. Kinetics of Y _Z Oxidation and Reduction	222
	VII. Kinetics of Y _D Oxidation and Reduction and Comparison	225
	VIII. Mechanisms for Y _Z Oxidation and Reduction	226
	IX. Concluding Remarks	227
	Acknowledgments	228
	References	228
10	The Catalytic Manganese Cluster: Organization of the Metal Ions	235–260
	<i>Vittal K. Yachandra</i>	
	Summary	235
	I. Introduction	236
	II. Oxidation States of the Manganese	237
	III. Structure of the Manganese Cluster	242
	IV. Structural Role of the Calcium Cofactor	249

V. Structural Role of the Chloride Cofactor	253
VI. Mechanism of Water Oxidation and O ₂ Evolution	254
Acknowledgments	256
References	256
11 The Catalytic Manganese Cluster: Protein Ligation	261–284
<i>Richard J. Debus</i>	
Summary	261
I. Introduction	262
II. The D1 Polypeptide	263
III. The CP43 Polypeptide	279
IV. Concluding Remarks	280
Acknowledgments	280
References	280
12 The Catalytic Manganese Cluster: Implications from Spectroscopy	285–306
<i>Karin A. Åhrling, Ronald J. Pace and Michael C. W. Evans</i>	
Summary	285
I. Introduction	286
II. S-State Spectroscopy	286
III. A Spectroscopic Model for the Catalytic Site	300
References	302
13 The Calcium and Chloride Cofactors	307–328
<i>Hans J. van Gorkom and Charles F. Yocum</i>	
Summary	308
I. Introduction	308
II. Chloride	309
III. Calcium	314
IV. Concluding Remarks	323
Acknowledgments	323
References	323
14 Bicarbonate Interactions	329–346
<i>Jack J. S. van Rensen and Vyacheslav V. Klimov</i>	
Summary	330
I. Introduction	330
II. Bicarbonate Requirement on the Electron Acceptor Side of Photosystem II	331
III. Bicarbonate Requirement on the Electron Donor Side of Photosystem II	336
IV. Conclusions	341
Acknowledgments	342
References	342

15	Side-Path Electron Donors: Cytochrome b_{559}, Chlorophyll Z and β-Carotene	347–365
	<i>Peter Faller, Christian Fufezan and A. William Rutherford</i>	
	Summary	348
	I. Introduction	348
	II. Location of Accessory Electron Donors	348
	III. Spectroscopic Studies	352
	IV. Electron Transfer Pathways	355
	V. Function of the Alternative Electron Transfer Pathway	359
	VII. Conclusions	362
	Acknowledgments	362
	References	362

Part IV: Structural Basis for Photosystem II

16	Molecular Analysis by Vibrational Spectroscopy	367–387
	<i>Takumi Noguchi and Catherine Berthomieu</i>	
	Summary	367
	I. Introduction	368
	II. Light-Induced Fourier Transform Infrared (FTIR) Difference Technique	369
	III. Cofactors on the Electron Donor Side	369
	IV. Cofactors on the Electron-Acceptor Side	377
	V. Cofactors in Secondary Electron-Transfer Pathways	381
	Acknowledgments	382
	References	382
17	Configuration of Electron Transfer Components Studied by EPR Spectroscopy	389–402
	<i>Robert Bittl and Asako Kawamori</i>	
	Summary	389
	I. Introduction	390
	II. Spectroscopic Background	390
	III. Orientation of Cofactor Molecules	392
	IV. Distances Between Cofactor Molecules	395
	V. Concluding Remarks	399
	Acknowledgments	400
	References	400
18	Structural Analysis of the Photosystem II Core/Antenna Holocomplex by Electron Microscopy	403–424
	<i>Ben Hankamer, James Barber and Jon Nield</i>	
	Summary	404
	I. Introduction	404
	II. Electron Cryo-Microscopy Techniques	405
	III. Structure of Higher Plant Photosystem II and Its Antenna System	410

IV. Organization and Dynamics of Higher Plant Photosystem II and Its Antenna In Vivo	417
V. Future Prospects and Concluding Remarks	420
Acknowledgments	421
References	421
19 Photosystem II: Structural Elements, the First 3D Crystal Structure and Functional Implications	425–447
<i>Horst T. Witt</i>	
Summary	425
I. Introduction	426
II. Transmembrane Charge Separation Events as Primary Acts of Light Energy Conversion and Spatial Organization of the Electron Donors and Acceptors — Analysis by a Molecular Voltmeter	428
III. The Primary Electron Donor Chlorophyll P680 and Its Stable Electron Acceptor Plastoquinone Q _A — The Engine Driving Water Oxidation	428
IV. The Membrane-Spanning Chlorophyll/Quinone Couple as a Reaction Center Model for Different Photosystems	429
V. Two Chlorins between the Chlorophyll/Quinone Couple as a Fast Path for Electrons Crossing the Membrane	429
VI. The Plastoquinone Pool as the Pathway for Transfer of Electrons from Q _A to Photosystem I and of Protons from the Outer Aqueous Phase to the Membrane Lumen	429
VII. Primary Electron Donors Organized as Chlorophyll Pairs	430
VIII. Identification of Photosystem II as a Dimer and Photosystem I as a Trimer	430
IX. Homology of the Photosystem II Core Complex with Photosystem I and the Bacterial Reaction Center	432
X. First 3-D Crystals of Photosystem II Capable of Water Oxidation and X-Ray Structure Analysis at 3.8–3.6 and 3.2 Å Resolution	432
XI. Manganese Valences, Proton Releases and Water States of the Quaternary S-State Cycle of the Light Driven Engine	438
XII. Functional Implications	441
Acknowledgments	443
References	443
20 3D Crystal Structure of the Photosystem II Core	449–467
<i>Jian-Ren Shen and Nobuo Kamiya</i>	
Summary	449
I. Introduction	450
II. Crystallization	450
III. Crystal Structure of Photosystem II from Thermophilic Cyanobacteria	454
IV. Future Prospects and Concluding Remarks	463
Acknowledgments	464
References	464

21 Refined X-Ray Structure of Photosystem II and Its Implications	469–489
<i>James Barber and So Iwata</i>	
Summary	469
I. Introduction	470
II. X-Ray Crystallography	470
III. Major Differences from Earlier Structures	471
IV. Overall Structure	472
V. Protein Subunits	472
VI. Pigments and Cofactors	476
VII. The Oxygen Evolving Center	479
VIII. General Implications of the Structure	482
IX. Water Oxidation Mechanism	482
X. Perspectives	485
Acknowledgments	485
References	485

Part V: Molecular Dynamics of Photosystem II

22 Energy Trapping and Equilibration: A Balance of Regulation and Efficiency	491–514
---	----------------

Laura M. C. Barter, David R. Klug and Rienk van Grondelle

Summary	492
I. Introduction	492
II. The Context for Solar Energy Conversion in Photosystem II	493
III. Rapid Energy Transfer and Equilibration within Isolated Complexes	494
IV. Conversion of Excited States into Charge Separated States	501
V. Concluding Remarks	508
Acknowledgments	509
References	509

23 The Role of Carotenoids in Energy Quenching	515–537
---	----------------

Barry J. Pogson, Heather M. Rissler and Harry A. Frank

Summary	515
I. Introduction	516
II. Biosynthesis and Photosystem Assembly	516
III. Carotenoids and Photoprotection	523
Acknowledgments	531
References	531

24 Flash-Induced Oxygen Evolution and Other Oscillatory Processes	539–565
--	----------------

Vladimir Shinkarev

Summary	540
I. Introduction	541
II. The Kok Model of Oxygen Evolution	541
III. Binary Oscillations in the Kok Model	561
IV. Conclusions	562

Acknowledgments	563
References	563
25 Mechanism of Photosynthetic Oxygen Production	567–608
<i>Warwick Hillier and Johannes Messinger</i>	
Summary	568
I. Introduction	568
II. Photosynthetic O ₂ Evolution Patterns and the Kok Model	569
III. Structures and Oxidation States of the Mn ₄ O _x Ca Complex	571
IV. Substrate Interactions	576
V. Energetic and Kinetic Considerations	582
VI. Mechanistic Overview of O-O Bond Formation Reactions	590
VII. A New Mechanistic Rendition of Photosynthetic Oxidation Production	597
Acknowledgments	600
References	600
 Part VI: Assembly and Biodynamics of Photosystem II	
<hr/> <hr/>	
26 Photo-Assembly of the Catalytic Manganese Cluster	609–626
<i>G. Charles Dismukes, Gennady M. Ananyev and Richard Watt</i>	
Summary	610
I. Introduction	610
II. Function of Photosystem II Subunits in Water Splitting and Photo-Assembly	610
III. Biogenesis of the Water Oxidizing Complex	613
IV. Roles of the Inorganic Cofactors from Photo-Assembly	616
V. Concluding Remarks	622
Acknowledgments	623
References	623
 27 Photoinactivation and Mechanisms of Recovery	 627–648
<i>Wah Soon Chow and Eva-Mari Aro</i>	
Summary	628
I. Introduction	628
II. The Inevitability of Photoinactivation of Photosystem II	629
III. Potential Agents of Photosystem II Photoinactivation	630
IV. The Variability of the Extent of Photosystem II Photoinactivation	632
V. Molecular Rearrangements Preceding the Degradation of the D1 Protein	635
VI. Degradation of the Damaged D1 Protein	636
VII. Biogenesis and Assembly of the New D1 Copy into Photosystem II	639
Acknowledgments	643
References	643
 28 Transcriptional and Translational Regulation of Photosystem II Gene Expression	 649–668
<i>Kenichi Yamaguchi, Stephen P. Mayfield and Mamoru Sugita</i>	
Summary	650
I. Introduction	650

II. Regulation of Photosystem II Gene Expression in Algae	651
III. Regulation of Photosystem II Gene Expression in Higher Plants	658
Acknowledgments	662
References	662
29 Protein Transport and Post-translational Processing in Photosystem II Biosynthesis and Homeostasis	669–682
<i>Steven M. Theg and Lan-Xin Shi</i>	
Summary	669
I. Introduction	670
II. Targeting Pathways Utilized by Different Photosystem II Subunits	670
III. Assembly of Subunits into Photosystem II	674
IV. Post-Translational Modifications	676
V. Concluding Remarks	679
Acknowledgments	679
References	679
 Part VII: Comparison of Photosystem II with Other Natural/Artificial Systems	
30 The Origin and Evolution of Photosynthetic Oxygen Production	683–695
<i>G. Charles Dismukes and Robert E. Blankenship</i>	
Summary	683
I. The Timetable and Biogeochemical Consequences of Oxygenic Photosynthesis	684
II. Minimal Cofactor Diversity in Water Oxidizing Complexes	685
III. Transitional Electron Donors and ‘Missing Links’	687
IV. Possible Evolution Pathways for the Photosystem II Water Oxidizing Complex	688
V. Concluding Remarks	693
Acknowledgments	693
References	693
31 Mechanistic Comparisons Between Photosystem II and Cytochrome c Oxidase	697–713
<i>Gary W. Brudvig and Mårten Wikström</i>	
Summary	697
I. Introduction	698
II. Protein Structure and Cofactors	698
III. Energetics of Water Oxidation and Oxygen Reduction	701
IV. Catalytic Mechanisms	702
V. Analogies between the Oxygen Chemistry of Photosystem II and Cytochrome c Oxidase	708
Acknowledgments	710
References	710

32 Mimicking the Properties of Photosystem II in Bacterial Reaction Centers	715–727
<i>László Kálmán, JoAnn C. Williams and James P. Allen</i>	
Summary	715
I. Evolutionary Developments	716
II. Achieving a Highly Oxidizing Electron Donor	717
III. Oxidation of Tyrosine Residues and Metals	719
IV. Designing a Manganese Cluster	725
Acknowledgments	725
References	725
33 De Novo Protein Design in Respiration and Photosynthesis	729–751
<i>Brian R. Gibney and Cecilia Tommos</i>	
Summary	729
I. Introduction	730
II. Construction of Proteins Containing Cofactors Involved in Energy Conversion	737
III. Perspective	747
Acknowledgments	748
References	748
34 Understanding Photosystem II Function by Artificial Photosynthesis	753–775
<i>Ann Magnuson, Stenbjörn Styring and Leif Hammarström</i>	
Summary	753
I. Introduction	754
II. Mimicking Photosystem II Reactions	758
III. Redox Properties in Natural and Artificial Photosynthetic Systems	769
IV. Future Outlook	772
Acknowledgments	772
References	772
Index	777