

Artificial Photosynthesis

From Basic Biology to Industrial Application

Edited by Anthony F. Collings and Christa Critchley



WILEY-VCH Verlag GmbH & Co. KGaA

Contents

	Foreword V
	Preface IX
	List of Contributors XXIII
Part I	The Context 1
1	Artificial Photosynthesis: Social and Political Issues 3 Ian Lowe
1.1 1.2 1.3 1.4 1.5	Introduction 3 The Need for a Transition to Artificial Photosynthesis 4 Some Associated Social and Political Issues 6 Using the Available Photons: Towards Sustainability Science Conclusions 11 References 11
2	An Integrated Artificial Photosynthesis Model 13 Ron J. Pace
2.1	Introduction 13
2.2	Natural Photosynthesis 13
2.3	Artificial Photosynthesis: An Integrated Strategy 17
2.4	A Technological Approach to Photosynthesis 19
2.5	Program 1: Biomimetic Photoelectric Generation 20
2.5.1	Milestones 24
2.6	Program 2: Electrolytic Hydrogen 24
2.6.1	Milestones 28
2.7	Programs 3 and 4: Waterless Agriculture 28
2.7.1	Program 3: Bioenergetic Converters 29
2.7.1.1	Milestones 30
2.7.2	Program 4: The CO_2 -fixing Enzyme Reactor 31
2.7.2.1	Milestones 32
2.8	Conclusions 33 References 33

Artificial Photosynthesis: From Basic Biology to Industrial Application Edited by Anthony F. Collings and Christa Critchley Copyright © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-31090-8 9

Part II Capturing Sunlight 35

3	Broadband Photon-harvesting Biomolecules for Photovoltaics 37 Paul Meredith, Ben J. Powell, Jenny Riesz, Robert Vogel, David Blake, Indriani Kartini, Geff Will, and Surya Subianto
3.1 3.2	Introduction 37 The Photoelectrochemical Grätzel Cell (Dye-sensitized Solar Cell) 39
3.3	Typical Components and Performance of a DSSC 41
3.3.1	Construction and Mode of Operation 41
3.3.2	Typical DSSC Performance 45
3.3.3	Device Limitations 47
3.4	Melanins as Broadband Sensitizers for DSSCs 48
3.4.1	Melanin Basics 48
3.4.2	Melanin Chemical, Structural, and Spectroscopic Properties 50
3.4.3	Melanin Electrical and Photoconductive Properties 58
3.4.4	Melanins as Broadband Photon-harvesting Systems 61
3.4.5	A DSSC Based Upon Synthetic Eumelanin 62
3.5	Conclusions 63
	References 64
4	The Design of Natural Photosynthetic Antenna Systems 67 Nancy E. Holt, Harsha M. Vaswani, and Graham R. Fleming
4 4.1	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67
4 4.1 4.2	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68
4 4.1 4.2 4.2.1	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69
4 4.1 4.2 4.2.1 4.2.2	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory: B800 to B850 Inter-band EnergyTransfer69
4 4.1 4.2 4.2.1 4.2.2 4.2.2 4.2.3	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory: B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70
4 4.1 4.2 4.2.1 4.2.2 4.2.2 4.2.3 4.2.4	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory: B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70Modified Redfield Theory: Intra-band B850 Exciton Dynamics72
4 4.1 4.2 4.2.1 4.2.2 4.2.3 4.2.3 4.2.4 4.3	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70Modified Redfield Theory: Intra-band B850 Exciton Dynamics72Energetic Disorder Within Light-harvesting Complexes73
4 4.1 4.2 4.2.1 4.2.2 4.2.2 4.2.3 4.2.4 4.3 4.3.1	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70Modified Redfield Theory: Intra-band B850 Exciton Dynamics72Energetic Disorder Within Light-harvesting Complexes73From Isolated Complexes to Membranes: Disorder in LH273
4 4.1 4.2 4.2.1 4.2.2 4.2.2 4.2.3 4.2.4 4.3 4.3.1 4.3.2	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70Modified Redfield Theory: Intra-band B850 Exciton Dynamics72Energetic Disorder Within Light-harvesting Complexes73From Isolated Complexes to Membranes: Disorder in LH273Photosystem I75
4 4.1 4.2 4.2.1 4.2.2 4.2.3 4.2.4 4.3 4.3.1 4.3.2 4.4	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory: B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70Modified Redfield Theory: Intra-band B850 Exciton Dynamics72Energetic Disorder Within Light-harvesting Complexes73From Isolated Complexes to Membranes: Disorder in LH273Photosystem I75Photochemistry and Photoprotection in the Bacterial Reaction
4 4.1 4.2 4.2.1 4.2.2 4.2.3 4.2.4 4.3 4.3.1 4.3.2 4.4	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory: B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory: B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70Modified Redfield Theory: Intra-band B850 Exciton Dynamics72Energetic Disorder Within Light-harvesting Complexes73From Isolated Complexes to Membranes: Disorder in LH273Photosystem I75Photochemistry and Photoprotection in the Bacterial ReactionCenter78
4 4.1 4.2 4.2.1 4.2.2 4.2.3 4.2.4 4.3 4.3.1 4.3.2 4.4 4.5	The Design of Natural Photosynthetic Antenna Systems67Nancy E. Holt, Harsha M. Vaswani, and Graham R. FlemingIntroduction67Confined Geometries: From Weak to Strong Coupling and Everythingin Between68Conventional Förster Theory. B800 to B800 Intra-band EnergyTransfer69Generalized Förster Theory. B800 to B850 Inter-band EnergyTransfer69Generalized Förster Theory with the Transition Density CubeMethod: Car to Bchl Inter-pigment Energy Transfer70Modified Redfield Theory: Intra-band B850 Exciton Dynamics72Energetic Disorder Within Light-harvesting Complexes73From Isolated Complexes to Membranes: Disorder in LH273Photosystem I75Photochemistry and Photoprotection in the Bacterial ReactionCenter78The Regulation of Photosynthetic Light Harvesting79

References 83

- 5 Identifying Redox-active Chromophores in Photosystem II by Low-temperature Optical Spectroscopies 87 Elmars Krausz and Sindra Peterson Årsköld
- 5.1 Introduction 87
- 5.2 Experimental Methods 89
- 5.2.1 Sample Preparation 89
- 5.2.2 Illumination 90
- 5.2.3 Spectra 90
- 5.3 Results and Discussion 91
- 5.3.1 Absorption and CD Signatures: Plant PSII Cores and BBYs 91
- 5.3.2 Absorption and CD Signatures: Plant and Cyanobacterial PSII Cores 94
- 5.3.3 Absorption Signatures: The Native and Solubilized Reaction Center 94
- 5.3.4 MCD Signatures: P680 and Chl_z 96
- 5.3.5 Electrochromic Signature: Pheo_{D1} in Active PSII 99
- 5.4 Conclusions 103
- 5.4.1 Low-temperature Precision Polarization Spectroscopies 103
- 5.4.2 Signatures of P680 and Chl_z 103
- 5.4.3 Electrochromism Signature of Pheo_{D1} 104
- 5.4.4 Coupling and Robustness in P680 and Biomimetic Systems 104 References 105

6 The Nature of the Special-pair Radical Cation Produced by Primary Charge Separation During Photosynthesis 109 Jeffrey R. Reimers and Noel S. Hush

- 6.1 Introduction 109
- 6.2 The Special Pair 109
- 6.3 The Hole-transfer Band 113
- 6.4 Initial Investigations of the Hole-transfer Band 116
- 6.5 Identification of the SHOMO to HOMO Band 118
- 6.6 Full Spectral Simulations Involving all Bands 119
- 6.7 Predicting Chemical Properties Based on the Spectral Analysis 121
- 6.8 Conclusions 125 References 125

7 Protein-based Artificial Photosynthetic Reaction Centers 127

Reza Razeghifard and Thomas J. Wydrzynski

- 7.1 Introduction 127
- 7.2 Natural Reaction Centers 127
- 7.2.1 Structure and Function 127
- 7.2.2 Creation of a Charge-separated State 129
- 7.2.3 Mutational Studies 129

- XVIII Contents
 - 7.3 Synthetic and Semi-synthetic Reaction Centers 130
 - 7.3.1 Multi-layered Films 131
 - 7.3.2 Synthetic Reaction Centers 132
 - 7.3.2.1 Electron Acceptor 134
 - 7.3.2.2 Electron Donor 136
 - 7.3.2.3 Photocatalyst: Photoactive Peptides 138
 - 7.4 Perspective 140 References 141
 - 8 Novel Geometry Polynorbornane Scaffolds for Chromophore Linkage and Spacing 147 Ronald N. Warrener, Davor Margetic, David A. Mann,

Zhi-Long Chen, and Douglas N. Butler

- 8.1 Introduction 147
- 8.2 Results and Discussion 151
- 8.2.1 Reaction at Carbonyl Groups to Form Unsymmetrical Type III Dvads 151
- 8.2.2 Extended-frame Dyads 154
- 8.3 Preliminary Results 155
- 8.3.1 The Use of Multicarbonyl Reagents for Dyad Formation 155
- 8.4 Conclusions 157
- 8.5 Dyad Nomenclature 158

References 165

- Part III Feeding the Grid from the Sun 167
- 9 Very High-efficiency in Silico Photovoltaics 169 Martin A. Green
- 9.1 Introduction 169
- 9.2 Silicon Wafer Approach 171
- 9.3 Thin-film Approaches 173
- 9.4 Third-generation Technologies 178
- 9.5 Conclusions 183
 - References 184

10 Mimicking Bacterial Photosynthesis 187

- Devens Gust, Thomas A. Moore, and Ana L. Moore
- 10.1 Introduction 187
- 10.2 Natural Photosynthesis 188
- 10.3 Artificial Photosynthesis 190
- 10.3.1 Artificial Antenna Systems 190
- 10.3.2 Artificial Reaction Centers 194
- 10.3.3 Antenna–Reaction Center Complexes 199
- 10.3.4 Transmembrane Proton Pumping 201

- 10.3.5 Synthesis of ATP 204
- 10.3.6 Transmembrane Calcium Transport 206
- 10.4 Conclusions 208 References 209
- Part IV Photohydrogen 211
- 11Development of Algal Systems for Hydrogen Photoproduction:
Addressing the Hydrogenase Oxygen-sensitivity Problem213Maria L. Ghirardi, Paul King, Sergey Kosourov, Marc Forestier,
Liping Zhang, and Michael Seibert213
- 11.1 Introduction 213
- 11.2 Sulfur Deprivation and Hydrogen Photoproduction 214
- 11.2.1 Background 214
- 11.2.2 Model of the Interactions Between Different Metabolic Pathways in Sulfur-deprived Cells 215
- 11.2.3 Confirmation of the Model 217
- 11.2.4 Limiting Factors for H₂ Photoproduction under Sulfur Deprivation 218
- 11.2.5 Mechanism of Regulation 220
- 11.3 Molecular Engineering of the Algal Hydrogenase 221
- 11.3.1 Algal Hydrogenases and H₂ Production 221
- 11.3.2 Cloning and Sequencing of the Two *C. reinhardtii* [FeFe]-Hydrogenases 221
- 11.3.3 Anaerobic Expression of the two C. reinhardtii Hydrogenases 223
- 11.3.4 Oxygen Inhibition of Hydrogenase Activity and Molecular Engineering for Increased O₂ Tolerance 224 References 226
- 12 Bioengineering of Green Algae to Enhance Photosynthesis and Hydrogen Production 229 Anastasios Melis
- 12.1 Introduction 229
- 12.2 Rationale and Approach 230
- 12.3 Physiological State of the Chl Antenna Size in Green Algae 231
- 12.4 The Genetic Control Mechanism of the Chl Antenna Size in Green Algae 232
- 12.5 Effect of Pigment Mutations on the Chl Antenna Size of Photosynthesis 233
- 12.6 Genes for the Regulation of the Chl Antenna Size of Photosynthesis 235
- 12.7 Conclusions 237 Acknowledgements 237 References 237

XX Contents

Part V	The Carbon Connection 241
13	Manipulating Ribulose Bisphosphate Carboxylase/Oxygenase in the Chloroplasts of Higher Plants 243 T. John Andrews and Spencer M. Whitney
13.1	Introduction 243
13.2	Why Manipulate Rubisco in Plants? 243
13.2.1	Genetic Manipulation of Higher-plant Rubisco Is Now Feasible 243
13.2.2	The Advantages of "Ecological" Studies of Rubisco "at Home" in Its Physiological Context 244
13.2.3	A Compelling Example of Genome–Phenome Interactions 244
13.2.4	An Improvement in the Resource-use Efficiency
13.3	What Constitutes an Efficient Rubisco? 245
13.3.1	Key Kinetic Parameters 245
13.3.2	Physiological Consequences of Rubisco Efficiency 246
13.3.3	Regulatory Properties 247
13.3.4	Evolution of Rubisco Efficiency 248
13.4	How to Find a Better Rubisco? 248
13.4.1	In Nature? 248
13.4.2	By Rational Design? 248
13.4.3	By in Vitro Evolution? 249
13.5	How to Manipulate Rubisco in Plants? 250
13.5.1	Nuclear Transformation 250
13.5.2	Plastid Transformation 252
13.6	What Have We Learned So Far? 252
13.6.1	Both Nuclear and Plastidic Genomes Are Able to Express Both
	rbcL and RbcS Genes 252
13.6.2	Photosynthesis and Growth Can Be Supported by a Foreign Rubisco 254
13.6.3	The Properties of a Mutated or Foreign Rubisco Are Reflected in the Leaf's Gas-exchange Properties 254
13.6.4	The Requirements for Folding and Assembly of the Subunits of Red-type, Form-I Rubisco Are Not Accommodated in Chloroplasts 255
13.6.5	A Better Strategy for Directed Mutagenesis of <i>thcl</i> 256
13.6.6	Subunit Hybrids Can Be Formed in vivo 256
13.7	Priorities for Future Manipulation of Rubisco in vivo 257
13.7.1	The Structural Foundations of Efficient Properties 257
13.7.2	Regulation of Rubisco Gene Expression 258
13.7.3	Folding and Assembly of Rubisco Subunits 258
13.8	Conclusions 259

References 260

14 Defining the Inefficiencies in the Chemical Mechanism of the Photosynthetic Enzyme Rubisco by Computational Simulation 263

Jill E. Gready

- 14.1 Introduction 263
- 14.1.1 Catalytic Inefficiencies 263
- 14.1.2 Evolutionary Constraints? 264
- 14.1.3 Experimental Limitations 265
- 14.1.4 Goals of Simulations 265
- 14.1.5 Simulation Options 266
- 14.2 Computational Methods 267
- 14.2.1 Computational Programs 267
- 14.2.2 Enzyme Models 268
- 14.2.3 Active-site Fragment Complexes 268
- 14.2.4 QM/MM Simulations 269
- 14.3 Results and Discussion 271
- 14.3.1 Fragment-complex Calculations 271
- 14.3.1.1 Enolization Step 271
- 14.3.1.2 Carboxylation Step 273
- 14.3.1.3 Hydration Step 275
- 14.3.1.4 Sequential Addition of CO₂ and H₂O 275
- 14.3.1.5 Alternative Conformations of the Gem-diol 275
- 14.3.1.6 C2-C3 Bond Cleavage: Pathway I 276
- 14.3.1.7 C2-C3 Bond Cleavage: Pathway II 276
- 14.3.1.8 Protonation of C2 276
- 14.3.1.9 Dissociation of Products 277
- 14.3.2 Summary of Main Findings 277
- 14.3.3 QM/MM+MD Calculations 277
- 14.3.3.1 CO2 Addition: Early vs. Late Protonation of the Carboxylate 278
- 14.3.3.2 Hydration of the β -Keto Acid 280
- 14.3.3.3 His294 Protects Intermediates from Decarboxylation 280
- 14.3.3.4 The Tightly Coupled Active-site Environment 280
- 14.4 Conclusions 281 References 281
- 15 Carbon-based End Products of Artificial Photosynthesis 283 Thomas D. Sharkey
- 15.1 Introduction 283
- 15.2 What Are the End Products of Plant Chloroplast Photosynthesis? 284
- 15.3 Does End-product Synthesis Ever Limit Photosynthesis? 285
- 15.4 What Would Be a Desirable Carbon-based End Product of Photosynthesis? 286 *References* 289

- XXII Contents
 - **16** The Artificial Photosynthesis System: An Engineering Approach 291 Dilip K. Desai
 - 16.1 Introduction 291
 - 16.2 Engineering Approach to APS 291
 - 16.3 Elements of the Engineering Approach 292
 - 16.3.1 Economic Value 292
 - 16.3.2 Limitations of Natural Photosynthesis Systems (NPS) 292
 - 16.3.2.1 Speed of NPS 292
 - 16.3.2.2 Energy Efficiency of NPS 292
 - 16.3.2.3 Water Requirements of NPS 293
 - 16.3.2.4 Land Use for NPS 293
 - 16.3.3 Scale of Operation 293
 - 16.3.4 Functional Specification 294
 - 16.4 Elements of Envisaged System 294
 - 16.5 Cyanobacteria 295
 - 16.6 Photo-bioreactor 296
 - 16.7 Theory 296
 - 16.8 Results 298
 - 16.9 Conclusions 299
 - References 299

17 Greenhouse Gas Technologies: A Pathway to Decreasing Carbon Intensity 301 Peter J. Cook

- 17.1 Introduction 301
- 17.2 CO₂ Capture 301
- 17.3 Storing CO₂ 303
- 17.4 Australian Initiatives: Capture and Storage Technologies 306
- 17.5 Conclusions 307 References 308

Subject Index 309