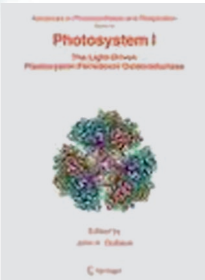
## Photosystem I




Advances in Photosynthesis and Respiration. Vol. 24. Edited by *John H. Golbeck*. Springer, Dordrecht 2006. 716 pp., hardcover € 266.00.—ISBN 978-1-4020-4255-3

Photosynthesis carried out by cyanobacteria, green algae, and higher plants is the fundamental biological process by which solar energy converts atmospheric $CO_2$ and water into biomass, thereby releasing, as a "waste" product, the molecular oxygen that is essential for all human and animal life on earth. The light-driven energy- and electron-transfer processes trigger reactions that finally lead to the oxidation of water, the reduction of $NADP^+$, and the build-up of a proton gradient across the photosynthetic membrane to produce ATP. These processes are catalyzed by two membrane-embedded pigment–protein complexes, which are called photosystems (PS) I and II. PSII contains the site of water-cleavage, and utilizes the electrons extracted from water to reduce plastoquinone to plastoquinol. The latter diffuses through the membrane until it is re-oxidized by another membrane protein, the cytochrome-$b_6f$-complex, which transfers the electrons to a water-soluble electron carrier (plastocyanin or cytochrome $c_6$). This carrier in turn is oxidized by PSI, which delivers the electrons via ferredoxin to the enzymes that produce NADPH.

The book reviewed here is concerned with PSI. It is the 24th volume of the series *Advances in Photosynthesis and Respiration* and complements Volume 22, which is about PSII. The book is edited by one of the leading experts in the field, John H. Golbeck of the Pennsylvania State University, and provides an up-to-date collection of 40 reviews written by 80 established researchers from 13 countries.

PSI is a pigment–protein complex consisting of many subunits, which binds more than a hundred cofactors (including chlorophylls, carotenoids, lipids, iron–sulfur clusters, phylloquinones). It combines the functions of light-harvesting and trans-membrane charge separation in one complex. Through this combination, each photon absorbed by the antenna pigments is funneled to the so-called reaction center (RC). The RC is comprised of two symmetry-related branches of redox-active cofactors. Here, the excitation energy is converted into an initial charge-separated state. The subsequent fast transport of an electron over a chain of successive electron acceptors stabilizes the charge separation, which is a prerequisite for the following slower redox reactions with the soluble electron carriers.

Understanding a complex molecular machinery such as PSI clearly requires an interdisciplinary approach. This is reflected in the broad perspective of the book, which covers areas that range from microbiology and mutagenesis, through structural analysis, spectroscopy, biochemistry, and theoretical modeling, to evolution. To guide the reader through this wide variety, the articles are grouped into eleven parts.

In the first part, an interesting survey of early discoveries in the field is presented. All authors of this section have contributed to the history of PSI research, and they describe their pioneering work in a vivid and informative way. The reader gains an impression of the difficulties that had to be overcome to elucidate details of the functional mechanisms of pigment–protein complexes without structural information. Thus, the determination of the structure of cyanobacterial PSI by X-ray diffraction at 2.5-Å resolution by Jordan et al. in 2001 was a real breakthrough that accelerated progress in understanding PSI. These beautiful structures are described in detail in Part II, along with more recent data on plant systems, and in Part III they are complemented by information about peripheral proteins that bind to PSI. The two rather short sections that follow are concerned with excitation and electron-transfer dynamics as studied by spectroscopic techniques (Part IV), and with genetic manipulations of PSI (Part V). At this point, the subdivision and ordering of sections appears somewhat arbitrary, since Part IV could well have been merged with Part VI about spectroscopy and Part VII about kinetics.

Not surprisingly, the most abundant studies of a light-driven redox enzyme are those that have applied spectroscopic techniques to reveal functional cofactor states and electron-transfer rates. Consequently, the emphasis of the book is on these topics, so that Parts VI and VII are the largest subsections. The focus is on optical, infrared, and electron paramagnetic resonance (EPR) spectroscopies, as well as on time-resolved optical and EPR techniques. Related to these issues is the hot and ongoing debate about the direction of electron transfer in the RC. The book provides a wealth of experimental data that are interpreted in terms of either one or both of the two cofactor branches being active in electron transfer. This is a good example of the situation that a knowledge of the X-ray structure is not sufficient to understand a protein.

Part VIII contains articles about genetics and assembly of PSI, while Part IX is about theoretical modeling. Here again, the ordering of topics is not entirely comprehensible, because Part IX is more related to spectroscopy and kinetics than to genetics and assembly. Part X describes related processes such as cyclic electron transfer around PSI and photoinhibition, while Part XI deals with the evolution of PSI and related proteins. The book is completed by a number of indexes. Besides indexes of authors and subjects, the book also provides an organism index, a mutant index, and a gene and gene-product index, all of which are very helpful.

Each article in the book is a thorough review of the current state of knowledge and of ongoing developments in a particular field, and in most cases includes an introduction to the field for nonspecialists. This ensures that the volume is not only a rich source of information for advanced researchers, contributing to a better communication between scientists of different disciplines, but also a valuable introduction for graduate students. The book appears at the right time, since structures are available and have already been used for some years to interpret data, and the work now provides a comprehensive review of recent developments concerning PSI. In conclusion, everybody who works with PSI or plans to do so in the near future should have the book on his or her desk.

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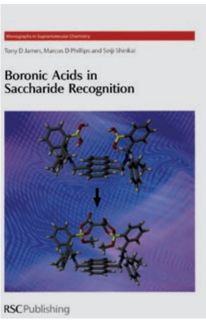
## *Boronic Acids in Saccharide Recognition*




By *Tony D. James*, *Marcus D. Phillips* and *Seiji Shinkai*. Royal Society of Chemistry, Cambridge 2006. 174 pp., hardcover £ 99.95.—ISBN 978-0-85404-537-6

Supramolecular chemistry is a broad area that encompasses many activities, but the design of synthetic receptors remains a core business. There are good specific reasons for wishing to have receptors that bind many substrates. For example, receptors may be used in analytical or separation systems, and may potentially have biological or catalytic activity. There is also a strong general motivation, in that the field serves as a proving ground for techniques and ideas in supramolecular chemistry. Just as synthetic chemists use natural products to hone their skills, supramolecular chemists can learn by setting themselves targets for binding and recognition. Among such targets, carbohydrates are both topical and challenging. On the one hand, the role of saccharide recognition in biology is under intensive investigation, and carbohydrate sensing (specifically glucose sensing) is important for the management of diabetes. At the same time, carbohydrates are quite "difficult" substrates, being large compared to other supramolecular targets, and only subtly different from each other. Moreover, their dominant functional group is hydroxy, which is very similar to the water molecules that surround them in their natural environment. Discrimination between substrate and solvent, the first job of a receptor, is therefore a major challenge.

Two strategies have been used to design synthetic carbohydrate receptors. One approach is essentially biomimetic, employing the noncovalent interactions used by carbohydrate-binding proteins such as lectins. Progress is being made, but it is only recently that receptors of this type have succeeded in water (as opposed to organic media, where substrate–solvent discrimination is far less challenging). The second strategy, which is discussed in this monograph, exploits the tendency of boronic acids to form cyclic boronate esters with 1,2- and 1,3-diols. This latter approach relies on the formation of covalent bonds, which raises the issue of whether it is truly "supramolecular", but complexation is kinetically fast, and most chemists would accept that this research conforms to the spirit of supramolecular chemistry. Importantly, the strategy works. Even simple boronic acids bind carbohydrates in water with quite respectable association constants, so molecular design can focus on controlling selectivity and improving affinity from a fairly high baseline. Reporter units (e.g., fluorophores) may also be incorporated, and the development of carbohydrate sensors is a key objective.

James and Shinkai were pioneers in this area, and have already written several reviews. It is appropriate that they should now expand their coverage to give a comprehensive account in book form. They begin with a short introduction and a brief chapter on carbohydrate recognition in general. In particular, they highlight the medical potential of a supramolecular nonbiological glucose sensor. Although the current enzyme-based methods are effective and user-friendly, improvements are certainly possible. For example, a synthetic receptor is likely to be more robust than a protein-based system, and therefore longer-lasting and amenable to sterilization. Chapter 3 provides a clear and detailed account of the principles behind the boronate–diol equilibrium. This is especially useful, as it was not covered in previous accounts in review journals. Chapters 4–7 then survey the large number of systems that have been reported in the primary literature. Chapters 4 and 5 focus on boronate-based fluorescent sensors for carbohydrates. The former chapter considers systems that employ internal charge transfer (ICT) and photoelectron transfer (PET). It also illustrates the value of ditopic structures to control selectivity, and intramolecular amine–borane interactions to mediate fluorescence detection. Developing these themes, Chapter 5 describes a modular approach to fluorescent carbohydrate sensors, which is currently being explored by one of the authors. Chapter 6 reviews other sensing strategies such as colorimetric and electrochemical detection. Chapter 7 covers "other systems for saccharide recognition", including receptors that operate at or across interfaces, CD receptors, and materials formed by molecular imprinting. Finally there is a short (two-page) conclusion.

Overall, the book does an excellent job of assembling the large body of literature in this area, explaining the operation of boronate-based carbohydrate receptors and suggesting routes to improved performance. This will be very valuable to workers in the field and interesting to many others. One might have welcomed a more substantial conclusion, perhaps discussing the medical application of these systems. For the nonspecialist reader, it is difficult to assess whether a clinical glucose sensor is just around the corner, or whether there are still major problems to be solved. However, this monograph certainly belongs on library shelves and in the laboratories of many supramolecular chemists.

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