1-11-1. Photosynthetic Reaction Center Complexes

Overview

Photosynthetic reaction centers are composed of photosystem I (PSI) and photosystem II (PSII), which perform a series of charge separation and electron transfer reactions, leading to the conversion of light energy into chemical energy. Owing to the development of X-ray crystallography and cryo-electron microscopic (cryo-EM) structural analysis techniques, the structures of both PSI and PSII in complex with light-harvesting protein complex (LHCs) have been solved from various organisms. In particular, the structure of the catalytic center for water oxidation in PSII (Fig. 1), as well as a number of reaction intermediate structures, have been solved, providing much information on the mechanism of water oxidation.

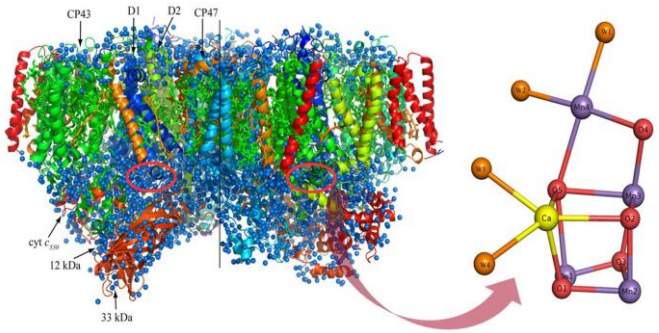

Figure 1. Structure of PSII (left side) and the catalytic center for water oxidation, the Mn_4CaO_5 cluster (Umena et al., *Nature*, 2011).

Current Status and Frontiers

Researches on reaction centers have been performed extensively, not only from the interests of basic research but also owing to the potential applications in artificial photosynthesis. Since the mid-2000, the structures of PSI and PSII from various organisms have been elucidated. In particular, researches into the mechanism of water oxidation in PSII and highly efficient utilization of light energy by PSI and PSII have seen great developments in recent years; they are introduced in the following.

1. Mechanism of water oxidation in PSII

Water oxidation in PSII proceeds through a Kok cycle, where the catalyst undergoes $S_1 \rightarrow S_2 \rightarrow S_3 \rightarrow (S_4) \rightarrow S_0$ state transition. The dark-stable S_1-state structure has been solved by X-ray crystallography in 2011 (Fig. 1), and the intermediate S_2, S_3-state structures are solved by a pump-probe approach using femtosecond X-ray free electron lasers. The results revealed that while there are several structural changes in the Mn_4CaO_5 cluster and

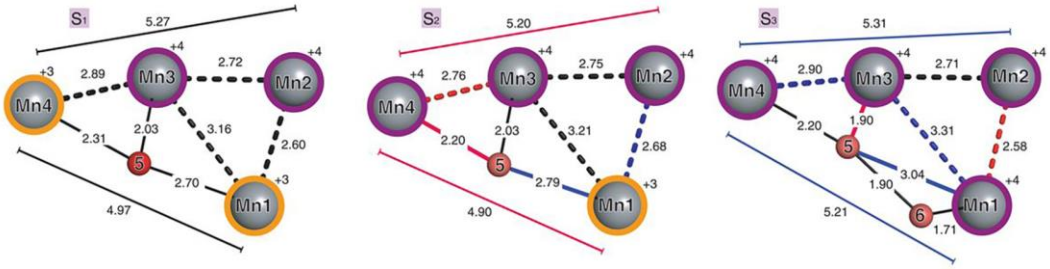

Figure 2. Structures of the Mn4CaO5 cluster at the S_1, S_2, S_3 states. Red circled numbers 5 and 6 indicates O5 and O6. The O6 atom can be seen to be inserted only in the S_3-state.

some of the its surrounding residues during the S_1-to-S_2 transition, a new oxygen atom named O6 appeared only in the S_3-state at a position close to O5 (Fig. 2). This indicates the formation of molecular oxygen between O6 and O5, providing the mechanism of molecular oxygen formation.

2. Highly efficient utilization of light energy in photosynthesis

Light energy is absorbed by various photosynthetic pigments bound to "light-harvesting protein complexes (LHCs)", and transferred to the reaction center to enable the charge separation reactions. These pigments contain chlorophyll *a, b, d, f*, various carotenes, etc., and they are bound to LHCs. Although LHCs belong to the *lhc* supergene family, they differ in sequences and structures greatly depending on the organisms, and form supercomplexes with both PSI and PSII. Owing to the development of cryo-EM structural analysis techniques, structures of PSI-LHCIs, PSII-LHCIIs from various organisms have been solved, providing much information regarding the energy absorption, transfer, and dissipation under excess light conditions.

References

1. Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature*, **473**, 55–60 (2011).
2. M. Suga, et al., *Nature*, **543**, 131–135 (2017).
3. M. Suga, et al., *Science,* **366**, 334–338 (2019).
4. H. Li, et al., *Nature*, **626**, 670–677 (2024).

Future Perspectives and Directions

Issues to be solved in 10 years: Complete elucidation of the water oxidation mechanism, proton channel/water channel, in cellular structures and dynamics of PSI-LHCIs, PSII-LHCIIs from various organisms, their changes in response to environmental changes, and applications of the water oxidation and highly efficient light-energy utilization mechanisms in artificial photosynthesis.

(Author: Jian-Ren Shen)