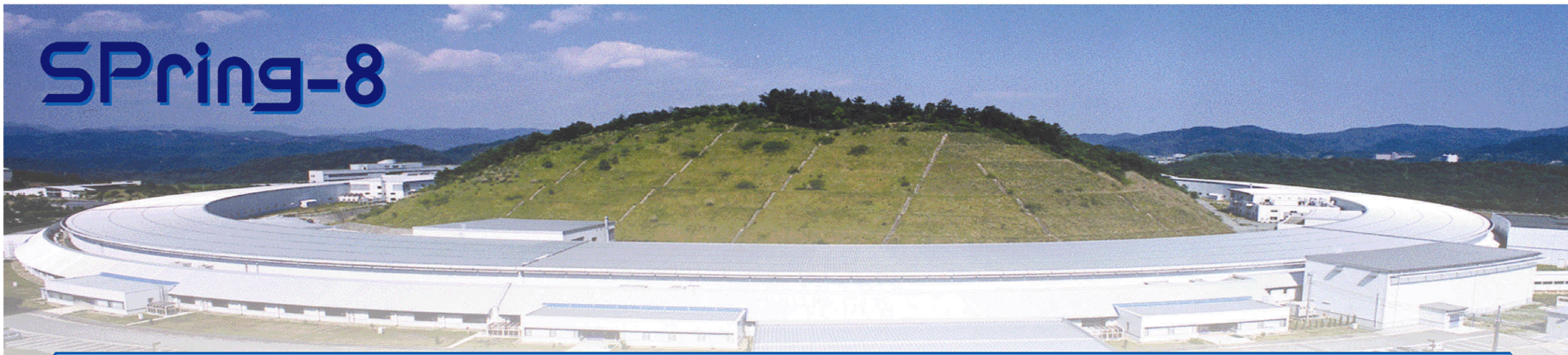

Mechanism behind Light-induced Water-splitting in Photosynthesis

Scientists of a research group led by Professor Jian-Ren Shen (Division of Bioscience, Graduate School of Natural Science and Technology, Okayama University) and Professor Nobuo Kamiya (The OCU Advanced Research Institute for Natural Science and Technology, Osaka City University) have elucidated the mechanism behind the splitting of water and the evolution of oxygen during photosynthesis by using solar energy.

In photosynthesis, organic substances such as glucose are generated from carbon dioxide using solar energy, which provide the energy source for almost all living organisms on the earth through respiration. Upon the absorption of solar light, photosystem II (PSII, Fig. 1) splits water to evolve oxygen molecules, protons and electrons simultaneously. These electrons are used to convert carbon dioxide to glucose. The water-splitting reaction by PSII is catalyzed by a metal-oxygen cluster consisting of four manganese (Mn) atoms and a calcium (Ca) atom linked by multiple oxygen (O) atoms. However, the accurate chemical composition and detailed atomic arrangement of the cluster remained unclear.

In this study, the scientists succeeded in improving the quality of PSII crystals significantly and carried out X-ray crystal structure analysis using three beamlines (BL44XU, BL41XU, and BL38B1) at SPring-8. It was found that the cluster has a chemical formula of Mn_4CaO_5 arranged in a distorted chair form, to which four water molecules are bound, with two being associated to one of the four Mn atoms and the other two to the Ca atom (Fig. 2). Some of these four water molecules are therefore considered to be incorporated into the oxygen molecules during the water-splitting reaction.

The successful analysis of the Mn_4CaO_5 cluster structure utilized by nature to split water will greatly inspire chemical synthesis of similar compounds that possess water-splitting activity, which may ultimately lead to the efficient conversion of solar energy to chemical energy through the synthesis of hydrogen molecules and methanol using electrons generated from water by the catalysts, to realize artificial photosynthesis. This is expected to contribute to solving problems related to energy, the environment, and food shortage that we will face in the near future.

Reference: Y. Umena, K. Kawakami, J.-R. Shen and N. Kamiya; *Nature* **473**, 55-60 (2011)

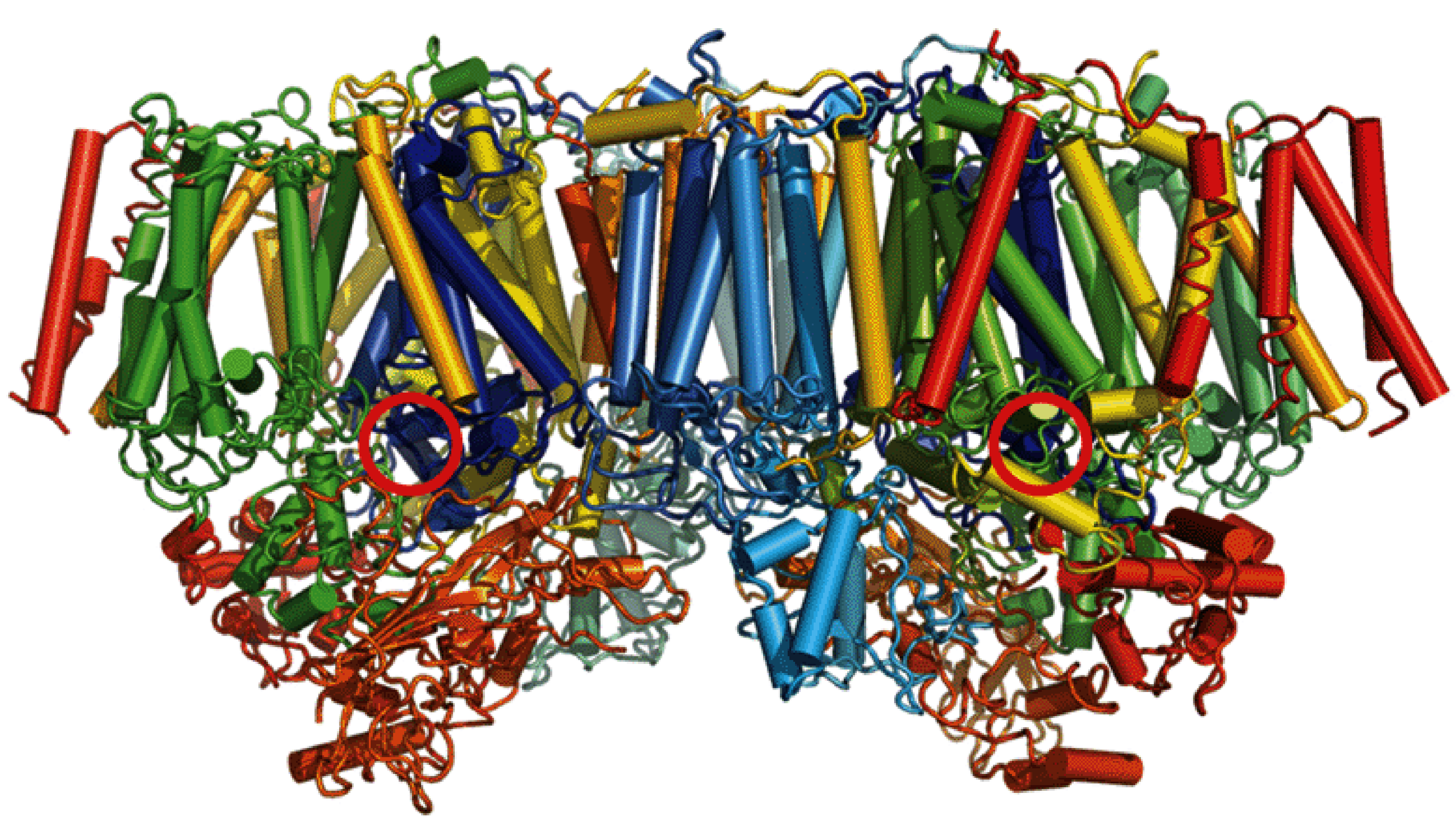

Fig. 1. Overall structure of PSII
PSII has a dimer structure consisting of two monomers. The oxygen-evolving centers are positioned at the sites indicated by two red circles.

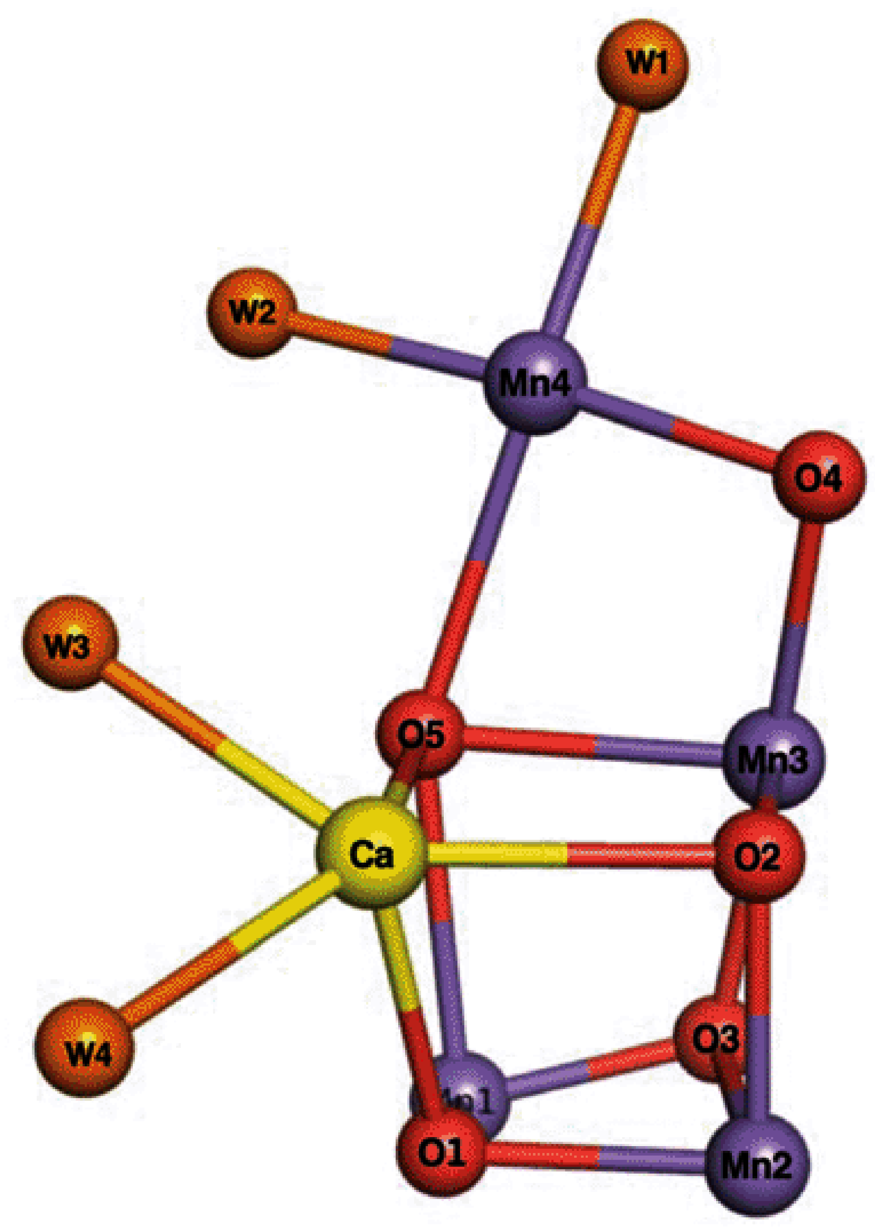

Fig. 2. Detailed chemical structure of the oxygen-evolving center
W1-W4 represent four water molecules bound to the Mn_4CaO_5-cluster.