Theoretical illumination of the proton wire for the $CaMn_4O_5$ cluster of photosystem II and elongation of Mn-Mn distances with hydrogen bonding. The UB3LYP geometry optimizations

M. Shoji[a*], H. Isobe[b], S. Yamanaka[c], Y. Umena[f], K. Kawakami[f], N. Kamiya[f], J.-R. Shen[b*], K. Yamaguchi[d,e*],

[a] *Center of Computational Sciences, Tsukuba University, Tsukuba, Ibaraki 305-8577, Japan*

[b] *Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan*

[c] *Graduate School of Science, Osaka University, Toyonaka, 560-0043*

[d] *Handairigaku Techno-Research, Toyonaka, Osaka 560-0043.*

[e] *NanoScience Design Center, Osaka University, Toyonaka, Osaka, 560-0043*

[f] *The OUC Advanced Research Institute for Natural Science and Technology (OCARNA), Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan.*

Abstract

Quantum mechanical (QM) and QM/molecular mechanics (MM) simulations of three different cluster models have been performed to illuminate hydrogen bonding networks for proton release pathways (PRP) of water oxidation reaction in the oxygen evolving complex (OEC) of photosystem II (PSII). Positions of all the hydrogen atoms in an extended QM Model III including the second coordination sphere for the active-site $CaMn_4O_5$ complex of OEC have been determined assuming the geometry of heavy atoms determined by the recent high-resolution X-ray diffraction (XRD) experiment of PSII refined to 1.9 Å resolution. Full geometry optimizations of the first coordination sphere model (QM Model I) embedded in the Model III and QM(QM Model I plus seven water molecules) /MM models, together with full QM Model III, have been also conducted to elucidate confinement effects for geometrical parameters of the $CaMn_4O_5$ cluster by proteins. Computational results by these methods have elucidated the O….O(N), O…H distances and O(N)-H…O angles for hydrogen bonds in PRP I and II that construct a proton wire from Asp61 toward His190. The hydrogen bonding structures illuminated have been also examined in relation to possibilities of protonation of bridge oxygen dianions within the $CaMn_4O_5$ cluster. The optimized Mn-Mn and Ca-Mn distances by QM Models I and III, together with QM(Model II)/MM, are examined for illumination of the confinements by protein. Implications of the computational results are discussed in relation to available EXAFS experiments and possible X-ray radiation damage of the $CaMn_4O_5$ cluster and long Mn-Mn distances of the high-resolution XRD that are current topics in the field of OEC of PSII.