1P248 シアノバクテリアのクリプトクロム DASH の変異体は二本鎖 CPD を修復する**Functional conversion of cryptochrome into photolyase**

Tomohiro Suzuki¹, Tatsuya Iwata¹, I Made Mahaputra Wijaya¹, Junpei Yamamoto², Tomoko Ishikawa³, Daichi Yamada¹, Elizabeth D. Getzoff⁴, Shigenori Iwai², Takeshi Todo³, Hideki Kandori¹ (¹*Nagoya Inst. Tech.*, ²*Grad. Sch. Eng. Sci., Osaka Univ.*, ³*Grad. Sch. Med., Osaka Univ.*, ⁴*The Scripps Res. Inst. USA*)

Cryptochrome (CRY) and photolyase (PHR) are flavoproteins whose structures are similar, but functions are entirely different. PHR repairs UV-induced DNA lesions, while CRY is involved in photomorphogenesis, biological clock and magnetoreception. Cryptochrome-DASH (CRY-DASH) is a new type of CRY originally found from cyanobacteria. In vitro experiment showed that CRY-DASH repairs CPD photoproduct in a single-strand DNA (ssCPD), but not in a double-strand DNA (dsCPD). In this study, we introduced mutation to CRY-DASH, and a mutant protein successfully repaired dsDNA, which was monitored by light-induced difference FTIR spectroscopy. Molecular mechanism of functional conversion of CRY into PHR will be discussed.

1P249 FTIR study of isotope-labeled CPD-Photolyase

I M. M. Wijaya¹, Tatsuya Iwata¹, Tilo Mathes², Junpei Yamamoto⁴, Kenichi Hitomi³, Elizabeth D. Getzoff³, Shigenori Iwai⁴, John T. Kennis², Hideki Kandori¹ (¹*Department of Frontier Materials, Nagoya Institute of Technology, Japan*, ²*Department of Physics and Astronomy, VU University, The Netherlands*, ³*Department of Integrative Structural and Computational Biology and The Skaggs Institute for Chemical Biology, The Scripps Research Institute, USA*, ⁴*Graduate School of Engineering Science, Osaka University, Japan*)

CPD-photolyases (PHRs) are flavoproteins that repair CPD-type UV-induced damaged DNA by use of near UV/blue light. We recently reported light-induced difference FTIR spectra of light-induced activation and DNA repair of *E. coli* CPD-PHR[1], whose signals originate from the chromophore (FAD), apo-protein or substrate. To identify vibrational signals, we prepared ¹³C- and ¹⁵N-labeled CPD-PHR enzymes whose chromophore is similarly labeled or unlabeled. Molecular mechanism of activation and DNA repair of CPD-PHR will be discussed on the basis of the FTIR spectral comparison of these systems.

[1] I M. M. Wijaya et al. *Biochemistry* 52, 1019 (2013).

1P250 光駆動ナトリウムポンプの低温赤外分光**Low-temperature FTIR spectroscopy of a light-driven sodium ion pump**

Hikaru Ono¹, Keiichi Inoue^{1,2}, Rei Abe-Yoshizumi¹, Kwang-Hwan Jung³, Hideki Kandori¹ (¹*Nagoya Ins. Of Technol.*, ²*JST PREST*, ³*Sogang Univ. Korea*)

Light-driven outward H⁺ pump bacteriorhodopsin (BR) and inward Cl⁻ pump halorhodopsin (HR) were discovered from Halophilic archaea 35-40 years ago. While HR can pump not only Cl⁻, but also other monovalent cations such as Br⁻, I⁻ and NO₃⁻; microbial rhodopsins can pump only H⁺, no other cations. It may be reasonable because the chromophore (protonated Schiff base of all-trans retinal) is positively charged, so that cations cannot stay in the Schiff base region except for the covalently attached H⁺. However, recent discovery of light-driven outward Na⁺ pump (Inoue et al. *Nature Commun.* 2013) challenges such common understanding in the field. Here we report low-temperature FTIR spectroscopy of a sodium ion pump, from which molecular mechanism will be discussed.

**1P251 霊長類色覚視物質の変異体に対する赤外分光研究
FTIR study of mutants of primate color pigments**

Kota Katayama¹, Daiki Kawata¹, Hiroo Imai², Akimori Wada³, Hideki Kandori¹ (¹*Department of Frontier Materials, Nagoya Institute of Technology*, ²*Primate Research Institute, Kyoto University*, ³*Organic Chemistry for Life Science, Kobe Pharmaceutical University*)

We human distinguish various colors using three proteins that contain a common chromophore, 11-cis-retinal, whereas structural information of color tuning by protein is little known. We have recently reported structural analysis of monkey red (MR) and green (MG) sensitive proteins by low-temperature FTIR spectroscopy. In this study, we prepared mutant proteins (S180A, Y277F and T285A MR, and N318Q MG), and the FTIR spectra were compared to those of MR and MG. We conclude that primate red-green discrimination primarily originates from dipolar interaction of specific amino acids, rather than structural difference. In contrast, we observed water-containing hydrogen-bonding network extended to the cytoplasmic domain, which differs between MR and MG.

1P252 OECのS3状態の反応活性部位の分子構造と酸化状態に関する理論的研究**Theoretical study on molecular structures and oxidation states of active site at the S3 state of OEC**

Tomoya Ichino, Masaki Mitani, Yasunori Yoshioka (*Grad. Sch. Eng., Univ. Mie*)

During the catalysis of water oxidation in nature, the oxygen evolving complex (OEC) passes through five oxidation states (S0 ~ S4). At the S3 state, the oxidation states of four Mn atoms were experimentally assigned as [4 Mn(IV) ions] or [Mn(III) and 3 Mn(IV) ions]. There are also proposals that substrate instead of Mn atom is oxidized to yield an oxygen radical species. In this study, the molecular structures and oxidation states of the active site at the S3 state of OEC have been investigated using B3LYP method. It is found that the most stable state in the triplet state is not the [4 Mn(IV) ions] but the [Mn(III) and 3 Mn(IV) ions] with the outer Mn(IV)-oxyl radical bond. The oxidation states with the Mn(IV)-OH radical or Ca(II)-OH radical bond are unstable.

**1P253 光化学系 II-電極による可視光照射下での水の酸化
Visible light-driven water oxidation by Photosystem II-immobilized electrodes**

Masaru Kato, Miwa Sugiura (*Proteo-Science Center, Ehime Univ.*)

Solar light-driven water splitting into molecular hydrogen and oxygen provides a sustainable route for the production of hydrogen, which is a potentially alternative fuel. The water oxidation reaction to molecular oxygen is known as the bottleneck in the development of water splitting devices, and many water oxidation catalysts including semiconductors and coordination compounds have been developed all over the world.

A photosynthetic protein Photosystem II is the natural water oxidation enzyme and sets the benchmark in terms of oxygen evolution rate under ambient conditions for the development of water oxidation catalysts. We report our progress on the development of metal oxide-based electrodes with PSII for visible light-driven water oxidation.