



# The 5<sup>th</sup> International Conference as the 2012 OCARINA Annual International Meeting.

The 5<sup>th</sup> International Conference as the 2012 OCARINA Annual International Meeting.

4<sup>th</sup>-6<sup>th</sup> March, 2013 Osaka City Univ. Media Center

4<sup>th</sup>-6<sup>th</sup> March, 2013  
Osaka City Univ. Media Center



## **PREFACE**

The OCU-Advanced Research Institute for Natural Science and Technology (OCARINA) sincerely invite you to its 5th International Conference as the 2012 OCARINA Annual International Meeting.

The annual meeting follows the very successful previous meetings. The 1st meeting was held at OCARINA in 2010. The third meeting was held just before the great East Japan Earth Quake (11 March 2011; The 4th meeting was held through 7-9 March). It past two and half years since the building and experimental facilities of OCARINA institute has been settled. Now we will have another facility at the 2nd floor of a newly built Comprehensive Science Research building. Even more the fully related Research Center for Artificial Photosynthesis (ReCAP) for the purpose of active Collaboration between Industry and University. Recently, it attracts very interest to utilize alternative and renewable energy sources. This Conference invites several important researchers from all over the world to discuss the real future of artificial/natural photosynthesis.

The Conference will cover the recent advances and novel progress in the field of Natural and Artificial Photosynthesis to celebrate the settlement of the ReCAP building. Our Institute, OCARINA and ReCAP will walk together with the Research Organization for the 21th Century of Osaka-Prefectural University (OPU). The project of Artificial Photosynthesis for practical achievement is so important and should be co-worked with vicinal Universities. It is our great pleasure to collaborate OPU for celebrating the future partnership.

Finally, we would like to express our sincere gratitude to Osaka City University for the financial support to host this important conference.

The OCU Advanced Research Institute for Natural Science and Technology(OCARINA)  
Director Prof.Dr.Isamu Kinoshita

## 挨拶

2013年3月4, 5, 6日の3日間, 大阪市立大学(杉本町キャンパス) 学術総合情報センターにおきまして, 大阪市立大学複合先端研究機構(OCARINA)の年次総会として第5回OCARINA国際会議を開催いたします。

第1回OCARINA国際会議は2010年に開催され, OCARINAが設立して約2年半経過いたしました。

近年, 再生可能なエネルギー資源への関心が高まる中, 大阪市立大学は産学連携の取組の一つである人工光合成研究センター(Research Center for Artificial Photosynthesis, "ReCAP")を設立し, 今後大阪府立大学の21世紀科学研究機構と協力して人工光合成プロジェクトを推進して行きます。本会議では, 世界各国から光合成研究に係る著名な先生方をお招きして, 人工光合成及びその関連分野における最新の研究成果を発表して頂くとともに, ReCAPの設立を記念することを主な目的としております。

大阪市立大学複合先端研究機構・機構長

木下 勇

Date

4-6th March, 2013

Venue

10thFloor, Osaka City Univ. Media Center

Organizing committee

- Prof. Dr. Hideki Hashimoto (Project Leader of OCARINA)
- Prof. Dr. Isamu Kinoshita (Director of OCARINA)
- Prof. Dr. Keisuke Kawakami (Special-appointment Associate Professor of OCARINA)

Advisory Board

- Prof. Dr. Richard J. Cogdell (FRS, University of Glasgow, UK)
- Prof. Dr. Masakazu Anpo (Vice-President of Osaka Prefecture University, JP)

Plenary speakers (Presentation: 50 mins, Question & Answer: 10 mins)

- Prof. Dr. Leroy Cronin (University of Glasgow, UK)
- Prof. Dr. Wolfgang Lubitz (Max Plank Institute for Chemical Energy Conversion, DE)
- Prof. Dr. Osamu Ishitani (Tokyo Institute of Technology, JP)
- Prof. Dr. Jun Miyake (Osaka University, JP)
- Prof. Dr. Bruno Robert (CEA Saclay, FR)
- Prof. Dr. Ryu Abe (Kyoto University, JP)
- Prof. Dr. Yutaka Amao (Oita University, JP)
- Prof. Dr. Jian-Ren Shen (Okayama University, JP)
- Prof. Dr. Nobuo Kamiya (Osaka City University, JP)

Invited speakers (Presentation: 25 mins, Question & Answer: 5 mins)

- Prof. Dr. Tim Storr (Simon Fraser University, CA)
- Dr. Rudi Berera (Vrije Universiteit Amsterdam, NL)
- Prof. Dr. Masakazu Anpo (Osaka Prefecture University, JP)
- Prof. Dr. Masako Kato (Hokkaido University, JP)
- Prof. Dr. Masahiro Sadakane (Hiroshima University, JP)
- Prof. Dr. Sachiko Matsushita (Tokyo Institute of Technology, JP)

- Prof. Dr. Shigeyuki Masaoka (Institute for Molecular Science, JP)
- Prof. Dr. Yuji Furutani (Institute for Molecular Science, JP)
- Prof. Dr. Hiroshi Isikita (Kyoto University, JP)
- Prof. Dr. Masayuki Yagi (Niigata University, JP)
- Prof. Dr. Toshio Asada (Osaka Prefecture University, JP)
- Prof. Dr. Miwa Sugiura (Ehime University, JP)
- Prof. Dr. Kentaro Ifuku (Kyoto University, JP)
- Prof. Dr. Mitsuo Shoji (University of Tsukuba, JP)
- Prof. Dr. Kenji Kano (Kyoto University, JP)

Invited speakers in OCARINA (Presentation: 25 mins, Question & Answer: 5 mins)

- Prof. Dr. Ritsuko Fujii
- Prof. Dr. Daisuke Kosumi
- Prof. Dr. Masakazu Hirotsu
- Prof. Dr. Yoshimasa Fukushima

## Programme

Monday, 4th March, 2013

- |             |  |
|-------------|--|
| 09:30~      | Opening reception  |
| 10:00~10:05 | Opening Remarks  |
| 10:05~10:15 | Message from Michio Miyano (Vice-President of Osaka City University) |
| 10:15~10:45 | Masakazu Anpo (Osaka Prefecture University)                          |
| 10:45~11:45 | Plenary lecture - Jun Miyake (Osaka University)                      |
| 11:45~12:45 | Poster sessions & Lunch Break  |
| 12:45~13:15 | Shigeyuki Masaoka (Institute for Molecular Science)                  |
| 13:15~13:45 | Tim Storr (Simon Fraser University)                                  |
| 13:45~14:15 | Sachiko Matsushita (Tokyo Institute of Technology)                   |
| 14:15~14:30 | Break  |
| 14:30~15:30 | Plenary lecture - Bruno Robert (CEA Saclay)                          |
| 15:30~16:00 | Ritsuko Fujii (Osaka City University)                                |
| 16:00~16:15 | Break  |
| 16:15~16:45 | Yuji Furutani (Institute for Molecular Science)                      |
| 16:45~17:15 | Miwa Sugiura (Ehime University)                                      |
| 17:15~18:15 | Plenary lecture - Nobuo Kamiya (Osaka City University)               |

Tuesday, 5th March, 2013

- 09:00~10:00 Plenary lecture - Wolfgang Lubitz (Max Plank Institute for  
Chemical Energy Conversion)  
10:00~10:30 Yoshimasa Fukushima (Osaka City University)  
10:30~10:40 Break  
10:40~11:10 Daisuke Kosumi (Osaka City University)  
11:10~11:40 Mitsuo Shoji (University of Tsukuba)  
11:40~13:40 Artificial photosynthesis forum, Poster sessions, & Lunch  
Break  
13:40~14:40 Plenary lecture - Leroy Cronin (University of Glasgow)  
14:40~15:10 Masahiro Sadakane (Hiroshima University)  
15:10~15:40 Rudi Berera (Vrije Universiteit Amsterdam)  
15:40~15:50 Break  
15:50~16:20 Kentaro Ifuku (Kyoto University)  
16:20~16:50 Hiroshi Ishikita (Kyoto University)  
16:50~17:50 Plenary lecture - Jian-Ren Shen (Okayama University)  
18:00~ Banquet

Wednesday, 6th March, 2013

- 09:00~10:00 Plenary lecture - Osamu Ishitani (Tokyo Institute of  
Technology)  
10:00~10:30 Masayuki Yagi (Niigata University)  
10:30~10:40 Break  
10:40~11:10 Masakazu Hirotsu (Osaka City University)  
11:10~11:40 Masako Kato (Hokkaido University)  
11:40~12:40 Poster sessions & Lunch Break  
12:40~13:40 Plenary lecture - Ryu Abe (Kyoto University)  
13:40~14:10 Toshio Asada (Osaka Prefecture University)  
14:10~14:20 Break  
14:20~14:50 Kenji Kano (Kyoto University)  
14:50~15:50 Plenary lecture - Yutaka Amao (Oita University)  
15:50~ Closing Remarks

#### 日時

2013年3月4日(月) 午前9時30分～午後6時15分

2013年3月5日(火) 午前9時～午後5時50分

2013年3月6日(水) 午前9時～午後4時(予定)

#### 会場

大阪市立大学学術情報総合センター10階

大阪市住吉区杉本3丁目3番138号 Tel:06-6344-9560

#### 主催

大阪市立大学複合先端研究機構 (OCARINA)

#### 後援

大阪市立大学・重点研究プログラム

物質分子系の組織的な大学院教育改革の推進と化学人材育成

#### 組織委員

- ・橋本 秀樹 (大阪市立大学複合先端研究機構・プロジェクトリーダー/大学院理学研究科・教授)
- ・木下 勇 (大阪市立大学複合先端研究機構・機構長/大学院理学研究科・教授)
- ・川上 恵典 (大阪市立大学複合先端研究機構・特任准教授)

#### 顧問委員

- ・Prof. Dr. Richard J. Cogdell (FRS, University of Glasgow, UK)
- ・安保 正一 (大阪府立大学・理事・副学長兼地域連携研究機構長)

#### 招待講演者

- ・Prof. Dr. Leroy Cronin (University of Glasgow, UK)
- ・Prof. Dr. Wolfgang Lubitz (Max Planck Institute for Chemical Energy Conversion, DE)
- ・Prof. Dr. Bruno Robert (CEA Saclay, FR)
- ・Prof. Dr. Tim Storr (Simon Fraser University, CA)
- ・Dr. Rudi Berera (Vrije Universiteit Amsterdam, NL)
- ・石谷 治 (東京工業大学大学院理工学研究科・教授)
- ・三宅 淳 (大阪大学大学院基礎工学研究科・教授)
- ・阿部 竜 (京都大学大学院工学研究科・教授)

- ・天尾 豊（大分大学工学部応用化学科・准教授）
- ・沈 建仁（岡山大学自然科学研究科・教授）
- ・安保 正一（大阪府立大学・理事・副学長兼地域連携研究機構長）
- ・加藤 昌子（北海道大学大学院理学研究院・教授）
- ・定金 正洋（広島大学大学院工学研究院・准教授）
- ・松下 祥子（東京工業大学大学院理工学研究科・准教授）
- ・正岡 重行（自然科学研究機構分子科学研究所・准教授）
- ・古谷 祐詞（自然科学研究機構分子科学研究所・准教授）
- ・石北 央（京大生命科学研究科キャリアパス形成ユニット・特定助教）
- ・八木 政行（新潟大学工学部・教授）
- ・麻田 俊雄（大阪府立大学理学部・准教授）
- ・杉浦 美羽（愛媛大学無細胞生命科学研究センター・准教授）
- ・伊福 健太郎（京都大学大学院生命科学研究科・助教）
- ・庄司 光男（筑波大学計算科学研究センター・助教）
- ・加納 健司（京都大学大学院農学研究科・教授）

#### 学内招待講演者

- ・神谷 信夫（大阪市立大学複合先端研究機構/大学院理学研究科・教授）
- ・廣津 昌和（大阪市立大学大学院理学研究科・准教授）
- ・藤井 律子（大阪市立大学複合先端研究機構・特任准教授）
- ・小澄 大輔（大阪市立大学複合先端研究機構・特任准教授）
- ・福島 佳優（大阪市立大学複合先端研究機構・特任助教）

#### プログラム

3月4日（月）

- 09:30～ 開場・受付
- 10:00～10:05 開会の辞
- 10:05～10:15 副学長挨拶/宮野 道雄（大阪市立大学・副学長）
- 10:15～10:45 安保 正一（大阪府立大学・理事・副学長兼地域連携研究機構長）
- 10:45～11:45 <基調講演 1>三宅 淳（大阪大学大学院基礎工学研究科・教授）
- 11:45～12:45 ポスターセッション & 昼食
- 12:45～13:15 正岡重行（自然科学研究機構 分子科学研究所・准教授）
- 13:15～13:45 Tim Storr (Simon Fraser University)
- 13:45～14:15 松下 祥子（東京工業大学大学院理工学研究科・准教授）

- 14:15~14:30 休憩
- 14:30~15:30 <基調講演 2> Bruno Robert (CEA Saclay)
- 15:30~16:00 藤井 律子 (大阪市立大学複合先端研究機構・特任准教授)
- 16:00~16:15 休憩
- 16:15~16:45 古谷 祐詞 (自然科学研究機構 分子科学研究所・准教授)
- 16:45~17:15 杉浦 美羽 (愛媛大学無細胞生命科学工学研究センター・准教授)
- 17:15~18:15 <基調講演 3> 神谷 信夫 (大阪市立大学複合先端研究機構/大学院理学研究科・教授)

2013年3月5日(火)

- 09:00~10:00 <基調講演 4> Wolfgang Lubitz (Max Plank Institute for Chemical Energy Conversion)
- 10:00~10:30 福島 佳優 (大阪市立大学複合先端研究機構・特任助教)
- 10:30~10:40 休憩
- 10:40~11:10 小澄 大輔 (大阪市立大学複合先端研究機構・特任准教授)
- 11:10~11:40 庄司 光男 (筑波大学計算科学研究センター・助教)
- 11:40~13:40 人工光合成フォーラム, ポスターセッション, 昼食
- 13:40~14:40 <基調講演 5> Leroy Cronin (University of Glasgow)
- 14:40~15:10 定金 正洋 (広島大学大学院工学研究院・准教授)
- 15:10~15:40 Rudi Berera (Vrije Universiteit Amsterdam)
- 15:40~15:50 休憩
- 15:50~16:20 伊福 健太郎 (京都大学大学院生命科学研究科・助教)
- 16:20~16:50 石北 央 (京大生命科学研究科キャリアパス形成ユニット・特定助教)
- 16:50~17:50 <基調講演 6> 沈 建仁 (岡山大学自然科学研究科・教授)
- 18:00~ 懇親会

2013年3月6日(水)

- 09:00~10:00 <基調講演 7> 石谷 治 (東京工業大学大学院理工学研究科・教授)
- 10:00~10:30 八木 政行 (新潟大学工学部・教授)
- 10:30~10:40 休憩
- 10:40~11:10 廣津 昌和 (大阪市立大学大学院理学研究科・准教授)
- 11:10~11:40 加藤 昌子 (北海道大学大学院理学研究院・教授)
- 11:40~12:40 ポスターセッション & 昼食
- 12:40~13:40 <基調講演 8> 阿部 竜 (京都大学大学院工学研究科・教授)

13:40~14:10 麻田 俊雄 (大阪府立大学理学部・准教授)  
14:10~14:20 休憩  
14:20~14:50 加納 健司 (京都大学大学院農学研究科・教授)  
14:50~15:50 <基調講演 9>天尾 豊 (大分大学工学部応用化学科・准教授)  
15:50~ 閉会の辞

# Invited Lectures



Monday, 4th March





## The Science and Technology of Artificial Photosynthesis-based on Ti-oxide Photocatalysts

Masakazu ANPO

Vice President & Executive Director, Osaka Prefecture University  
1-1 Gakuen-cho, Sakai-city, Osaka 599-8531, Japan

Osaka Prefecture University is a partner of the Artificial Photosynthesis Research Center of Osaka City University and, in this presentation, the science and technology of artificial photosynthesis incorporating our newly developed visible light-responsive Ti-oxide photocatalysts will be introduced.

Environmentally harmonious, clean, safe and sustainable chemical technology and processes are required to address pollution and climate change and are, thus, the subject of much research and discussion. Artificial photosynthesis, in which abundant and clean solar energy can be harnessed, would be a major advance in the development of sustainable, non-hazardous and cost-efficient technologies. The development of highly functional Ti-oxide photocatalytic materials is especially promising and, significantly, the photo-induced super-hydrophilic properties of TiO<sub>2</sub> thin films for such applications as self-cleaning and anti-fogging in mirrors and bone-titanium integration with high bio-compatibility have already been realized.

Unlike the natural photosynthesis in green plants, conventional photocatalytic materials can make use of only 3-4% of the sunlight reaching earth, necessitating the use of a UV light source. However, as we have reported since 2000, visible light-responsive Ti-oxide photocatalytic materials which enable the absorption of visible light and can operate under sunlight irradiation have been successfully developed. These developed Ti-oxide materials were found to work as effective environmentally-friendly photocatalysts, leading to the efficient use of solar energy for production of clean energies and other significant reactions.

This lecture introduces the most promising approaches in the development of highly functional TiO<sub>2</sub> thin film materials for applications in photocatalytic devices for the solar splitting of H<sub>2</sub>O into H<sub>2</sub> and O<sub>2</sub> by separate evolution as well as the design of solid solar cells and photo-induce fuel cells without the use of any organic dye sensitizers.

- 1) M. Anpo, M. Takeuchi, *J. Catal.*, **216** 505 (2003) and references therein.
- 2) M. Anpo, M. Matsuoka, *Annu. Rev. Mater. Res.*, Ed., J.M. Thomas, **35**, 233 (2005).
- 3) M. Matsuoka, M. Anpo, *Green Catalysis*, Ed., P.T. Anastas, Wiley-VCH, 59 (2009).
- 4) M. Anpo, P. V. Kamat, *Environmentally Benign Photocatalysts*, Springer (2010).

## Pathway for BioHydrogen Realization



**Jun Miyake and Kazumi Hakamada**

*Graduate School of Engineering Science, Osaka University  
1-3 Machikaneyama, Toyonaka, Osaka 560-8531 Japan*

Diversification of energy is required to stabilize the supply other than oil, gas and nuclear power. However, renewable natural power sources, such as sunlight and wind force, have low energy density, and it is a fault that a time jitter occurs. The entropic problems in wind and solar cell as collection and stabilization requires much energy.

Biomass is the most abundant energy source available in the world. Problem is the cost for the collection of biomass. A conceptual classification is given below based on the size of the biomass accumulation. I should like to explain the scientific evaluation of the difficulty and the possible technological directions, based on the table below.

Table 1. Scale and Possibility of BioEnergy Production

- 
1. Abundant Biomass Available (as Ethanol Production Waste in Brazil)  
→ Realistic application possible with a large scale (Very low entropy state)
  2. Large Amount of Biomass Accumulation as Factory/Municipal Wastes  
→ Application possible for special purpose (Low entropy state)
  3. Community Scale Waste  
→ The most difficult situation (High entropy state)
  4. Very Remote Area without Any Other Energy Supply  
→ Biomass Could be the Primal Energy Source
- 

The most difficult technology should be in the category No.3. Entropic view gives us the mechanism of the difficulty. Collection of biomass of a large amount needs energy, which would be very high in some situation. The application study of biohydrogen for the community is being studied by many researchers.

Bacteria are the system changed as energy which can exploit natural power sources. Photosynthesis bacteria can be used for the large-scale reactor which changes light energy into hydrogen by little investment, in order to carry out self-multiplication.

Accumulation of the hydrogen also reduces a time jitter. That is, it is thought that the energy transduction of bacteria has a meaning as technology corresponding to a difficult subject (entropy) in engineering of an energy collection and equalization.

Equipment and an energy investment -- the large-scale equipment for appearing natural power sources and securing the amount of collections of cargo for using in society is needed, and a large-scale accumulation of electricity is required to also cover a time jitter, and there is in it -- become large and difficult to serve as realistic technology easily.

It is thought that creation of an energy transduction method which is called the equalization of energy which carries out a time jitter to the thermodynamic entropy problem of accumulation of thin energy and which can similarly conquer an entropy problem is needed.

We should like to show a system design of a grid composed of several elements (Electric Grid, Wind Turbine, Solar Cell and BioHydorgen). Effect of the reduction of entropic loss is going to be examined theoretically and experimentally.

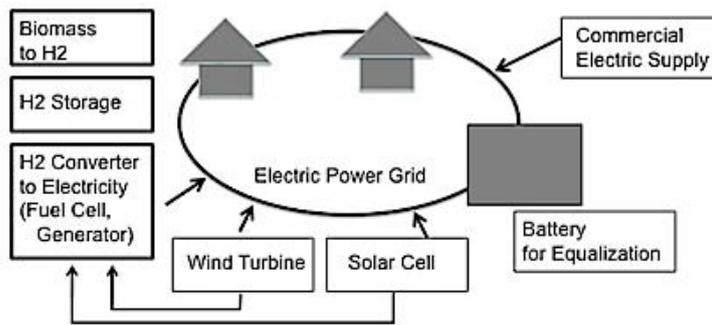


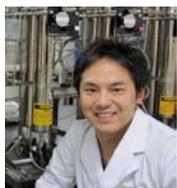
Fig. BioHydrogen as an Equalization Element for Power Grid

Acknowledgements:

This work was supported by Strategic China-Japan Cooperative Programme on “Science and Technology (S&T) for Environmental Conservation and Construction of a Society with Less Environmental Burden” “Energy Recycling Technology for Waste and Exhaust Heat” (Jun Miyake, Osaka and Katsutoshi Hori, Nagoya, Japan and Xin-Hui Xing, Tsinghua, China).

**References:**

- 1) T. Kihara, X.Y. Liu, C. Nakamura, K.M. Park, S.W. Han, D.J. Qian, K. Kawasaki, N.A. Zorin, S. Yasuda, K. Hata, T. Wakayama, J. Miyake, Direct electron transfer to hydrogenase for catalytic hydrogen production using a single-walled carbon nanotube forest, *Int. J. Hydrogen Energy* 36, 7523-7529 (2011).
- 2) Asada, Y., Tokumoto, M., Aihara, Y., Oku, M., Ishimi, K., Wakayama, T., Miyake, J., Tomiyama, M., Kohno, H., Hydrogen production by co-cultures of *Lactobacillus* and a photosynthetic bacterium, *Rhodobacter sphaeroides* RV, *Int. J. hydrogen Energy* 31, 1509-1513 (2006).
- 3) K. Hori, M. Ishikawa, M. Yamada, A. Higuchi, Y. Ishikawa, and H. Ebi; Production of peritrichate bacterionanofibers and their proteinaceous components by *Acinetobacter* sp. Tol 5 cell affected by growth substrates, *J. Biosci. Bioeng.* 111, 31-36 (2010).
- 4) Feng Q, Wang Y, Wang T, Zheng H, Chu L, Zhang C, Chen H, Kong X, Xing XH. , Effects of packing rates of cubic-shaped polyurethane foam carriers on the microbial community and the removal of organics and nitrogen in moving bed biofilm reactors. *Bioresour Technol.* 117, 201-7 (2012).



## Water Oxidation by Mono- and Multinuclear Metal Complexes

Shigeyuki Masaoka

*Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan, and PRESTO, Japan Science and Technology Agency (JST), Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan*

Water splitting to H<sub>2</sub> and O<sub>2</sub> using sunlight is one of the most important chemical processes to provide the solution for the energy and environmental problems encountered in our society. Water oxidation ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ), one of two half-reactions for water splitting, provides electrons and protons for the other half-reaction (hydrogen evolution). The water oxidation step has long been considered as the bottleneck of the water-splitting process, so the development of highly active and robust water oxidation catalysts is a key step to accomplish light-driven water splitting.

We recently reported that some mononuclear ruthenium complexes serve as highly active water oxidation catalysts [1], although it has long been believed that only dinuclear metal complexes are active for water oxidation. We have also investigated the reaction mechanism of water oxidation catalyzed by the mononuclear catalysts, revealing that these catalysts can be classified into two groups that have different rate-determining steps (RDS). In one class, the RDS is a homolytic radical coupling between two catalyst species. For the other class, the step is a heterolytic radical coupling between the catalyst and the oxidant. Based on these reaction mechanisms, new multinuclear metal complexes were designed and developed as candidates for a new class of water oxidation catalysts. In this talk, recent progress of our study will also be presented [2].

[1] (a) S. Masaoka, K. Sakai, *Chem. Lett.*, **2009**, 38, 182. (b) M. Yoshida, S. Masaoka, K. Sakai, *Chem. Lett.*, **2009**, 38, 702. (c) M. Yoshida, S. Masaoka, J. Abe, K. Sakai, *Chem. Asian J.*, **2010**, 5, 2369. (d) J. Kiyota, J. Yokoyama, M. Yoshida, S. Masaoka, K. Sakai, *Chem. Lett.*, **2010**, 39, 1146. (e) A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka, K. Sakai, *Chem. Commun.*, **2012**, 48, 239. (f) M. Okamura, M. Yoshida, R. Kuga, K. Sakai, M. Kondo, S. Masaoka, *Dalton Trans.*, **2012**, 41, 13081.

[2] (a) M. Kobayashi, S. Masaoka, K. Sakai, *Angew. Chem. Int. Ed.*, **2012**, 51, 7431. (b) K. Kuroiwa, M. Yoshida, S. Masaoka, K. Kaneko, K. Sakai, N. Kimizuka, *Angew. Chem. Int. Ed.*, **2012**, 51, 656. (c) K. Yamauchi, S. Masaoka, K. Sakai, *J. Am. Chem. Soc.*, **2009**, 131, 8404. (d) T. Yamaguchi, S. Masaoka, K. Sakai, *Chem. Lett.*, **2009**, 38, 434.

# Oxidized Metal Phenoxide Complexes - Correlation of Electronic Structure and Reactivity



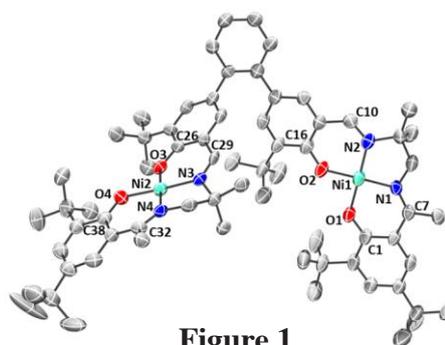
Tim Storr,\* Linus Chiang, Tim J. Dunn

Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A-1S6, Canada \*Corresponding author: tim\_storr@sfu.ca

The interplay of redox-active transition metal ions and pro-radical ligands in metalloenzyme sites is an area of considerable research interest. Galactose oxidase (**GOase**), a mononuclear copper enzyme with a Cu(II)-phenoxyl radical active oxidant, is the archetypical example. The simplicity of the single copper active site of the enzyme galactose oxidase,[1] which functions by catalyzing the oxidation of primary alcohols to aldehydes while reducing dioxygen to hydrogen peroxide, has inspired efforts to develop small molecule mimics capable of mild and selective alcohol oxidation. Recent developments show that ligands serving as electron reservoirs offer opportunities to expand catalysis, especially by conferring to first-row transition metals a “noble metal-like” reactivity.[2] To this end, we have investigated the chemistry of a series of simple oxidized mono- and bis-phenoxide metal complexes, which demonstrate that small variations of the ligand structure affect the locus of oxidation.[3] Characterization of the oxidized complexes has afforded significant insight into the electronic structure of these ligand radical systems.

We are currently investigating both monometallic and bimetallic ligand radical complexes (Figure 1). The oxidized forms are characterized by both experimental (low temperature UV-Vis-NIR spectroscopy, electrochemistry, x-ray crystallography, resonance Raman) and theoretical methods. DFT calculations provide insight into the oxidation locus, providing further information of the electronic structure.

We have shown that small changes to ligand structure influences ligand radical localization. We are now using this information to probe the effect of radical localization on reactivity for a large number of mono- and bi-metallic systems.



**Figure 1**

**References:** [1] N. Ito, S. E. V. Phillips, C. Stevens, Z. B. Ogel, M. J. McPherson, J. N. Keen, K. D. S. Yadav and P. F. Knowles, *Nature*, **1991**, 350, 87. [2] P. J. Chirik and K. Wieghardt, *Science*, **2010**, 327, 794. [3] L. Chiang, A. Kochem, O. Jarjayes, T. J. Dunn, H. Vezin, M. Sakaguchi, T. Ogura, M. Orio, Y. Shimazaki, F. Thomas and T. Storr, *Chem. Eur. J.*, **2012**, 18, 14117; T. J. Dunn, M. I. Webb, K. Hazin, P. Verma, E. C. Wasinger, Y. Shimazaki and T. Storr, *Dalton Trans.*, **2013**, DOI:10.1039/C2DT32632A.



## Preparation of Mesoporous Oxide Monoliths and the Photocatalytic Activity

Sachiko Matsushita\*, Takashi Nogawa, Toshihiro Isobe, Akira Nakajima

Department of Metallurgy & Ceramics Science, Tokyo Institute of Technology,  
2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, JAPAN Tokyo Institute of Technology,  
JAPAN

e-mail: matsushita.s.ab@m.titech.ac.jp

An organic monolith is a continuous interconnected skeleton with large through-pores. This structure reduces the diffusion path and provides high permeability, resulting in excellent separation efficiency. Such organic monolith, which can be produced by self-organization in polymer phase separation, might be an excellent template as a catalyst.[1] In this research, porous spherical metal oxide particles were prepared by impregnation of a Titanium precursor and Si precursor solution into the organic monolith sphere particles (8  $\mu\text{m}$  diameter, MBP-8, Sekisui Plastics Co. Ltd.) at room temperature, with subsequent calcining in air. The scanning electron microscopy (SEM), and  $\text{N}_2$  adsorption-desorption isotherms and BJH equation analysis revealed that our samples were porous spheres mainly sized pores of around 2 and 10 nm (Fig. 1). Larger pores of around 55 nm were also convinced by SEM observations.

Addition of Si precursor decreased the  $\text{TiO}_2$  crystallinity and increased the specific surface area and the width of bandgap (Fig. 2). The photocatalytic reduction activities of these samples were examined using  $\text{CO}_2$ -vapor under UV light irradiation. The generation of CO was convinced.

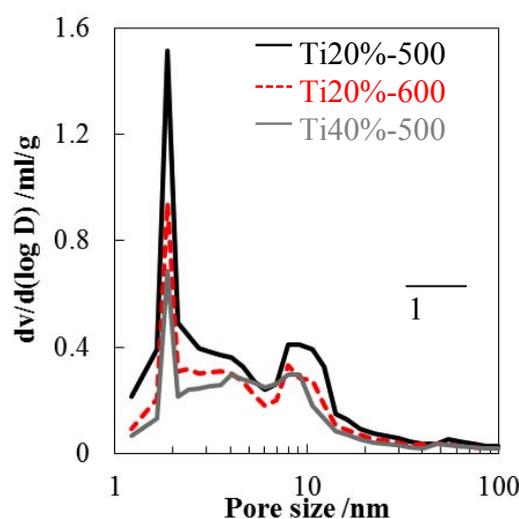


Figure 1. Ti precursor concentration and calcining temperature dependence of pore size distribution for obtained  $\text{TiO}_2$ – $\text{SiO}_2$  composite particles. The SEM image of the samples sintered at 500°C is shown in inset.

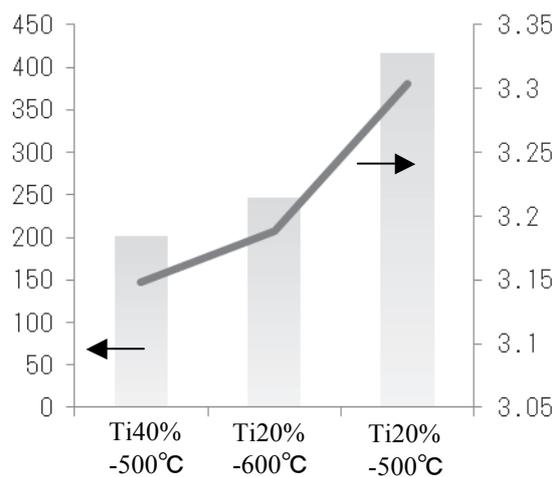


Figure 2. Total pore area and bandgap for obtained  $\text{TiO}_2$ – $\text{SiO}_2$  composite particles. The volume percentage of titanium precursor in raw materials and the sintered temperature were noted at bottom.

**References:** [1] Uchiyama, S.; Isobe, T.; Matsushita, S.; Nakajima, K.; Hara, M.; Nakajima, A., *J. Mater. Sci.* **2011**, *47* (1), 341.



## Molecular Basis of Photoprotection

Bruno Robert

*Institute of Biology and Technology CEA Saclay, 91191 Gif/Yvette Cedex. France  
bruno.robert@cea.fr*

Through their light-harvesting antenna, plants frequently absorb more solar energy than they can use in photosynthesis. This excess energy has the potential to cause cell damage, such as pigment bleaching and protein inactivation. To minimise photodamage, a number of protection mechanisms exist, which we have characterized at a molecular/functional level. I will discuss the following mechanisms in the light of our most recent results

*Protection against photooxidative stress induces by high light environments : shaping proteins in large multimolecular architectures*

Excitation energy quenchers rapidly appear in the photosynthetic membrane of plants and algae when these organisms are exposed to high illumination conditions. Until recently, this mechanism was still poorly understood. In the last years, combined use of advanced spectroscopic methods, first applied on isolated light-harvesting complexes then developed for their application on systems as complicated as whole leaves, have yielded a precise picture of the molecular events which underlie this important mechanism of photoprotection in higher plants. I will report recent results showing that these mechanisms actually occur upon the build-up of the large macrocomplexes of photosystem II, *i.e.* that the protein-protein interactions in these complexes shape the structure and function of antenna proteins.

*Triplet-triplet transfers between chlorophyll and carotenoid molecules : from natural to artificial photosynthesis*

We recently showed that in most light-harvesting proteins of oxygenic organisms, the pigment organization dramatically modify the properties of the triplet states, in order to minimize the production of singlet oxygen. I will report the excitation energy cascade in these complexes, as well as in artificial systems such as phtalocyanin/carotenoid dyads, and how we can access to the structure of these triplet states.



## Structure of siphonaxanthin bound to the newly isolated photosynthetic antenna from a deep-sea green alga, *Codium intricatum*

○FUJII, Ritsuko<sup>1,2</sup>; SHIGEMATSU, Yusuke<sup>3</sup>; OKA, Naohiro<sup>4</sup>; IHA, Masahiko<sup>4</sup>; HASHIMOTO, Hideki<sup>1,3,5</sup>

<sup>1</sup>OCARINA/OCU; <sup>2</sup>JST-PRESTO; <sup>3</sup>Osaka City Univ.; <sup>4</sup>South Product Inc.; <sup>5</sup>JST-CREST

**Abstract:** One of an issue of the Solar-fuel system is how to utilize the low-density photon from the sun. Natural photosynthetic organisms have developed a variety of light-harvesting system, so-called "photosynthetic antenna", to collect the photon to transfer the excited energy to the reaction center in a proper time scale. At 10-20 m below the sea level, only a dim blue-green light can penetrate. Thus the photosynthetic antenna of deep-sea phototrophs shows highly efficient light-harvesting function. We aimed to extract the essence of the efficient energy utilization system to make use of the result for the Solar-fuel system.

Some of green alga from deep sea shows olive drab color and they are called "siphonous" green alga because they have a unique pigment, siphonaxanthin (Sx). It is bound to the photosynthetic antenna, Sx-chlorophyll *a/b* protein (SCP), and harvest blue-green region of light. The Sx content were quite scattering among the collected alga from the seashore. We have been recently successful to optimize the Sx content by culturing one of the siphonous green alga, *Codium intricatum* Okamura as its filamentous body. In this study, we purified the SCP and determined its partial primary structure by MALDI-TOF-MS/PSD, and its quaternary structure by Blue Native-PAGE, as well as its pigment compositions by a combination of HPLC, LC-MS, and <sup>1</sup>H-NMR. The SCP forms a trimer consists of a subunit, whose partial sequences show high homology to the well-studied light-harvesting complex from higher plants, LHCII. Pigment analyses revealed that both Sx and Sx C12:O ester (see the figure) were equally bound to the SCP and the pigment composition was identical to that of the LHCII except for Sx and Sx ester is the substitutes for the two molecules of lutein. Therefore the structure of Sx (and Sx ester) in the SCP can be estimated by using the X-ray structure of the pea LHCII at 2.5Å resolution [1].

**References:** [1] Standfuss, J.; van Scheltinga, A.C. T.; Lamborghini, M; Kühlbrandt, W. *Embo J.* **2005**, 24, 919.

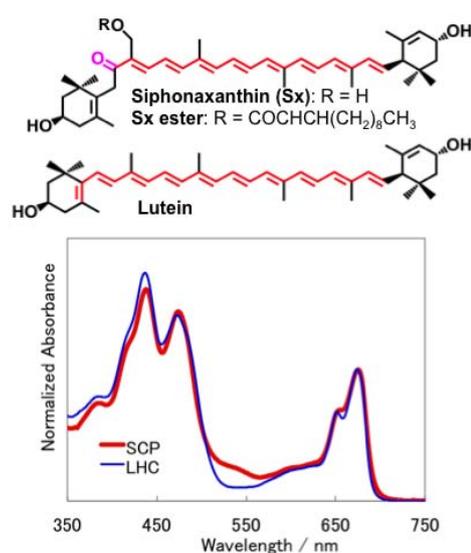
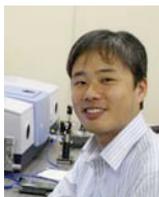


Fig. Chemical structures of carotenoids and absorption spectra of corresponding photosynthetic antennae



## Water Molecules and Ions in Membrane Proteins Studied by FTIR Spectroscopy

Yuji Furutani<sup>1,2,3</sup>

<sup>1</sup>*Department of Life and Coordination-Complex Molecular Science,  
Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan*

<sup>2</sup>*Department of Structural Molecular Science, The Graduate University for Advanced  
Studies (SOKENDAI), Myodaiji, Okazaki 444-8585, Japan*

<sup>3</sup>*PRESTO, Japan Science and Technology Agency(JST),  
4-1-8 Honcho Kawaguchi, Saitama, 332-0012, Japan*

**Abstract:** Membrane proteins play crucial roles for receiving external stimuli, transporting and permeating protons and ions to generate biological energy and signal, and incorporating nutrients and excreting unfavorable chemicals, and so on. The molecular mechanisms of membrane proteins have been deepened with the progress in structural biology. Elucidation of atomic structures of various kinds of G protein coupled receptors (GPCRs) and its active form complex with G protein is a milestone, leading to the Nobel prize in chemistry 2012. Another great progress was done by Japanese groups (Profs. Kamiya and Shen). They revealed the precise coordination structure of the Mn cluster in photosystem II, which impacted on chemists in various fields, especially the researchers aiming to realize artificial photosynthesis. However, X-ray crystallography captures a static structure of protein restricted by steric constraint in the crystal lattice. The structural changes which connect the inactive and active states of protein should be elucidated by using other physicochemical methods.

Fourier-transform infrared (FTIR) spectroscopy is one of powerful method for investigating molecular structures in the level of chemical bonds. In general, large number of atoms in a protein molecule hampers resolving each normal mode in the infrared spectrum. Therefore, stimulus-induced difference infrared spectroscopy has been applied to extract structural changes of protein in response to various stimuli. Light is one of important stimulus for life and can be easily controlled by modern electronics and laser techniques. Inorganic ions permeate ion channels and are vectorially transported by pumps and transporters. The selectivity of ions, especially discrimination between potassium and sodium ions, is important for understanding the molecular mechanisms of the ion channels and transporters.

In this talk, I'd like to introduce my recent studies on a light-driven chloride ion pump, *pharaonis* halorhodopsin (*pHR*), and a potassium ion channel, KcsA. The structural changes of *pHR* including water molecules inside protein has been revealed by time-resolved FTIR spectroscopy. We analyzed the dynamics of the dangling bonds of water molecules, which

are free from the hydrogen-bonding network, and discussed the relationship with the ion-transporting mechanism [1]. KcsA is a well-known potassium ion channel whose precise X-ray structures in various conditions have been reported. We have applied attenuated total reflection FTIR (ATR-FTIR) spectroscopy to reveal the ion-protein interaction of the selectivity filter of KcsA, which is a special part for discriminating potassium ions from sodium ions. We succeeded to assign the C=O stretching vibrations of the selectivity filter in the amide I region [2]. By analyzing the bands, we characterized the coordination structure of the carbonyl groups and the affinity for potassium ions.

FTIR spectroscopy could be a complementary method for investigating the structural changes of protein as a result of reception of various stimuli and specific interactions with ions, ligands, and inhibitors. After revealing X-ray crystal structures of proteins, FTIR spectroscopy would help the researchers to investigate the molecular mechanisms of the proteins in more detail.

#### **References:**

- [1] Furutani, Y.; Fujiwara, K.; Kimura, T; Kikukawa, T.; Demura, M.; Kandori, H. *J. Phys. Chem. Lett.* **2012**, 3, 2964.
- [2] Furutani, Y.; Shimizu, H.; Asai, Y.; Fukuda, T.; Oiki, S.; Kandori, H. *J. Phys. Chem. Lett.* **2012**, 3, 3806.



## Regulation of electron transfer in Photosystem II

Miwa SUGIURA

*Cell-Free Science and Technology Research Center, Ehime University  
JST-PRESTO*

In the photosynthetic primary process of plants, algae and cyanobacteria, Photosystem II (PSII) cooperates in series to convert photon energy into chemical energy through light-induced charge separation and subsequent electron transfers. The light-driven water oxidation by PSII enzyme is responsible for the production of  $O_2$  on Earth, and is at the origin of the synthesis of most of the biomass. PSII is a supracomplex that consists with 17 membrane-spanning proteins and 3 extrinsic proteins involving over 80 cofactors such as chlorophylls,  $\beta$ -carotenes, non-heme irons, plastoquinones, lipids, and so on [1]. The reaction centre proteins, D1 and

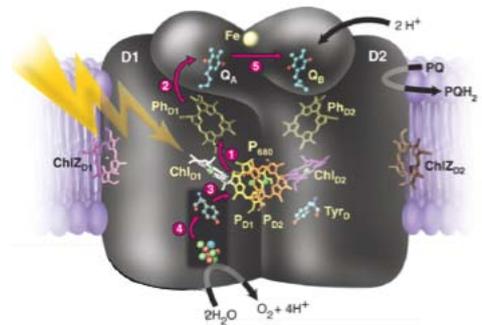


Fig. 1. Electron transport and water oxidation in PSII.

D2, bind all the redox-active cofactors involved in the energy conversion process and the following sequence of reactions occurs. As shown in Fig. 1, firstly, a special form of Chl $a$ ,  $P_{680}$ , acts as an exciton trap and converted to a strong reducing agent after excitation ( $P_{680}^*$ ). Within a few picoseconds,  $P_{680}^*$  reduces a pheophytin (Pheo) to form the radical par state  $P_{680}^{+*}Pheo^{\cdot-}$ , then  $Pheo^{\cdot-}$  reduces a primary plastoquinone  $Q_A$  to produce  $P_{680}^{+*}Pheo^{\cdot-}$ . The  $P_{680}^{+*}$ , which has a very high redox potential ( $> 1.2$  V), oxidises a  $Tyr_Z$  to form  $Tyr_Z^{+*}P_{680}PheoQ_A^-$  on a nanosecond. On a millisecond scale,  $Q_A^-$  reduces a second plastoquinone  $Q_B$  to form  $Tyr_Z^{+*}P_{680}PheoQ_AQ_B^-$ . The oxidised  $Tyr_Z^{+*}$  extracts an electron and proton from a  $Mn_4CaO_5$  cluster. A second photochemical turnover reduces  $Q_B^-$  to  $Q_B^{2-}$ . Two further photochemical turnovers provide the  $Mn_4CaO_5$  cluster with a total of four oxidising equivalents.

The main cofactors involved in the function of PSII are borne by the D1 and D2 proteins. In cyanobacteria, the D1 protein may be encoded by several *psbA* genes which are known to be possibly expressed differentially depending on the environmental conditions. In the cyanobacterium *Thermosynechococcus elongatus* there are 3 different *psbA* genes coding for D1. Among the 344 residues constituting D1 there are 21 differences between PsbA1 and PsbA3, 31 between PsbA1 and PsbA2 and 27 between PsbA2 and PsbA3. By those substitutions functions of PSII are modified especially in water oxidation rate and redox potentials of cofactors[1-6]. In this symposium, regulation system of D1 gene expression and functional difference due to the partial modification of structure in PSII complexes.

#### References:

- [1] Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N. *Nature* **2011**, 473, 55.
- [2] Sugiura, M.; Kato, Y.; Takahashi, R.; Suzuki, H.; Watanabe, T.; Noguchi, T.; Rappaport, F.; Boussac, A. *Biochim. Biophys. Acta* **2010**, 1797, 1491.
- [3] Ogami, S.; Boussac, A.; Sugiura, M. *Biochim. Biophys. Acta* 2012, 1817, 1322.
- [4] Sugiura, M.; Ogami, S.; Kusumi, M.; Un, S.; Rappaport, F.; Boussac, A. *J. Biol. Chem.* **2012**, 287, 13336.
- [5] Kato, Y.; Sugiura, M.; Oda, A.; Watanabe, T. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, 106, 17365.
- [6] Kato, Y.; Shibamoto, T.; Yamamoto, S.; Watanabe, T.; Ishida, N.; Sugiura, M.; Rappaport, F.; Boussac, A. *Biochim. Biophys. Acta* **2012**, 1817, 1998



## Structure and Function of $\text{Mn}_4\text{CaO}_5$ Cluster in Water-Splitting and Oxygen-Evolving Photosystem II

Nobuo Kamiya, *The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University, Osaka 558-8585, Japan.* E-mail: [nkamiya@sci.osaka-cu.ac.jp](mailto:nkamiya@sci.osaka-cu.ac.jp)

Photosystem II (PSII) performs light-induced electron transfer and water-splitting reactions leading to the formation of molecular oxygen. PSII from thermophilic cyanobacteria consists of seventeen membrane-spanning subunits, three hydrophilic, peripheral subunits, and many cofactors with a total molecular weight of 350 kDa for a monomer. Recently, crystal quality of PSII from *Thermosynechococcus vulcanus* has been improved significantly, and the crystal structure has reported by our group at a resolution of 1.9 Å [1]. Electron density distributions for each of the five metal ions in the water-splitting and oxygen-evolving  $\text{Mn}_4\text{Ca}$ -cluster are clearly separated to locate the individual metal ions and all of the ligands to the metal cluster unambiguously. Five oxygen atoms forming oxo-bridges between the metal ions are identified, and four water molecules are found to be associated with the metal cluster, some of which may serve as substrates in the oxygen-evolving reaction. The most significant structural feature of the  $\text{Mn}_4\text{CaO}_5$  cluster is its distorted chair form. The large distortion from a symmetric cubane is principally caused by the existence of Ca and O5, the fifth oxo-bridge connecting three Mn and one Ca ions. The distances between the three Mn ions and O5 are remarkably longer than those between the other oxygen and Mn ions. This suggests that the bonds between O5 and each of the Mn ions are weak, implying that O5 is apparently different from the other four oxygen atoms. It may also suggest that O5 may exist as a hydroxide ion in the S1-state of the Kok cycle, as supported recently by DFT calculations [2]. In order to elucidate the mechanism of PSII oxygen evolution, it is crucial to identify the two substrate-water molecules participating in the O-O bond formation. Based on the above structural features revealed, O5 may form part of the reaction site. Among the four water molecules bound to the  $\text{Mn}_4\text{CaO}_5$  cluster, two are located most closely to O5, with their distances to O5 around 3 Å. In addition, these two water molecules have a distance of 3.3 Å between each other. Thus, there is a possibility that O-O bond formation is taken place within these two water molecules and O5.

Based on the detailed structure of the  $\text{Mn}_4\text{CaO}_5$  cluster, many researchers may be at present making their efforts towards developing novel water-splitting and oxygen-evolving catalysts. The most difficult problem may be how to realize the asymmetry like the  $\text{Mn}_4\text{CaO}_5$  cluster in their catalysts.

[1] Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **473** (2011) 55-60.

[2] H. Isobe, M. Shoji, S. Yamanaka, Y. Umena, K. Kawakami, N. Kamiya, J.-R. Shen, K. Yamaguchi, *Dalton Trans.*, **41**, (2012) 13727-13740.



Tuesday, 5th March





## Light-Induced Water Splitting and Hydrogen Production: Learning from Nature

Wolfgang Lubitz

*Max Planck Institute for Chemical Energy Conversion (CEC), Stiftstrasse 34-36,  
45470 Mülheim an der Ruhr, Germany*

Storage of the sun's energy in "solar fuels" like molecular hydrogen or related molecules using water as basic material is a research topic of great importance for our society.

A promising starting point for the development of synthetic sun light-driven water splitting catalyst, is to use Nature's approach for inspiration, which is realized in *oxygenic photosynthesis*. [1] In this process, found in green plants, algae and cyanobacteria, water oxidation occurs in a unique biological supercomplex (Photosystem II, PSII). This harbours an oxygen-bridged tetra-nuclear manganese/calcium cluster as catalytic site embedded in a smart protein matrix. [2] Many green algae and bacteria also contain enzymes that enable hydrogen evolution from excess protons, the hydrogenases. [3,4]

The implementation of "artificial photosynthesis" represents a major challenge as chemists are at present not yet able to design and synthesize devices that are able to mimic the natural processes in an efficient way, i.e. with low overpotential, high turnover rates and sufficient stability (long lifetimes) of the catalysts. One major difficulty is the poorly understood coupling of the light-induced one-photon/one-electron charge separation to the multi-electron catalytic processes leading to water oxidation and fuel production. In addition, Nature uses the protein surrounding to optimize the enzymatic process; the matrix is also protection and allows efficient repair *in vivo*. In this respect chemically synthesized systems are currently by far inferior to the native ones.

In recent years high resolution X-ray crystallographic structures of PSII [2] and different hydrogenases [3-6] have been obtained and additional spectroscopic and electrochemical experiments have very significantly increased our knowledge about the structure and function of the native enzymes. Slowly, a mechanistic understanding of the underlying processes is developing. [3,7] This knowledge will help to advance the field of *artificial photosynthesis*, aiming at synthesizing new catalysts for large scale water splitting, hydrogen production or energy storage in other chemical compounds, processes that are of key importance for a sustainable energy future.

In this lecture the native enzymes *wateroxidase* and *hydrogenase* are presented and their working mechanisms are discussed. [1] Prospects of native biological and chemical systems to solve the energy problem will also be addressed.

## References:

- [1] Cox, N.; Lubitz, W. Molecular Concepts of Water Splitting: Nature's Approach. In: *Chemical Energy Storage*, R. Schlögl (ed.), De Gruyter, Berlin/Boston **2013**, pp.185 - 224.
- [2] Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N. *Nature* **2011**, 473, 55.
- [3] Lubitz, W.; Ogata, H.; Reijerse, E.; Higuchi, Y. Structure and Function of Hydrogenase Enzymes. In: *Molecular Solar Fuels*, T.W. Wydrzynski, W. Hillier (eds.), RSC Publishing; Cambridge **2012**, pp. 288 - 325.
- [4] Fontecilla-Camps, J.C.; Amara, P. ; Cavazza, C.; Nicolet, Y.; Volbeda, A. *Nature* **2009**, 460, 814.
- [5] Fritsch, F.; Scheerer, P.; Frielingsdorf, S.; Kroschinsky, S.; Friedrich, B.; Lenz, O.; Spahn, C.M.T. *Nature* **2011**, 479, 249.
- [6] Shomura, Y.; Yoon, K.-S.; Nishihara, H.; Higuchi, Y. *Nature* **2011**, 479, 253.
- [7] Cox, N.; Pantazis, D.; Neese, F.; Lubitz, W. *Acc. Chem. Res.* **2013**, in press

## Photoreaction analysis of flavin photoreceptor BLUF domain by cryogenic spectroscopy



Yoshimasa Fukushima

*The OCU Advanced Research Institute for Natural Science and Technology  
Osaka city university, 3-3-138, Sugimoto, Sumiyoshi, Osaka, 558-8585 Japan*

BLUF (sensor of Blue Light Using Flavin) domain is a class of flavin-binding photoreceptor that is distributed among genomes of bacteria and some eucaryotes. Cyanobacterial BLUF-domain protein PixD is related to the cell motility. Three types of flavin protein families, BLUF, LOV (Light, Oxygen and Voltage sensing) and PHR (Photolyase Homology Region) domains are known to function as a photoreceptor. They show somewhat different photoreactions. The photoreaction of the BLUF-containing protein TePixD of a cyanobacterium *Thermosynechococcus elongatus* BP-1 have been studied by cryogenic spectroscopy, nano second time-resolved spectroscopy, and site-directed mutagenesis on the conserved residues around the flavin chromophore.

Absorption spectrum of flavin in TePixD shows the ~10 nm red shift upon the illumination at 283 K [1]. H-bondings between flavin and the surrounding amino acid seem to be modified coupled to the red-shift as also shown for other BLUF domain proteins by FTIR or Raman spectroscopy. The red-shifted form was found to appear at 10 ns after the laser flash excitation suggesting the fast photoconversion to the red-shifted form from the singlet-excited state of flavin at room temperature. This type of photoreaction is different from the other flavin-binding proteins LOV and PHR domains that form triplet state or electron transferred state of flavin. Illumination of wild-type protein at 10 K, on the other hand, induced only the 5 nm red shift of flavin. The 5 nm-shifted form was stable at 10 K, and was converted to the ~10 nm-shifted form on warming to 50-240 K in the dark. The 5 nm-shifted form, thus, seems to be an intermediate state with a small conformational changes around flavin. The mutant proteins, in which either Tyr8 or Gln50 is replaced, did not show the proper photoconversion at room temperature [2]. Gln50 is directly H-bonded to flavin but Tyr8 indirectly interacts with flavin via H-bond with Gln50. Y8F and Y8A mutant proteins formed higher extents of triplet state of flavin as found in the LOV domain proteins. We concluded that conformational or redox change of flavin itself is very limited in the red-shifted intermediates. We will discuss how the protein environment determines the photoreaction of flavin.

### References:

- [1] Fukushima, Y.; Okajima, K.; Shibata, Y.; Ikeuchi, M.; Itoh, S. *Biochemistry* **2005**, 44, 5149.
- [2] Okajima, K.; Fukushima, Y.; Suzuki, H.; Kita, A.; Ochiai, Y.; Katayama, M.; Shibata, Y.; Miki, K.; Noguchi, T.; Itoh, S.; Ikeuchi, M. *J. Mol. Biol.* **2006**, 363, 10.



# Ultrafast Excited State Dynamics of Fucoxanthin: A Role of Intramolecular Charge Transfer in Brown Algal Light-harvesting

Daisuke Kosumi<sup>1,2</sup>, Ritsuko Fujii<sup>1,3</sup>, Mitsuru Sugisaki<sup>2,4</sup>, Masahiko Iha<sup>5</sup>, Shigeo Katsumura<sup>6</sup>, and Hideki Hashimoto<sup>1,2,4</sup>

<sup>1</sup>The Osaka City University Advanced Research Institute for Natural Science and Technology (OCARINA), 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

<sup>2</sup>JST/CREST, 4-1-8 Hon-chou, Kawaguchi, Saitama 332-0012, Japan

<sup>3</sup>JST/PRESTO, 4-1-8 Hon-chou, Kawaguchi, Saitama 332-0012, Japan

<sup>4</sup>Department of Physics, Graduate School of Science, Osaka City University

<sup>5</sup>South Product Co. Ltd., 12-75 Suzaki, Uruma-shi, Okinawa 904-2234, Japan

<sup>6</sup>Department of Chemistry, Kwansei Gakuin University, Hyogo 669-1337, Japan

Fucoxanthin-chlorophyll *a/c* protein (FCP) complexes from brown algae, *Cladosiphon okamuranus* TOKIDA (Okinawa Mozuku in Japanese), contain the carbonyl-carotenoid, fucoxanthin [1], which exhibits spectral characteristics attributed to an intramolecular charge transfer (ICT) state located nearby the lowest S<sub>1</sub> excited state in polar environments due to the presence of the carbonyl group in its polyene backbone as shown in Fig. (A) [2]. In the FCP complexes, fucoxanthin molecules absorb light energy in the blue-green region of the spectrum (Fig. (B)) and transfer it to nearby chlorophylls rapidly and efficiently [1,3]. Recent ultrafast spectroscopic techniques have revealed the ultrafast dynamics of the ICT state of carbonyl-carotenoids and its role in excitation energy transfer of aquatic algal photosynthetic antennas [3]. However, details of the nature and function of the ICT state have been still matters of debate. In this study, we investigated (1) the role of the ICT property of fucoxanthin in ultrafast energy transfer to chlorophyll *a/c* in brown algal photosynthetic antennas and (2) the molecular nature of the ICT state of fucoxanthin molecules with various conjugation lengths [4] in solvent environments using femtosecond pump-probe spectroscopic measurements.

[1] R. Fujii *et al.*, *Photosynth. Res.*, 111, 165, 2012.

[2] D. Kosumi *et al.*, *Phys. Chem. Chem. Phys.*, 13, 10762, 2011.

[3] T. Polívka and V. Sundström, *Chem. Rev.*, 104, 2021, 2004.

[4] T. Kajikawa *et al.*, *Org. Lett.*, 14, 808-811, 2012.

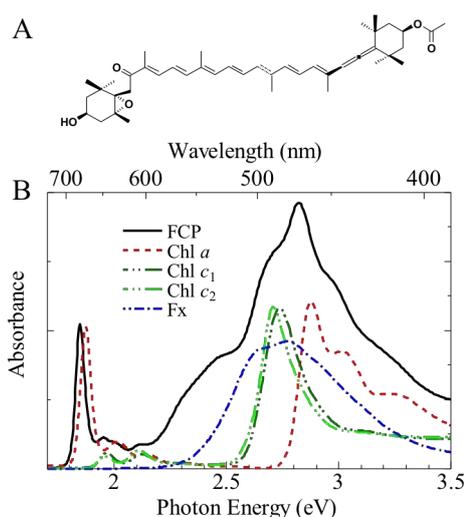


Figure: (A) A chemical structure of fucoxanthin and (B) the steady-state absorption spectrum of the isolated FCP complex.

# A QM/MM study on the $S_2$ spin state of the oxygen-evolving complex

Mitsuo Shoji,<sup>1</sup> Hiroshi Isobe,<sup>2</sup> Shusuke Yamanaka,<sup>2</sup>

Jian-Ren Shen,<sup>3</sup> Kizashi Yamaguchi<sup>2</sup>

<sup>1</sup> Graduate School of Pure and Applied Science, University of Tsukuba

<sup>2</sup> Graduate School of Science, Osaka University

<sup>3</sup> Graduate School of Natural Science and Technology, Okayama University

Oxygen-evolving complex (OEC) is a key reaction center in photosystem II (PSII) for the oxidation reaction of water to dioxygen. The OEC cycles through five redox states ( $S_i$ ,  $i = 0-4$ ) with the extraction of four electrons and four protons. Umena and co-workers have determined the high-resolution x-ray structure at the 1.9Å, and revealed the fine 3D structure of OEC, including the  $\text{CaMn}_4\text{O}_5$  cluster and close waters [1]. The OEC forms many hydrogen-bonds with neighboring waters and residues, it is not obvious for the electronic and spin structure at the ground state.

In this study, the ground spin state of OEC at the  $S_2$  state was examined by using a QM/MM approach. Ground spin state is one of the important characters to check the validity of computational results. The high-resolution x-ray structure was used as a starting model (Fig. 1). A large QM region was used including second coordination amino acids and waters. Geometry optimizations were performed for the QM/MM model. We found that calculated ground spin state is  $(4/2, -3/2, 3/2, -3/2)$  at the (III, IV, IV, IV) charge state for Mn centers, respectively. This result is consistent to the recent EPR result. The magnetic interactions between Mn centers were evaluated to evaluate the Heisenberg exchange parameters following the generalized spin projection scheme [2].

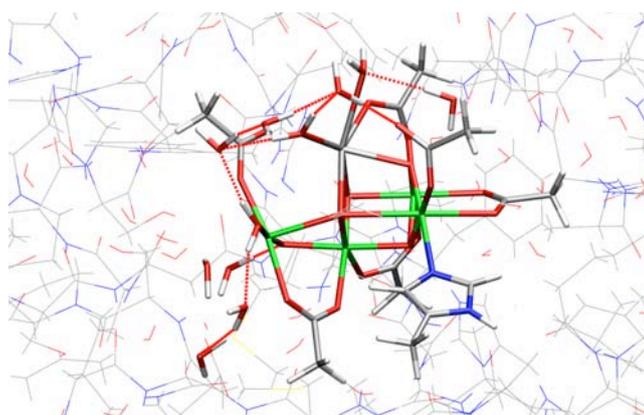


Figure 1. QM atoms used in the QM/MM calculations.

## References:

- [1] Umena, Y.; Kawakami, K.; Shen, J-R; Kamiya, N. *nature* **2011**, 473, 55.
- [2] Shoji, M. et al. *Chem. Phys. Lett.* **2006**, 432,343.



## New Paradigms in Water Splitting

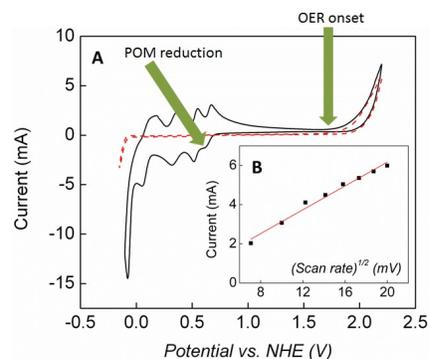
Lee Cronin, School of Chemistry, University of Glasgow,  
Glasgow, G12 8QQ, UK

Email: [Lee.Cronin@glasgow.ac.uk](mailto:Lee.Cronin@glasgow.ac.uk)

Web: [www.chem.gla.ac.uk/staff/lee](http://www.chem.gla.ac.uk/staff/lee)

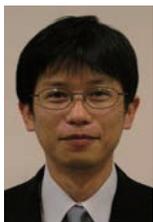
The need for sustainable, carbon-neutral technologies to meet the world's growing demand for energy has become a widely acknowledged imperative. However, despite this realization, renewable energy sources such as wind and solar power remain under-exploited as large-scale replacements for fossil fuels.<sup>[1]</sup> This is largely due to the intermittency of supply: a reliable way of storing the energy generated by renewable sources must be found in order to compensate for periods during which the wind does not blow or the sun does not shine. An especially attractive solution to this problem is to store sustainably-generated energy in the form of chemical bonds by the electrochemical or photochemical splitting of water to produce oxygen and hydrogen. Here we describe the development of 'proton-electron-buffers' (PEBs) using redox-active polyoxometalate (POM) clusters that are able to address the problem of simultaneous oxygen and hydrogen production during the electrolysis of water, Figure 1.

Figure 1 shows the CV of 0.5 M  $H_3Mo_{12}PO_{40}$  (black line) and 1 M  $H_3PO_4$  (dashed line, to show where OER and HER onset occur). A three-electrode, single compartment setup was used, with a 2 mm diameter Pt disc working electrode, Pt wire counter electrode and an Ag/AgCl reference electrode at a scan rate of  $100\text{ mVs}^{-1}$ . The green arrows highlight the oxidation and reduction peaks associated with the first reduced state of  $H_3Mo_{12}PO_{40}$ .



Using a PEB in an electrolyser could also bring significant advantages with regards to intermittent power supplies (such as renewables) by reducing the instantaneous voltages required for electrolysis to occur. In addition to exploring water splitting through the paradigm of the proton-electron-buffer, we will also describe the use of reduced polyoxometalate clusters as an intermediate "fuel source", by reacting the reduced PEBs with reducible chemical substrates (possibly including low grade organic waste products) to produce storable fuels.

1. R. J. Cogdell, T. H. Brotsudarmo, A. T. Gardiner, P. M. Sanchez, L. Cronin, *Biofuels*, **2010**, *1*, 861-876.
2. D. -L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.*, **2010**, *49*, 1736-1758.



## Catalytic activity of $\mu$ -oxo dimer of mono-ruthenium substituted $\alpha$ -Keggin-type heteropolytungstates for water oxidation.

Masahiro Sadakane<sup>a)b)</sup>, Hiroaki Kitatomi<sup>a)</sup>, Shuhei Ogo<sup>a)</sup>, Tsuneji Sano<sup>a)</sup>

*a) Applied Chemistry, Graduate School of Engineering, Hiroshima University*

*b) PRESTO JST*

**Abstract:** We present  $\mu$ -oxo dimeric species of the mono-ruthenium substituted heteropolytungstates,  $[\{XW_{11}O_{39}Ru\}_2O]^{n-}$  ( $X = Si$  or  $Ge$ ) (Fig 1 (right)), show WOC activity using CAN as an oxidant without decomposition to the monomeric species.

Development of efficient and robust water oxidation catalyst (WOCs) is one of the most important keys for realization of artificial photosynthesis which could be a solution for the energy problem worldwide. Heteropolytungstates are discrete tungsten-oxide molecules with other elements that have recently been attracting increasing interest because of their WOC activities [1]. Bonchio and Hill groups reported another sandwich-type heteropolytungstate with tetranuclear ruthenium core,  $[(\gamma-SiW_{10}O_{36})_2Ru_4O_4(OH)_2(H_2O)_4]^{10-}$ , showed high catalytic activity for water oxidation using cerium ammonium nitrate (CAN) or  $[Ru^{III}(bpy)_3]^{3+}$  as an oxidant. Hill group reported high catalytic activity of a sandwich-type heteropolytungstate with tetranuclear cobalt core,  $[(PW_9O_{34})_2Co_4(H_2O)]^{10-}$ , using  $[Ru^{III}(bpy)_3]^{3+}$  as an oxidant. Fukuzumi group reported that mononuclear ruthenium substituted heteropolytungstates,  $[XW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$  ( $X = Si$  or  $Ge$ ) (Fig 1 (left)), show WOC activity using CAN as an oxidant. They proposed that oxo-Ru species is active species [2].

We reported that the mono-ruthenium substituted heteropolytungstates (Fig 1 (left)) dimerized to form  $\mu$ -oxo dimeric species,  $[\{XW_{11}O_{39}Ru\}_2O]^{n-}$  ( $X = Si$  or  $Ge$ ) (Fig 1 (right)) [3]. We present WOC activity of these dimeric species.

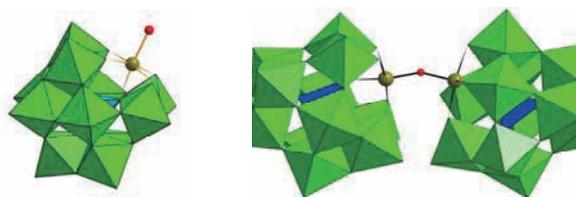


Fig 1. Structure of (left)  $[XW_{11}O_{39}Ru(H_2O)]^{n-}$  and (right)  $[\{XW_{11}O_{39}Ru\}_2O]^{n-}$  ( $X : Si$  or  $Ge$ ).

The dimer showed catalytic activity for water oxidation using CAN as an oxidant (Fig 2). Ru in the dimeric species was coordinated by five oxygen of polyoxotungstate and one  $\mu$ -oxo bridged two mono-ruthenium substituted polyoxotungstates. There is no example where such  $\mu$ -oxo dimer is active as WOC. Therefore, it could be considered that monomeric species generated by dissociative decomposition of the dimer acted as an active species. However, we

## Template for the abstract

indicated that the dimer worked as a real catalyst.

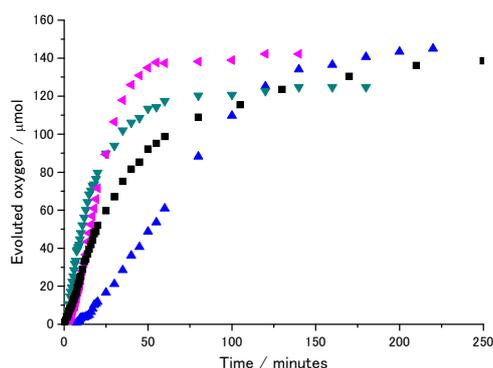


Fig 2. Time course of oxygen evolution catalyzed by (green) Si-monomer, (blue) Si-dimer, (black) Ge-monomer, and (pink) Ge-dimer. Ru concentration: 60  $\mu\text{M}$ , CAN concentration: 6 mM in 100 mL of 0.1 M  $\text{HNO}_3$ .

Fig 2 shows time course of oxygen evolution catalyzed by monomers and dimers in same Ru concentration. Oxygen evolution rate using Si-monomer catalyst is faster than Si-dimer catalyst but reaction rate became slower in the course of reaction. Amount of oxygen produced using Si-dimer catalyst became larger than amount of oxygen using Si-monomer catalyst in the course of reaction. Furthermore, catalytic activity of Ge-dimer is higher than Ge-monomer. These results indicated that dimer is a real catalyst.

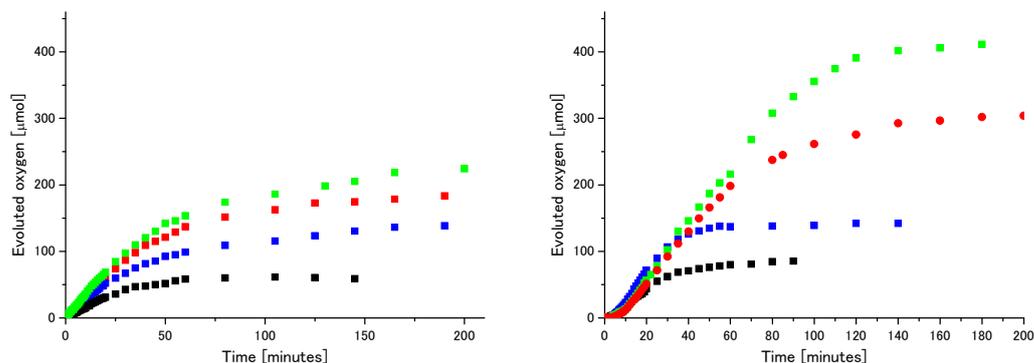


Fig 3. CAN concentration effect on oxygen evolution using (left) Ge-monomer and (right) Ge-dimer. CAN concentration: (green) 18 mM, (red) 12 mM, (blue) 6 mM, (black) 3 mM Ru concentration: 60  $\mu\text{M}$ , CAN concentration: 6 mM in 100 mL of 0.1 M  $\text{HNO}_3$ .

Fig 3 shows effect of CAN concentration on the oxygen evolution rate. Initial reaction rate decreased by decreasing CAN concentration in the case of Ge-monomer which agreed with result reported by Fukuzumi group [2]. On the other hand, initial reaction rate did not change by decreasing CAN concentration in the case of Ge-dimer. This result indicate that reaction mechanism of dimer is different from reaction mechanism of monomer.

- References** [1] Miras, H. N.; Yan, J.; Long, D.-L.; Cronin, L. *Chem. Soc. Rev.* **2012**, *41*, 7403.  
[2] Murakami, M.; et al. *J. Am. Chem. Soc.* **2011**, *133*, 11605.  
[3] Sadakane, M.; et al. *Dalton Trans.* **2007**, 2833.



## The excited states of the inactive and active forms of the Orange Carotenoid Protein

Rudi Berera<sup>1</sup>, Michal Gwizdala<sup>2,3</sup>, Ivo HM van Stokkum<sup>1</sup>, Diana Kirilovsky<sup>2,3</sup>  
and Rienk van Grondelle<sup>1</sup>

*1 Division of Physics and Astronomy, Department of Biophysics, VU University Amsterdam,  
The Netherlands*

*2 Commissariat a l'Energie Atomique, Institute de Biologie et Technologie de Saclay and  
3Centre National de la Recherche Scientifique, 91191 Gif sur Yvette, France*

Too much light in photosynthesis is just an example of how too much of a good thing can be extremely harmful. In fact while light is the lifeblood of the photosynthetic process, too much of it can be lethal. In order to cope with the deleterious effects of excess illumination photosynthetic organisms have developed photoprotective mechanisms generally known as nonphotochemical quenching (NPQ).

The orange carotenoid protein (OCP) is a crucial player in NPQ in a large number of cyanobacteria. This water soluble protein binds one pigment only, the keto carotenoid 3'-hydroxyechinenone and needs to be photoactivated by strong (blue-green) light in order to induce energy dissipation within or from the phycobilisome, the main light harvesting system of these organisms. We performed transient-absorption spectroscopy on OCP samples frozen in the inactive and active forms at 77 K. By making use of target analysis we determined the excited state properties of the active form. Our results show that OCP photoactivation modifies the carotenoid excited state energy landscape. More specifically the photoactivated OCP is characterized by one state with predominantly ICT character (ICT/S<sub>1</sub>) and a lifetime of 2.3 ps, and another state with mainly S<sub>1</sub> character (S<sub>1</sub>/ICT) with a lifetime of 7.6 ps. We also show that the kinetic model is fully consistent with the RT data obtained earlier<sup>(1)</sup>. We propose that this ICT/S<sub>1</sub> state acts as the quencher in the OCP mediated NPQ.

1. Berera, R., van Stokkum, I. H. M., Gwizdala, M., Wilson, A. I., Kirilovsky, D., and van Grondelle, R. (2012) The Photophysics of the Orange Carotenoid Protein, a Light-Powered Molecular Switch, *The Journal of Physical Chemistry B* 116, 2568-2574.



## Molecular Functions of the Membrane-Extrinsic Subunits of Photosystem II in Higher Plants

Kentaro Ifuku

Graduate School of Biostudies, Kyoto University, Kyoto 606-8502, Japan / JST-PRESTO

### Abstract:

Photosystem II (PSII) is a light-driven water-plastoquinone oxidoreductase and a major source of energy on earth. Recently, the crystal structure of PSII from thermophilic cyanobacteria was resolved at atomic resolution, which allows us to analyze and understand its functions in great detail [1]. However, the structural information of cyanobacterial PSII cannot be necessarily generalized to PSII of other eukaryotes, because eukaryotic PSII has developed specific subunits during evolution. In particular, the compositions of the PSII membrane-extrinsic subunits, which are associated with the luminal side of PSII and involved in oxygen evolution, are significantly different among the oxygenic photosynthetic organisms. The PsbP and PsbQ protein are PSII extrinsic subunits characteristically developed in green plants and required for  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  retention in PSII, essential cofactors for water-splitting reaction [2]. We have characterized molecular functions of PsbP and PsbQ in higher plants and suggest that PsbP, but not PsbQ, is essential for the oxygen-evolving activity [3]. In vitro reconstitution and cross-linking experiments suggest that PsbP directly interacts with the cytochrome  $b_{559}$   $\alpha$  subunit of PSII (PsbE protein), and the conserved His-144 residue in the central  $\alpha\beta\alpha$  structure of PsbP has a critical role to maintain this interaction [4]. The substitution of His-144 to alanine particularly lowered the  $\text{Cl}^-$ -retention ability of PsbP, suggesting that the interaction between PsbP and PsbE is required for the optimal PSII activity. Molecular evolution and the specific role of PsbP in regulating the function of the PSII-light-harvesting complex II supercomplex will be discussed.

### References:

- [1] Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N. *Nature*. **2011**, 473, 55-60.
- [2] Ifuku, K.; Ido, K.; Sato, F. *J. Photochem. Photobiol. B*. **2011**, 104, 158-164.
- [3] Kakiuchi, S.; Uno, C.; Ido, K.; Nishimura, T.; Noguchi, T.; Ifuku, K.; Sato, F. *Biochim. Biophys. Acta (Bioenergetics)* **2012**, 1817, 1346-1351.
- [4] Ido, K.; Kakiuchi, S.; Uno, C.; Nishimura, T.; Fukao, Y.; Noguchi, T.; Sato, F.; Ifuku, K. *J. Biol. Chem.* **2012**, 287, 26377-26387.

# Proton transfer mediated by hydrogen bonds in proteins

Hiroshi Ishikita<sup>1,2</sup>

(1) 202 Building E, Career-Path Promotion Unit for Young Life Scientists, Graduate School of Medicine, Kyoto University, Yoshida-Konoe-cho, Sakyo-ku, Kyoto 606-8501, Japan

(2) Japan Science and Technology Agency (JST), PRESTO, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

## Abstract:

In a protein environment, protons can be transferred along a proton transfer pathway, where each ionizable or polar site is arranged at a hydrogen-bond (H-bond) distance. Thus, formation of an H-bond between proton donor and acceptor moieties is essential for proton transfer.

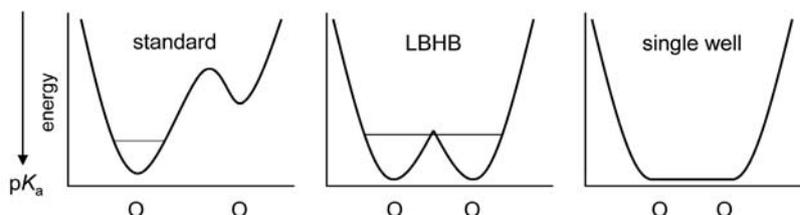


Fig 1. Potential-energy profiles of standard H-bond (left), low-barrier H-bond, LBHB (middle), and single-well H-bond (right).

In photoactive yellow protein (PYP), the H-bond between Glu46 and *p*-coumaric acid is a standard H-bond in the ground state. Upon photo-excitation, the H-bond becomes an unusually short, single-well H-bond (Fig 1), facilitating proton transfer (Fig 2) [1, 2]. Formation of a single-well H-bond has also been observed in proton-coupled electron transfers via quinone in the O<sub>2</sub>-evolving complex, Photosystem II [3]. Formation of a single-well H-bond appears to be prerequisite for proton transfer events in proteins.

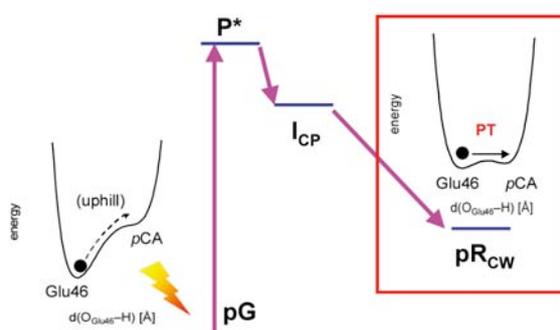


Fig 2. Formation of a single-well H-bond in PYP.

## References:

- [1] K. Saito and H. Ishikita, Proc Natl Acad Sci U S A 109 (2012) 167-172.
- [2] K. Saito and H. Ishikita, Biochim Biophys Acta 1827 (2013) 387-394.
- [3] K. Saito, A.W. Rutherford and H. Ishikita, Proc Natl Acad Sci U S A 110 (2013) 954-959.

## Structure of photosystem II and the mechanism of light-induced water-oxidation



**Jian-Ren Shen**

*Graduate School of Natural Science and Technology/Faculty of Science,  
Okayama University, Okayama 700-8530, Japan*

Photosystem II is a multi-subunit membrane protein complex containing 19-20 subunits with a total molecular mass of 350 kDa, and forms a dimer in cyanobacterial cells. PSII catalyzes light-induced water splitting, leading to the evolution of molecular oxygen. The catalytic center of water-oxidation is a  $\text{Mn}_4\text{CaO}_5$ -cluster. In this talk, I will introduce the high resolution structure of PSII analyzed at a resolution of 1.9 Å [1], with the emphasis on the structure of the oxygen-evolving complex (OEC), which is organized in a distorted chair form with a cubane-like structure. The cubane-like core of the metal cluster is composed of  $\text{Mn}_3\text{CaO}_4$  linked via  $\mu$ -oxo bridges to a fourth Mn (Mn4) outside of the cubane. The distortion in the cubane structure makes it unstable, or flexible, which may be important for the structural changes to occur accompanying the water-oxidation cycle, namely, the S-state cycle. In order to examine the role of the only  $\text{Ca}^{2+}$  ion within the cubane core, we replaced it with  $\text{Sr}^{2+}$ , and analyzed its structure [2]. Our analysis showed that the structure of the resulted  $\text{Mn}_4\text{SrO}_5$ -cluster is very similar to that of the  $\text{Mn}_4\text{CaO}_5$ -cluster. However, among the two water molecules W3 and W4 ligated to the  $\text{Ca}^{2+}$  ion, the position of W3 was affected by the  $\text{Sr}^{2+}$ -substitution, leading to an elongated distance between W3 and  $\text{Sr}^{2+}$  as well as that of W2-W3; whereas the position of W4 was not much affected. This result suggests that W3 binds to  $\text{Ca}^{2+}$  more weakly than W4, and is more mobile than W4. The change in the position of W3 may therefore be one of the reasons for the decrease in the oxygen-evolving activity upon  $\text{Sr}^{2+}$ -substitution, which implies the possible involvement of this water in the O-O bond formation.

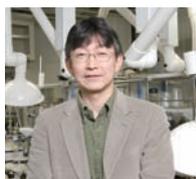
This work was performed in collaboration with Yasufumi Umena, Keisuke Kawakami, Fasal Hammad Mekky Koua, and Nobuo Kamiya. I thank them for their great contributions.

### References

- [1] Umena Y., Kawakami K., Shen J.-R., Kamiya N. *Nature* **2011**, 473, 55-60.
- [2] Koua K.M.H., Umena Y., Kawakami K., Shen J.-R. *Proc. Natl. Acad. Sci. USA* **2013**, in press.

Wednesday, 6th March





## Artificial Photosynthesis Using Homogeneous and Heterogeneous Photocatalytic Systems.

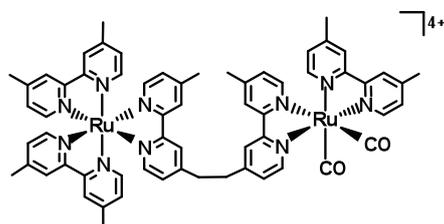
Osamu Ishitani

*Department of Chemistry, Tokyo Institute of Technology, Japan*

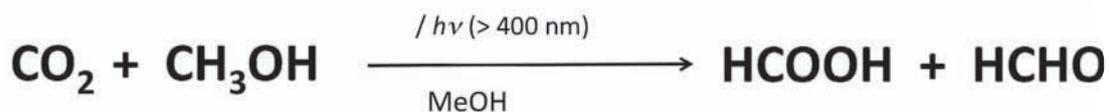
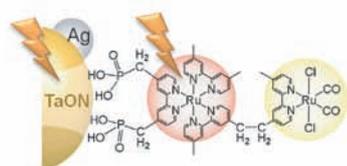
**Abstract:** Both the problems of the global warming and shortage of the fossil fuels have brought about great interest in photochemical utilization of CO<sub>2</sub> with solar energy. Efficient photocatalysts for CO<sub>2</sub> reduction must be necessary for development of such an important technology.

We have developed novel types of photocatalytic systems using metal complexes and/or semiconductors as a photocatalyst.<sup>1</sup> I will focus on the following systems in my presentation.

- (1) Architecture of supramolecular photocatalysts driven with visible light, which can efficiently reduce CO<sub>2</sub> selectively to CO or HCOOH.<sup>2-6</sup>



- (2) Z-scheme type photocatalysts by using hybrids composed with the supramolecular photocatalyst and a semiconductor, which can reduce CO<sub>2</sub> with methanol as an electron donor.



## References:

1. Yui, T.; Tamaki, Y.; Sekizawa, K.; Ishitani, O., Photocatalytic reduction of CO<sub>2</sub>: from molecules to semiconductors. *Top. Curr. Chem.* **2011**, *303*, 151-84.
2. Gholamkhash, B.; Mametsuka, H.; Koike, K.; Tanabe, T.; Furue, M.; Ishitani, O. *Inorg. Chem.* **2005**, *44*, 2326.
3. Sato, S.; Koike, K.; Inoue, H.; Ishitani, O. *Photochem. Photobiol. Sci.* **2007**, *6*, 454.
4. Koike, K.; Naito, S.; Sato, S.; Tamaki, Y.; Ishitani, O. *J Photochem. Photobiol. A: Chem.* **2009**, *207*, 109.
5. Tamaki, Y.; Watanabe, K.; Koike, K.; Inoue, H.; Morimoto, T.; Ishitani, O. *Faraday Discuss.* **2012**, *155*, 115.
6. Tamaki, Y.; Morimoto, T.; Koike, K.; Ishitani, O. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15673.



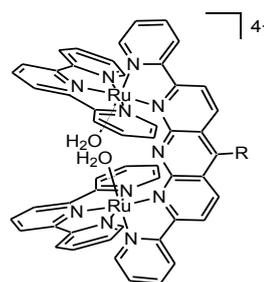
## Molecular design of catalysts for water oxidation toward artificial photosynthesis.

Masayuki Yagi

Department of Materials Science and Technology, Faculty of Engineering and Center for Transdisciplinary Research, Niigata University, 8050 Ikarashi-2, Niigata 950-2181, Japan  
§ PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Ruthenium(II) complexes with polypyridyl ligands have been extensively studied because of diverse variety of excited-state phenomena, including photoluminescence, photoredox chemistry, and photosubstitution process. The luminescent excited state is usually a triplet metal-to-ligand charge transfer ( $^3\text{MLCT}$ ) state. In some case, thermal excitation of  $^3\text{MLCT}$  is known to allow a triplet ligand field ( $^3\text{d-d}$ ) excited state, and the latter state is assumed to be involved in a dissociative mechanism for photosubstitution. Recently, much attention has been given to poly(pyridyl)ruthenium aquo complexes as water oxidation catalyst. Most of these complexes undergo proton coupled electron transfer reactions to give  $\text{Ru}^{\text{V}}=\text{O}$  species which have been pointed out as a key intermediate in the catalytic cycle of water oxidation. One could expect that dinuclear ruthenium complexes capable of being intramolecular coupling of  $\text{Ru}^{\text{V}}=\text{O}$  moieties work as a highly water oxidation catalyst. We design a new dinuclear ruthenium complex (denoted as **Ru<sub>2</sub>**, see Fig.1) shown in the below scheme. However, the thermochemical reaction of  $\text{Ru}(\text{tpy})\text{Cl}_3$  with the bridging ligand (**L**) having an anthridine moiety selectively produces *trans*- $[\text{Ru}(\text{tpy})(\text{L})\text{Cl}]^+$  (*trans*-**RuLCl**). The subsequent reaction of *trans*-**RuLCl** with additional  $\text{Ru}(\text{tpy})\text{Cl}_3$  can not give **Ru<sub>2</sub>** due to the steric hindrance between tpy ligands on *trans*-**RuLCl** and  $\text{Ru}(\text{tpy})\text{Cl}_3$ . To overcome the problem on the thermochemical synthesis, we focus on the utilization of photoisomerization reactions of poly(pyridyl)ruthenium(II) aquo complexes which was recently reported in our earlier paper.[1]

The thermochemical reaction of **L** and  $\text{Ru}(\text{tpy})\text{Cl}_3$  in water gave a green solid of *trans*-**RuLCl**, which is identified from single X-ray crystallography and NMR data. *trans*- $[\text{Ru}(\text{tpy})(\text{L})\text{OH}_2]^{2+}$  (*trans*-**RuLH<sub>2</sub>O**) was obtained by reflux with  $\text{AgNO}_3$  in water. Next, the aqueous solution of *trans*-**RuLH<sub>2</sub>O** was irradiated with visible light to give *cis*- $[\text{Ru}(\text{tpy})(\text{L})\text{OH}_2]^+$  (*cis*-**RuLH<sub>2</sub>O**). The photoisomerization reaction was monitored by UV-vis and  $^1\text{H}$  NMR spectroscopy techniques, and the quantum yield of the reaction was  $4.6 \times 10^{-2}$  %. **Ru<sub>2</sub>** was synthesized by the following two methods. (1) It was given from the reaction of *cis*-**RuLH<sub>2</sub>O** with 1 equivalent of  $\text{Ru}(\text{tpy})\text{Cl}_3$  by reflux with microwave radiation (yield 20 %) (2) It was also given by one-pot synthesis, where  $\text{Ru}(\text{tpy})\text{Cl}_3$  and **L** were irradiated with visible light at  $70^\circ\text{C}$  followed by the reflux with microwave radiation for 30 min. (yield 16 %). **Ru<sub>2</sub>** was characterized by mass spectroscopic data, exhibiting a peak at  $m/z = 371.98$  which can be assigned to  $[\text{Ru}^{\text{II}}_2(\text{tpy})_2\text{L}(\text{OH})(\text{OH}_2)]^{3+}$  ( $m/z = 372.05$ ). The  $^1\text{H}$  and  $^1\text{H}$ - $^1\text{H}$  COSY NMR data suggest a high symmetric configuration of *cis,cis*- $[\text{Ru}^{\text{II}}_2(\text{tpy})_2\text{L}(\text{OH})(\text{OH}_2)]^{3+}$  in  $\text{D}_2\text{O}$ .



*cis,cis*- $[\text{Ru}(\text{tpy})(\text{OH}_2)]_2\text{L}]^{4+}$   
Fig. 1 Structure of a dinuclear ruthenium complex.

- [1] Yamazaki, H.; Hakamata, T.; Komi, M.; Yagi, M. *J. Am. Chem. Soc.* **2011**, *133*, 8846-8849.



## Redox Behavior of High-Valent Polynuclear Manganese Complexes with Xanthene-Bridged Schiff Base Ligands

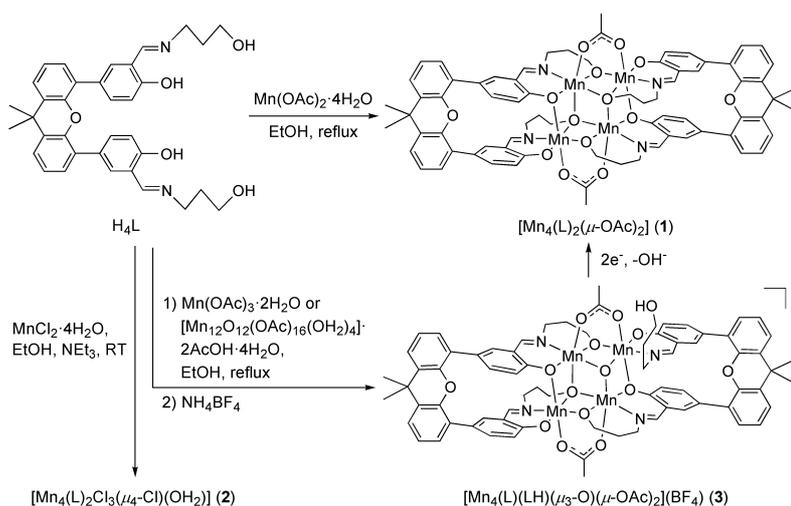
Masakazu Hirotsu

Graduate School of Science, Osaka City University, Osaka, 558-8585, Japan

Photosynthetic water oxidation is catalyzed by the oxygen evolving complex (OEC) containing a manganese cluster in photosystem II (PSII). X-ray diffraction studies of PSII revealed that the active site of the OEC has a  $\text{Mn}_4\text{CaO}_5$  cluster [1]. Biomimetic manganese complexes for the OEC have not been fully established. We recently developed a xanthene-bridged Schiff base ligand,  $\text{H}_4\text{L}$ , which effectively forms tetranuclear manganese complexes (Scheme 1) [2]. Redox behavior of the tetramanganese complexes supported by the xanthene-bridged ligands is presented.

The reaction of  $\text{H}_4\text{L}$  with 2 equiv of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  under reflux in ethanol afforded the mixed-valence  $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2$  complex  $[\text{Mn}_4(\text{L})_2(\mu\text{-OAc})_2]$  (**1**), which has an incomplete double-cubane structure of  $\text{Mn}_4\text{O}_6$  with four alkoxide and two phenolate O atoms. The analogous reaction using  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  gave the chloride-bridged  $\text{Mn}^{\text{III}}_4$  complex  $[\text{Mn}_4(\text{L})_2\text{Cl}_3(\mu_4\text{-Cl})(\text{OH}_2)]$  (**2**). The xanthene-bridged ligand L has a propensity to incorporate four manganese ions by dimerization. When  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  or  $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{OH}_2)_4] \cdot 2\text{AcOH} \cdot 4\text{H}_2\text{O}$  was used as a starting manganese complex with higher oxidation states, the  $\text{Mn}^{\text{III}}_4$  complex  $[\text{Mn}_4(\text{L})(\text{HL})(\mu_3\text{-O})(\mu\text{-OAc})_2](\text{BF}_4)$  (**3**) was obtained. Complex **3** has a bridging oxide ligand and a non-coordinated propanol arm of HL, and its  $\text{Mn}_4\text{O}_6$  core structure is similar to that of **1**.

Cyclic voltammograms of **1** and **3** in  $\text{CH}_2\text{Cl}_2$  exhibit four redox processes in the range of  $-1.2$  to  $0.7$  V vs  $E^\circ(\text{Fc}^{+/0})$ . The oxide-bridged complex **3** stabilizes higher oxidation states compared with **1**. Reduction of **3** gave **1** through proton abstraction from the non-coordinated propanol arm by the bridging oxide ligand.



Scheme 1. Synthesis of Manganese Complexes

[1] Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N. *Nature* **2011**, *473*, 55.

[2] Hirotsu, M.; Shimizu, Y.; Kuwamura, N.; Tanaka, R.; Kinoshita, I.; Takada, R.; Teki, Y.; Hashimoto, H. *Inorg. Chem.* **2012**, *51*, 766.



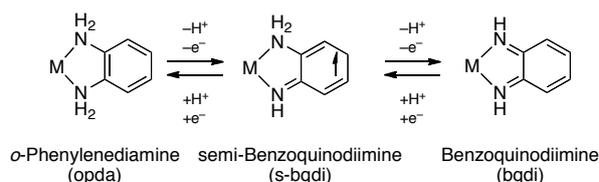
## Construction of Photochemical Hydrogen Evolution Systems Based on the Effective Utilization of 3d Metals

Masako Kato

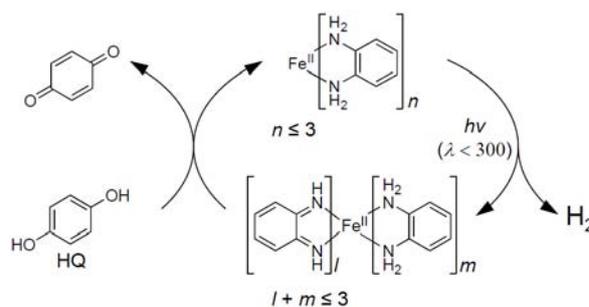
Department of Chemistry, Faculty of Science, Hokkaido University,  
Sapporo 060-0810, Japan

The strategy of our group to contribute to the energy issues is to construct novel photocatalytic systems using common metals instead of precious metals. For this challenging subject, we developed metal complexes containing redox active ligands such as benzenedithiolato and catecholato ions [1]. As shown in Scheme 1,

*o*-phenylenediamine (opda) also acts as a redox active ligand taking part in the multiple proton/electron transfer of the metal complexes. By using this ligand, we found a simple metal-complex system for photochemical hydrogen evolution without extra photosensitizers. On photoirradiation with the UV light, the hydrogen evolution occurred from the suspension formed by the mixing of  $\text{Fe}(\text{ClO}_4)_2$  and opda in THF. It is clear that the complexation of Fe ion and opda is essential for the reaction because very little hydrogen was evolved in the absence of Fe(II) ion. The hydrogen molecules would be produced by the photochemical activation of opda coordinated to Fe (II) ion. Interestingly, the hydrogen evolution increased by adding hydroquinone (HQ) indicating that the catalytic process proceeded by the supply of both protons and electrons from HQ as shown in Scheme 2. The results demonstrate a novel photoinduced hydrogen production/storage system comprised of completely precious-metal free materials.



Scheme 1. Multi-step redox properties of M-opda complexes.



Scheme 2. Proposed photocatalytic hydrogen evolution cycle.

### References:

- [1] Matsumoto, T.; Chang, H.-C.; Kobayashi, A.; Uosaki, K.; Kato, M. *Inorg. Chem.* **2011**, *50*, 2859-2869; Matsumoto, T.; Wakizaka, M.; Yano, H.; Kobayashi, A.; Chang, H.-C.; Kato, M. *Dalton Trans.* **2012**, *41*, 8201-8478.



## Development of Visible-Light-Responsive Photocatalysts for Solar Hydrogen Production

Ryu Abe

*Department of Energy and Hydrocarbon Chemistry, Graduate School of Science and Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. email: ryu-abe@scl.kyoto-u.ac.jp*

Photocatalytic water splitting into  $H_2$  and  $O_2$  using a semiconductor photocatalyst has received much attention recently due to the potential of this method for the clean production of  $H_2$  from water utilizing solar energy.<sup>[1, 2]</sup> Although a number of metal oxides have been reported to be active photocatalysts for the water-splitting reaction, most only function under ultraviolet (UV) light ( $\lambda < 400$  nm) owing to the large band gap energy of the materials ( $> 3$  eV). Because almost half of all incident solar energy at the Earth's surface falls in the visible region ( $400 < \lambda < 800$  nm), the efficient utilization of visible light remains indispensable for realizing practical  $H_2$  production based on photocatalytic water splitting. However, it is intrinsically difficult to develop an oxide semiconductor having both a sufficiently narrow bandgap ( $< 3.0$  eV) allowing visible light absorption and a highly negative conduction band level for  $H_2$  production.

In order to split water under visible light, we have developed new type of water splitting system based on two-step photoexcitation between two different photocatalyst materials, as shown in Fig. 1. This process was inspired by

natural photosynthesis in green plants and is known as the Z-scheme. In two-step systems, the water splitting reaction is broken up into two stages: one for  $H_2$  evolution and the other for  $O_2$  evolution; these are combined by using a shuttle redox couple (Red/Ox) in the solution. Over a  $H_2$  evolution photocatalyst (referred to as a  $H_2$  photocatalyst), the photoexcited electrons reduce water to  $H_2$  and holes in the valence band oxidize the reductant (Red) to an oxidant (Ox). The oxidant is reduced back to the reductant by photoexcited electrons generated over an  $O_2$  evolution photocatalyst (referred to as an  $O_2$  photocatalyst), where the holes oxidize water to  $O_2$ . This system lowers the energy required for photocatalysis, allowing visible light to be utilized more efficiently than in conventional water-splitting systems. In other words, it enables a semiconductor to be used that has either a water reduction or oxidation potential on one side of the system. For example, visible-light-responsive oxides such as  $WO_3$  can be used as  $O_2$  photocatalysts if they can reduce the oxidant to a reductant. Similarly, non-oxide photocatalysts (e.g., sulfides, oxynitrides, and dyes) can be used as  $H_2$  photocatalysts if they can oxidize the reductant to an

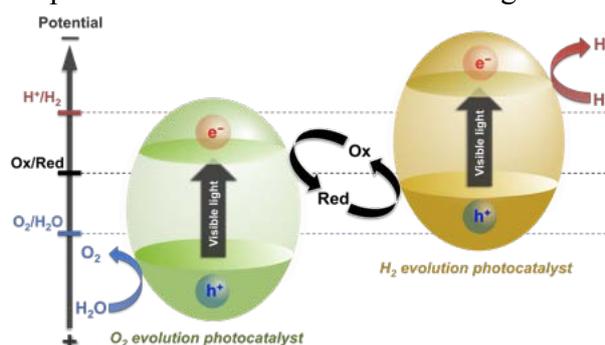


Fig. 1. Conceptual scheme for two-step water

oxidant. Based on the strategy, we have achieved overall water splitting using various visible light responsive photocatalysts, such as SrTiO<sub>3</sub> doped with Cr,<sup>[3]</sup> tantalum oxynitrides (TaON or BaTaO<sub>2</sub>N),<sup>[4-7]</sup> and organic dyes,<sup>[8]</sup> which work as a H<sub>2</sub> evolution photocatalyst, combined with tungsten oxide (WO<sub>3</sub>) for O<sub>2</sub> evolution in the presence of a shuttle redox mediator such as iodate/iodide (IO<sub>3</sub><sup>-</sup>/I<sup>-</sup>). The use of BaTaO<sub>2</sub>N or coumarin organic dye was demonstrating to be photoactive at wavelength up to ca. 700 nm. These results demonstrate the potential of a two-step water-splitting system for utilizing a broader band of visible spectrum.

Some oxynitride materials possess appropriate band levels for water splitting as well as a narrow band gap that permits visible light absorption. The top of valence band of these oxynitrides is much more negative than those of the corresponding oxides due to hybridization of the N 2p and O 2p orbitals. On the other hand, the bottom of the conduction band in these tantalum oxynitrides consists predominantly of empty tantalum orbitals. For example, tantalum oxynitride (TaON; band gap: ca. 2.5 eV, corresponding to light absorption up to 500 nm) has conduction and valence band edges at ca. -0.3 and +2.2 V vs. NHE, respectively, which are suitable for both water reduction and oxidation. However, the introduction of N 2p orbitals in the valence band generates a new problem in stability that need to be solved. Most oxynitrides undergo self-oxidative deactivation some degree, in which photogenerated holes oxidize nitrogen anions (N<sup>3-</sup>) to N<sub>2</sub> (2N<sup>3-</sup> + 6h<sup>+</sup> → N<sub>2</sub>). Recently, we have developed a simple method for fabricating an efficient oxynitride TaON, in which the TaON particles are first deposited on a conductive substrate using electrophoretic deposition, and then a necking treatment is applied to form effective contacts between the TaON particles.<sup>[9]</sup> It was also demonstrated that highly dispersed CoO<sub>x</sub> nanoparticles on the TaON photoanode efficiently scavenge photogenerated holes and effectively suppress self-oxidative deactivation of the TaON surface, resulting in a stable photocurrent.<sup>[10]</sup> This enabled us to stably split water into H<sub>2</sub> and O<sub>2</sub> under visible light irradiation at a relatively low applied bias (0.6 V vs. Pt counter electrode).

## References:

- [1] Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253
- [2] Abe, R. *J. Photochem. Photobiol. C: Photochemistry Reviews* **2010**, *11*, 179.
- [3] Abe, R.; Sayama, K.; Sugihara, H. *J. Phys. Chem. B* **2005**, *109*, 16052.
- [4] Abe, R.; Takata, T.; Sugihara, H.; Domen, K. *Chem. Commun.* **2005**, 3829.
- [5] Higashi, M.; Abe, R.; Takata, T.; Domen, K. *Chem. Mater.* **2005**, *21*, 1543.
- [6] Maeda, K.; Higashi, M.; Lu, D.; Abe, R.; Domen, K. *J. Am. Chem. Soc.* **2010**, *132*, 5858.
- [7] Abe, R.; Higashi, M.; Domen, K. *ChemSusChem*. **2011**, *4*, 228.
- [8] Abe, R.; Shinmei, K.; Hara, K.; Ohtani, B. *Chem. Commun.* **2009**, 3577.
- [9] Abe, R.; Higashi, M.; Domen, K. *J. Am. Chem. Soc.* **2010**, *132*, 11828.
- [10] Higashi M.; Domen K.; Abe, R. *J. Am. Chem. Soc.*, **2012**, *134*, 6968.



## Theoretical Study of Charge Transfer Process in Condensed Matter

Toshio Asada

*Osaka Prefecture University, The Research Institute for Molecular  
Electronic Devices (RIMED)*

*1-1, Gakuen-cho, Naka-ku, Sakai-city, Osaka, 599-8531 Japan*

### **Abstract:**

The simulation of chemical processes in proteins, condensed materials, and solutions require the coupling of quantum chemical methods and statistical mechanics approaches. The computational code[1] has been developed for molecular dynamics (MD) simulations using combined quantum mechanical/molecular mechanical (QM/MM) methods. Using the program, physical properties relating to charge transfer processes in complexes such as the degradation mechanism of the electron transporting layer in organic light-emitting diode (OLED)[2] or environmental effects on the redox potential of Q<sub>B</sub> plastoquinone in photosystem II (PSII) have been investigated.

Organic electro-luminescent (EL) and OLED electronic devices have recently been used as displays in mobile phones, televisions, electronic papers, and organic EL illuminations. In these OLED displays, emission is triggered by charge recombinations of electrons and holes in the light-emitting layer. It is known that the light emission efficiency of OLED devices is reduced as a function of time. This phenomenon is usually explained by penetration of Li ions into the electron-transporting layer. The degradation mechanism of the electron-transporting layer of Alq<sub>3</sub> is theoretically investigated [2] based on charge transfer rate constants.

The redox potential is also important to explain the charge transfer pathways in proteins. The environmental effects on the redox potential is evaluated using QM/MM MD simulations which can take the dynamical effects into consideration. Theoretical evaluation of redox potentials of Q<sub>B</sub>, and of the bromacil in PSII will be discussed.

### **References:**

- [1] Okamoto, T.; Yamada, K.; Koyano, Y.; Asada, T.; Koga, N.; Nagaoka, M.; *J. Comp. Chem.* **2011**, *32*, 932-942.
- [2] Asada, T.; Ohta, K.; Koseki, S.; *Theo. Chem. Acc.* **2011**, *130*, 439-448.



## Bioelectrochemical Approach in Energy Conversion

Kenji Kano

*Division of Applied Life Sciences, Graduate School of Agriculture, Kyoto University, Japan*

Bioelectrocatalytic systems, in which several biological redox reactions are coupled with electrode reactions, may be utilized for bio-sensing and energy conversion systems. One of the most popular biosensors is commercially available blood glucose sensor. On the other hand, biofuel cell becomes attracting attention as one of next-generation energy conversion systems. In order to couple biological redox reactions with electrode reactions, there are two types of strategies; direct electron transfer (DET)-type communication without mediator and mediated electron transfer (MET)-type one with mediators to assist the electron transfer between biological redox function and electrode.

Multi-copper oxidases (MCO) including laccase, bilirubin oxidase, and copper efflux oxidase would be the best catalyst for oxygen-reducing cathodes without release of O<sub>2</sub>-derived intermediates. The current density of DET-type bio-cathode has reached about 40 mA cm<sup>-2</sup> at 0 V (vs. Ag|AgCl electrode) at pH 5 under passive mode in atmosphere by controlling the hydrophobicity for oxygen transport and hydrophilicity for enzymatic reaction of meso-porous carbon electrodes.

On the other hand, there are a wide variety of strategies for anode. One of simple bio-anodes is microbe-catalyzed one, in which several microbes such as *Shewanella* sp. may be utilized to oxidize several organic and inorganic compounds and the electron is transferred to the cathode preferably in DET mode. This system is called microbial fuel cell (MFC). The weak points of this system is the low current density and that some inorganic cathode catalysis including specific carbon material such as Co-containing graphene will be required for field-type MFCs.

Photo-current can be observed in the presence of cyanobacteria as a catalyst and quinone as a mediator in anode on usual materials, and the coupling of the photo-anode system with MCO-catalyzed cathode leads to a bio-solar system, which can convert the photo-energy into the electric energy.

Glucose/O<sub>2</sub> biofuel cell has also been constructed in cooperation with Sony. NAD-dependent glucose dehydrogenase/NAD/diaphorase/quinone system is utilized as an anode catalyst. The cell power has reached about 10 mW cm<sup>-2</sup>, which is the world record in the MET system. Fructose/O<sub>2</sub> biofuel cell works as a noble DET-type biofuel cell, in which membrane-bound fructose dehydrogenase is utilized as an anode catalyst. The cell power has reached 2 mW cm<sup>-2</sup>, which is also the world record in the DET system.

The weak point of these enzymatic sugar/O<sub>2</sub> fuel cells may be that the complete oxidation of sugar fuels is difficult. In this sense, hydrogen and formate may be utilized as

fuels for complete oxidation. Hydrogen oxidation can be accelerated by *Desulfovibrio vulgaris* (Hildenborough) as a catalyst and methyl viologen as a mediator. The true mediator is of course hydrogenase. The H<sub>2</sub>-reducing anode has been coupled with MCO-catalyzed cathode to construct an H<sub>2</sub>/O<sub>2</sub> biofuel cell. Electrochemistry of isolated hydrogenase is also receiving a great attention.

Membrane-bound [NiFe] hydrogenase gives DET-type H<sub>2</sub>-oxidation current. The activity is reversibly inhibited at positive potential. However, the system may be utilized to construct gas-diffusion DET-type H<sub>2</sub>/O<sub>2</sub> biofuel cells.

Soluble NAD<sup>+</sup>-reducing hydrogenase and W- or Mo-containing NAD<sup>+</sup>-linked formate dehydrogenase has sequence homology very close to that of complex I. These are also useful to construct hydrogen-oxidizing and formate-oxidizing anodes, respectively.

These variety of anode strategies for energy conversion system are also very important to construct biosensors.



## Solar Fuel Production Based on the Bio-hybrid Artificial Photosynthesis System

Yutaka Amao

*Department of Applied Chemistry, Oita University, Oita 870-1192, Japan, and Precursory Research for Embryonic Science and Technology (PREST), Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan*

**Abstract:** Major purpose of this presentation is to achieve the “Artificial Photosynthesis for Solar Fuel Production”. In this presentation, production technologies of low-carbon fuels are classified into two categories[1-3]. First category is the solar hydrogen production from water based on the artificial photosynthesis using bioinspired system consisting of an electron donor, a photosensitizer, an electron relay and a platinum nano-particle. Second category is the artificial photosynthesis system for solar fuel production from CO<sub>2</sub>. CO<sub>2</sub> fixation is a potential technology for photocatalytic CO<sub>2</sub> reduction and synthesis of organic compounds from CO<sub>2</sub> as the starting material. For example, the low-carbon fuel, methanol production from CO<sub>2</sub> is accomplished using the artificial photosynthesis system consisting of the photosensitizer molecule and three dehydrogenases (formate, aldehyde and alcohol dehydrogenases). For example, methanol production from CO<sub>2</sub> using the artificial photosynthesis system is introduced. A sample solution containing ZnTPPS (0.1 μM), MV<sup>2+</sup> (0.1 mM), TEOA (0.3 M) FDH (12.5 units), AldDH (12.5 units) and ADH (12.5 units) is deaerated and then flushed with argon gas for 5 min. NaHCO<sub>3</sub> (0.01 mM) is added to the sample solution and then irradiated. The produced methanol is measured by gas chromatography. When the sample solution is irradiated with a tungsten lamp, methanol is produced with irradiation time. The methanol production was 0.55 μM after 4 h irradiation. The conversion yield of HCO<sub>3</sub><sup>-</sup> to methanol is estimated to be 5.5% after 4 h irradiation. In contrast, no methanol production is observed without irradiation or in the absence of HCO<sub>3</sub><sup>-</sup>. Thus, the produced methanol is not the oxidized TEOA but the origin from HCO<sub>3</sub><sup>-</sup> reduction with three dehydrogenases. These results indicate that the photochemical synthesis of methanol from HCO<sub>3</sub><sup>-</sup> with FDH, AldDH and ADH via the photoreduction of MV<sup>2+</sup> using ZnTPPS photosensitisation.

### References:

- [1] Amao, Y. *ChemCatChem* **2011**, 3, 458.
- [2] Amao, Y. *Current Nanoscience* **2008**, 4, 45.
- [3] Amao, Y., Maki, Y., Fuchino, Y. *J. Phys. Chem. C* **2009**, 113, 16811.



# Poster Presentations

## **Titles of Poster Presentations**

- PS01. Mutual relationships between structural and functional changes in the PsbM-deletion mutant of photosystem II**  
Sayaka Utoh, Keisuke Kawakami, Yasufumi Umena, Masako Iwai, Masahiko Ikeuchi, Jian-Ren Shen, Nobuo Kamiya
- PS02. Theoretical Simulation of Carotenoid Absorption Spectrum**  
Chiasa Uragami, Hideki Hashimoto
- PS03. Three catalysis achieved by ADP ribose pyrophosphatase**  
Yoshihiko Furuike, Yuka Akita, Ikuko Miyahara, and Nobuo Kamiya
- PS04. Synthesis of a sugar-incorporated C-C-N pincer palladium complex and their catalytic ability toward Suzuki-Miyaura reaction in water**  
Yosuke Imanaka, Hideki Hashimoto, Isamu Kinoshita, and Takanori Nishioka
- PS05. Reactions of Dibenzothiophene Derivatives Containing Bidentate Chelate Moieties with Iron Carbonyl Complexes**  
Kiyokazu Santo, Masakazu Hirotsu, and Isamu Kinoshita
- PS06. Dynamic structure change of phenothiazine trimer radical cation in its photo-induced charge separated state**  
Ayumu Karimata
- PS07. Molecular assembly of photosynthetic antenna pigment complexes on a gold electrode by using recombinant light-harvesting polypeptides with His-tag**  
Syunsuke Sakai
- PS08. Pigments and protein composition of the photosynthetic antenna from a siphonous green alga (*Codium intricatum* Okamura)**  
SHIGEMATSU, Yusuke; FUJII, Ritsuko; OKA, Naohiro; IHA, Masahiko; HASHIMOTO, Hideki
- PS09. Crystal enlargement of ADPRase and neutron diffraction experiments to elucidate the proton transfer pathway**  
Yusuke Komatsu, Yoshihiko Furuike, Ikuko Miyahara, and Nobuo Kamiya
- PS10. Sugar-coated N-heterocyclic carbene complexes incorporated with long alkyl Chains**  
Akiya Oda, Hideki Hashimoto, Isamu Kinoshita, and Takanori Nishioka
- PS11. Elucidation of the photosynthetic function of carbonylcarotenoids in the Chloroplast Genome-Modified lettuce**  
Masahiro Shirota, Ritsuko Fujii, Norihiko Misawa, Hideki Hashimoto
- PS12. Optical properties of photoexcited states of oceanic photosynthetic antenna pigment, chlorophylls *c* (Chls *c*)**  
Naoki Senju, Ritsuko Fujii, Tadashi Mizoguchi, Masahiko Iha, Akio Ichimura, Hideki Hashimoto
- PS13. Applications of Peptide Gemini Surfactants as Novel Solubilization Surfactants for Photosystems I and II of Cyanobacteria**  
S. Koeda, T. Mizuno, T. Noji, T. Dewa, T. Tanaka, M. Nango

- PS14. How iodide ions inhibit the oxygen evolution of photosystem II?**  
Keisuke Kawakami, Daisuke Hgiwara, Yasufumi Umena, Jian-Ren Shen, Nobuo Kamiya
- PS15. Syntheses of sulfur bridged Mo complexes with dithiophosphate ligand and the stability controlled by functional ligand**  
KAWAMOTO, Keisuke; ICHIMURA, Akio; KINOSHITA, Isamu
- PS16. Syntheses and Characterization of Novel Sulfido PtM<sub>2</sub> (M = Rh, Ir) Type Trinuclear Complexes with Chelated N-Heterocyclic Carbene Ligands**  
Yuri Maeda, Hideki Hashimoto, Isamu Kinoshita, and Takanori Nishioka
- PS17. Exciton-exciton annihilation in light harvesting complexes from a purple bacterium**  
Yuya Nagaoka, Daisuke Kosumi, Ritsuko Fujii, Mitsuru Sugisaki, and Hideki Hashimoto
- PS18. Towards Catalytic Water Oxidation: Synthesis of a Cobalt(III)-Oxon Cuban Cluster with protected-*p*-pyridylphosphonato ligand**  
Tomoyuki HASEGAWA, Keisuke KAWAMOTO, Isamu KINOSHITA
- PS19. Computational analysis of the electron-transfer inhibitors in Photosystem II**  
Ayako Tanaka, Satoshi Suzuri, Asada Toshio, Keisuke Kawakami, Yasufumi Umena, Jian-Ren Shen, Miyahara Ikuko, Nobuo Kamiya
- PS20. Regulation of the receptor ability of Zn-porphyrin by the formation of Fe complexes**  
Yoshikazu Ninomiya, Masatoshi Kozaki, Shuichi Suzuki, Keiji Okada
- PS21. Structural study on the Mn atoms in the oxygen-evolving complex of Photosystem II by X-ray absorption techniques**  
UMENA, Yasufumi, KAWAKAMI, Keisuke, Tanka, Ayaka, SHEN, Jian-Ren, KAMIYA, Nobuo
- PS22. The pH titration experiment in the crystals of ADPRase-ADPR binary complexes**  
Yurie Tomita, Yoshihiko Furuike, Ikuko Miyahara, and Nobuo Kamiya
- PS23. Design of Polyoxometalates Aimed to Artificial Photosynthesis**  
Hitoshi Yoneda, Keisuke Kawamoto, Toshio Asada, Isamu Kinoshita, and Hideki Hashimoto
- PS24. Synthesis and Magnetic Properties of Iron and Cobalt Complexes Containing a  $\pi$ -Radical Ligand with Photo-Excited High-Spin State**  
Koichi Katayama
- PS25. Relationship of charge of heads group of lipid and photochemical activity of photosystem II in reconstituted lipid bilayer**  
Tomoyasu Noji, Masaharu Kondo, Keisuke Kawakami, Jian-ren Shen, Mamoru Nango, Takehisa Dewa
- PS26. Construction of Carotenoid Molecularly-Oriented Film: A Model System of Photosynthetic Antenna**  
Shouhei Kita

**PS27. Photoinduced Electron Transfer of Platinum Bipyridine Diacetylides Linked by Triphenylamine and Naphthalenediimide and its application to photoelectric conversion system**

Shuichi Suzuki, Yuma Matsumoto, Mai Tsubamoto, Masatoshi Kozaki, Kenshi Kimoto, Munetaka Iwamura, Koichi Nozaki, Naoki Senju, Chiasa Uragami, Hideki Hashimoto, and Keiji Okada

**PS28. Syntheses and Properties of Nickel and Zinc Complexes with a Tripodal Ligand, 1-(pyridine-2-yl)-2,2-bis(pyridine-2-ylthio)ethanone**

Yu Masuda

**PS29. A Trial for Developing the Hybrid Artificial Photosynthesis**

Yui Takemoto, Keisuke Kawakami, Isamu Kinoshita

## **PS01. Mutual relationships between structural and functional changes in the PsbM-deletion mutant of photosystem II**

Sayaka Utoh<sup>1</sup>, Keisuke Kawakami<sup>2</sup>, Yasufumi Umena<sup>2,3</sup>, Masako Iwai<sup>4</sup>, Masahiko Ikeuchi<sup>5</sup>, Jian-Ren Shen<sup>6</sup>, Nobuo Kamiya<sup>2,1</sup>

<sup>1</sup> *Graduate School of Science, Osaka City University;* <sup>2</sup> *The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University;* <sup>3</sup> *JST-PRESTO;* <sup>4</sup> *Center for Biological Resources and Informatics, Tokyo Institute of Technology;* <sup>5</sup> *Department of Life Sciences (Biology), Graduate School of Arts and Science, The University of Tokyo;* <sup>6</sup> *Division of Bioscience, Graduate School of Natural Science and Technology/Faculty of Science, Okayama University*

Photosystem II (PSII) is a membrane protein complex that performs light-induced oxygen evolution from water. PSII consists of 20 subunits and various cofactors such as chlorophyll a, carotenoid, plastoquinone, and lipids. PsbM is one of the low molecular weight subunits of PSII, and is located in the monomer-monomer interface of PSII dimer. The function of PsbM has been reported to stabilize the PSII dimer and to relate to electron transfer efficiency of PSII. In order to elucidate the role of PsbM, we purified oxygen-evolving PSII complex from a PsbM-deletion mutant of *Thermosynechococcus vulcanus*, and started its structural and biochemical analysis.

## **PS02. Theoretical Simulation of Carotenoid Absorption Spectrum**

Chiasa Uragami<sup>1</sup>, Hideki Hashimoto<sup>1,2</sup>

- 1. JST/CREST and Department of Physics, Graduate School of Osaka City University*
- 2. Osaka City University Advanced Research Institute for Natural Science and Technology (OCARINA)*

In general, the absorption spectrum of carotenoid depends on its chemical structure. However, when we compare the absorption spectrum of the  $\beta$ -carotene with lycopene and astxanthin, which all of them has same number of conjugated double bond, not only the maximum wavelength, but also the spectral shapes are obviously different. Thus, we could see that the absorption spectra dose not depends only on the chemical structure. There must be some other factors that make difference in spectrum. In this study we consider that the factor is interaction between the carotenoid and neighboring molecules, hence we theoretically simulate the absorption spectrum and tried to get some kind of information that which kind of interaction contributes to the absorption spectrum.

### **PS03. Three catalysis achieved by ADP ribose pyrophosphatase**

°Yoshihiko Furuike<sup>1</sup>, Yuka Akita<sup>1</sup>, Ikuko Miyahara<sup>1</sup>, and Nobuo Kamiya<sup>2</sup>

<sup>1</sup>*Graduate School of Science, Osaka City University*

<sup>2</sup>*The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University*

ADP ribose pyrophosphatase (ADPRase) hydrolyzes ADP ribose to AMP and ribose-5'-phosphate (R5P) with the help of divalent metal cations. Although the existence of the concerted general acid-base catalysis and the metal ion catalysis has been expected, the detail of their chemical mechanisms hasn't been described. In order to reveal the ADPRase's chemical function, we conducted the time resolved X-ray crystallography at atomic resolutions. Consequently, the ADPRase mechanism could be described in three important points; the metal assisted regulations of configurations and reactivities for the electrophilic pyrophosphate and the nucleophilic water molecule, the participation of Glu residues in the deprotonation of the water molecule around  $\alpha$ -phosphorus, and the well-designed hydrogen bonding network including the low barrier hydrogen bond around  $\beta$ -phosphorus.

### **PS04. Synthesis of a sugar-incorporated C-C-N pincer palladium complex and their catalytic ability toward Suzuki-Miyaura reaction in water**

Yosuke Imanaka,\* Hideki Hashimoto, Isamu Kinoshita, and Takanori Nishioka

*Division of Molecular Materials Science, Graduate School of Science, Osaka City University, The OCU Advanced Institute of Natural Science and Technology (OCARINA), Osaka City University*

We demonstrated that the click chemistry is one of the useful methods to introduce sugar units into NHC ligands. The obtained C-C-N pincer NHC Pd complex with an acetyl protected D-glucose unit exhibited efficient catalytic activity in the Suzuki-Miyaura coupling reaction in aqueous media with excellent TON (91000) and TOF (30000 h<sup>-1</sup>). The acetylated complex, whose solubility is limited in water, should be deprotected under the reaction condition. These results imply that the click chemistry open a new way for the development of novel green asymmetric catalysts via incorporation of a variety of sugar units including mono-, di-, and poly-saccharides into metal complexes.

## PS05. Reactions of Dibenzothiophene Derivatives Containing Bidentate Chelate Moieties with Iron Carbonyl Complexes

Kiyokazu Santo, Masakazu Hirotsu, and Isamu Kinoshita

*Department of Chemistry, Graduate School of Science, Osaka City University  
(Molecular Design Laboratory)*

Hydrogenases are enzymes that catalyze the reversible oxidation of dihydrogen. The active site of the [FeFe]-hydrogenase has two iron centers, a bridged-dithiolate ligand, and biologically unusual carbonyl and cyanide ligands. A Schiff base containing an N,S-bidentate chelate moiety was synthesized by the reaction of 4-formyldibenzothiophene with 2-(methylthio)aniline. The photochemical reaction of the dibenzothiophene derivative with Fe(CO)<sub>5</sub> was performed to give two products, [Fe(L<sub>S,C,N</sub>)(CO)<sub>2</sub>Fe(CO)<sub>3</sub>] (**1**) and [Fe(L<sub>S,C,N,S</sub>)(CO)Fe(CO)<sub>3</sub>] (**2**), where L is a ligand formed by C-S cleavage of the Schiff base ligand precursor. These complexes have two iron centers, a bridged-thiolate ligand, and carbonyl ligands. Complex **2** acts as an electro-catalyst for proton reduction in the presence of acetic acid.

## PS06. Dynamic structure change of phenothiazine trimer radical cation in its photo-induced charge separated state

Ayumu Karimata

*Osaka City University*

We investigated photo-induced electron transfer of anthraquinone-phenothiazine trimer dyad (AQ-B-PTZ1-PTZ2-PTZ3) linked by bicyclo[2.2.2]octane (B) by means of pico- and nano- second transient absorption spectroscopies. Irradiation of 355 nm laser-pulse immediately gave a 620 nm band which is attributed to the spectral overlap of anthraquinone radical anion and meta-stable edge phenothiazine radical cation (PTZ1<sup>+</sup>-PTZ2-PTZ3). During 0.5-6 ns after the laser-pulse, the 620 nm band was converted to a 940 nm band that is assigned to the most stable phenothiazine trimer cation radical (PTZ1-PTZ2<sup>+</sup>-PTZ3), showing a hole-shift process with structural relaxation in the phenothiazine trimer radical cation.

**PS07. Molecular assembly of photosynthetic antenna pigment complexes on a gold electrode by using recombinant light-harvesting polypeptides with His-tag**

Syunsuke Sakai

*Graduate School of Engineering, Nagoya Institute of Technology*

The light-harvesting (LH) complexes containing reaction center (RC) from purple bacteria capture visible and near-infrared light energy, funnel the excited energy into the RC and convert it into charge separation with high efficiency. This energy transfer system is very useful to develop artificial photosynthetic devices mimicking the photosynthetic system. In this study, we produced recombinant LH apoproteins bearing His-tag by *E. coli* expression system and reconstituted artificial photosynthetic protein/pigment complexes using the recombinant LH apoproteins and Zn-porphyrin derivatives as a pigment cofactor. The reconstituted complex was immobilized on a Ni-nitrilotriacetic acid modified gold electrode for photocurrent measurement.

**PS08. Pigments and protein composition of the photosynthetic antenna from a siphonous green alga (*Codium intricatum* Okamura)**

○SHIGEMATSU, Yusuke; FUJII, Ritsuko; OKA, Naohiro; IHA, Masahiko;  
HASHIMOTO, Hideki

*OCARINA/OCU; Osaka City Univ.; JST-PRESTO; South Product Inc.; JST-CREST*

The protein and pigment analyses were performed to the siphonaxanthin-chlorophyll *a/b* protein(SCP) isolated from mass-cultured filamentous body of the siphonous green alga, *Codium intricatum* Okamura. The SCP consists of three 27 kDa homogeneous subunits, which binds both siphonaxanthin and its C12:0 ester equivalently. The amino-acid sequence of SCP was partially determined. As its consequence, the SCP is quite similar to the major photosynthetic antenna of higher plants, LHCII, except that it binds siphonaxanthin as a substitute of lutein.

**PS09. Crystal enlargement of ADPRase and neutron diffraction experiments to elucidate the proton transfer pathway**

Yusuke Komatsu<sup>1</sup>, Yoshihiko Furuike<sup>1</sup>, Ikuko Miyahara<sup>1,2</sup>, and Nobuo Kamiya<sup>1,2</sup>

<sup>1</sup>*Department of chemistry, Graduate School of Science, Osaka City University;* <sup>2</sup>*The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University*

ADPRase is a divalent-metal dependent enzyme which hydrolyzes ADP-ribose (ADPR) to AMP and ribose-5'-phosphate (R5'P). Our group has proposed a reaction mechanism of ADPRase based on the *in situ* observations of crystalline-state reaction. In order to prove the proton transfers predicted in the steps, we planned time-resolved neutron crystallography of ADPRase-ADPR system triggered by Mn<sup>2+</sup> soaking.

In order to experiment time-resolved neutron crystallography, we have to solve 3 problems.

1. Enlargement of ADPRase crystal 0.3mm<sup>3</sup> at least.
2. Replacement water to deuterium in ADPRase crystal.
3. The condition for Mn<sup>2+</sup> soaking should be examined in it.

Solve these problems, We experiment time-resolved neutron crystallography.

**PS10. Sugar-coated N-heterocyclic carbene complexes incorporated with long alkyl Chains**

Akiya Oda, Hideki Hashimoto, Isamu Kinoshita, and Takanori Nishioka

*Department of Chemistry, Faculty of Science, Osaka City University, Division of Molecular Materials Science, Graduate School of Science, Osaka City University, The OCU Advanced Institute of Natural Science and Technology (OCARINA), Osaka City University*

A palladium complex was synthesized using an NHC ligand precursor having an acetyl-protected b-D-glucopyranosyl unit and a dodecyl group. There are two possible isomers due to arrangement of two NHC moieties and the ethylene bridge. <sup>1</sup>H NMR spectrum of the complex indicates that two diastereomers of the palladium complex exist in solution. Since deprotection of the acetyl groups is essential for higher water solubility, a reaction of the palladium complex with sodium methoxide in methanol was also performed. Deprotection was confirmed using <sup>1</sup>H NMR spectroscopy and electrospray mass spectrometry. Isolation of the deprotected complex is currently in progress.

## **PS11. Elucidation of the photosynthetic function of carbonylcarotenoids in the Chloroplast Genome-Modified lettuce**

Masahiro Shirota<sup>1</sup>, Ritsuko Fujii<sup>2,3</sup>, Norihiko Misawa<sup>4</sup>, Hideki Hashimoto<sup>5</sup>

<sup>1</sup> *Department of Physics, Science, Osaka City University,* <sup>2</sup> *OCARINA,* <sup>3</sup> *JST-PRESTO,* <sup>4</sup> *Ishikawa Prefectural College,* <sup>5</sup> *JST-CREST*

In photosynthetic pigment protein complexes, carotenoids absorb sunlight and transfer it to chlorophylls. The high efficiency of the energy transfer has been reported for the photosynthetic antenna from some marine algae which bounds unique carbonyl carotenoids.<sup>1),2)</sup> Misawa et al. developed the chloroplast-genome modified (CGM) lettuce which accumulates carbonyl carotenoids in 95% of total carotenoids.<sup>3)</sup> The CGM lettuce grows in normal irradiation conditions, however the function of those carbonyl carotenoids has not been clarified yet. In this work, we prepared the major photosynthetic pigment protein complexes from the CGM lettuce and investigated the carotenoid to chlorophyll energy transfer.

Reference

- 1) Polívka and Sundström, *Chem. Rev.* **104** (2004) 2021
- 2) Kosumi et al., *J. Phys. Chem. Lett.*, **3**(2012) 2659
- 3) N.Misawa et al, patent pending 2012-198865

## **PS12. Optical properties of photoexcited states of oceanic photosynthetic antenna pigment, chlorophylls *c* (Chls *c*)**

Naoki Senju<sup>1</sup>, Ritsuko Fujii<sup>2,3</sup>, Tadashi Mizoguchi<sup>4</sup>, Masahiko Iha<sup>5</sup>, Akio Ichimura<sup>2</sup>, Hideki Hashimoto<sup>1,2,6</sup>

<sup>1</sup>*Department of Physics, Graduate School of Science, Osaka City University,* <sup>2</sup>*OCARINA,* <sup>3</sup>*JST-PRESTO,* <sup>4</sup>*Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritumeikan University,* <sup>5</sup>*South Product Ltd.,* <sup>6</sup>*JST-CREST*

Chlorophylls *c* (Chls *c*) are characterized by a fully conjugated porphyrin  $\pi$ -system as well as a unique acrylate acid at the 17-position (17-CH=CH-COOH). Therefore it is expected that protonation/de-protonation at the acrylate acid of Chls *c* affect their optical properties. In this study, absorption and fluorescence spectra of both Chl *c*<sub>1</sub> and Chl *c*<sub>2</sub> in 80% ethanol/water were compared under various pH values. The relative absorbances and fluorescence quantum yields of both Chl *c*<sub>1</sub> and Chl *c*<sub>2</sub> exhibited clear pH dependencies. Their acid dissociation counts were determined. The optical properties of methyl ester-substituted Chl *c*<sub>1</sub> (17-CH=CH-COOCH<sub>3</sub>) were found not to show the pH dependencies, indicating the pH dependencies originated from protonation/de-protonation at the acrylate acid.

### PS13. Applications of Peptide Gemini Surfactants as Novel Solubilization Surfactants for Photosystems I and II of Cyanobacteria

S. Koeda,<sup>1</sup> T. Mizuno,<sup>1\*</sup> T. Noji,<sup>1</sup> T. Dewa,<sup>1</sup> T. Tanaka,<sup>1</sup> M. Nango<sup>2</sup>

<sup>1</sup>*Graduate School of Engineering, Nagoya Institute of Technology,*

<sup>2</sup>*OCARINA, Osaka City University,*

<sup>1</sup>*Gokiso-cho, showa-ku, Nagoya, Aichi 466-8555, Japan*

<sup>1</sup>*Phone/Fax: +81-52-735-5237; E-mail: [cjk15042@stn.nitech.ac.jp](mailto:cjk15042@stn.nitech.ac.jp)*

Recently, we have studied novel gemini-type peptide surfactants (PG-surfactants), and the oligo-Asp series of PG-surfactants, **D<sub>3</sub>C<sub>12</sub>** and **D<sub>4</sub>C<sub>12</sub>**, are found to exhibit higher micelle-formation properties and tend to form bilayer morphologies. On the other hand, photosystems I and II (PSI and PSII) are two of the representative photosynthetic membrane proteins and these play key roles in absorbing photons from sunlight and producing electrons or holes *via* charge separation at the reaction center. In the thylakoid membrane, PSI and PSII take homotrimer and homodimer as a stable supramolecular complex, respectively. In this study, we designed new PG-surfactants, **DKDKC<sub>12</sub>K** and **DKDKC<sub>12</sub>D**, that could be utilize as a novel solubilization surfactant for membrane proteins, especially PSI trimer and PSII dimer.

From the comparison of absorption spectra of PSI trimer and PSII dimer solubilized with 0.1 wt% b-DDM and 0.1 wt% **DKDKC<sub>12</sub>K** or **DKDKC<sub>12</sub>D**, we confirmed that these PG-surfactants were able to solubilize PSI trimer and PSII dimer without denaturation. Using the dynamic light scattering measurements, these PG-surfactants can solubilize PSI trimer and PSII dimer without further aggregations. With respect to the activities of light-induced electron transfer initiated from reaction center, PSI trimer and PSII dimer solubilized with these PG-surfactants retained the original electron transfer activities.

## **PS14. How iodide ions inhibit the oxygen evolution of photosystem II?**

Keisuke Kawakami<sup>1</sup>, Daisuke Hgiwara<sup>2</sup>, Yasufumi Umena<sup>1</sup>, Jian-Ren Shen<sup>3</sup>,  
Nobuo Kamiya<sup>1,2</sup>

<sup>1</sup>*The OCU Advanced Research Institute for Natural Science and Technology, Osaka City university,* <sup>2</sup>*Graduate School of Science, Osaka City University,* <sup>3</sup>*Graduate School of Natural Science and Technology, Okayama University.*

Oxygen-evolving photosystem II (PSII) is the site of light-induced water-splitting and provides us with molecular oxygen indispensable for life on the earth. Chloride ion (Cl<sup>-</sup>) is an essential cofactor for oxygen evolution of PSII, and is closely associated with the Mn<sub>4</sub>CaO<sub>5</sub>-cluster. Substitution of Cl<sup>-</sup> with iodide ion (I<sup>-</sup>) completely inhibited oxygen evolution of PSII, whereas substitution of Cl<sup>-</sup> with Bromide ions (Br<sup>-</sup>) did not inhibit oxygen evolution. In this symposium, we will discuss the conformational changes around the Mn<sub>4</sub>CaO<sub>5</sub>-cluster due to the substitution of Cl<sup>-</sup> with I<sup>-</sup>.

## **PS15. Syntheses of sulfur bridged Mo complexes with dithiophosphate ligand and the stability controlled by functional ligand**

○KAWAMOTO, Keisuke; ICHIMURA, Akio; KINOSHITA, Isamu

*Osaka City Univ., OCARINA*

The syntheses and the X-ray structure of incomplete cubane-type complex [Mo<sub>3</sub>S<sub>4</sub>(dtp)<sub>3</sub>- (μ<sub>2</sub>-dtp)(pyrazine)] have been reported. In the cyclic voltammetry, the mixture of the complex and CF<sub>3</sub>COOH shows catalytic current after overnight. The catalytic current increased with the concentration of CF<sub>3</sub>COOH. The <sup>1</sup>H NMR spectra of the complex at various temperatures indicate the structure in solution as follows: 1) a pyrazine coordinated species is in equilibrium with a pyrazine uncoordinated one in solution. 2) the equilibrium is strongly shifted to the dissociated species at room temperature. 3) the all pyrazine hydrogen atoms can distinguish at -30°C and lower because of a restricted rotation about the Mo-N (pyrazine) bond.

## PS16. Syntheses and Characterization of Novel Sulfido PtM<sub>2</sub> (M = Rh, Ir) Type Trinuclear Complexes with Chelated N-Heterocyclic Carbene Ligands

Yuri Maeda,\* Hideki Hashimoto, Isamu Kinoshita, and Takanori Nishioka

*Division of Molecular Materials Science, Graduate School of Science, Osaka City University The OCU Advanced Research Institute of Natural Science and Technology (OCARINA)*

A bottom up method to construct sulfido bridged multinuclear complexes with N-heterocyclic carbene ligands using the hydrosulfido platinum complexes, [Pt(bisNHC-C<sub>n</sub>-R)(SH)<sub>2</sub>], was performed. From X-ray structural analyses of the trinuclear complexes, the M<sub>2</sub>Pt triangle cores are isosceles triangles with shorter M–M distances. The cyclic voltammetry of the heterometallic trinuclear complexes showed two reversible reduction peaks and only the second reduction potentials were affected by the lengths of the bridging alkyl chains of the bisNHC ligands. No significant differences were observed for the absorption maxima with the variation of N-substituents but small differences were found with the different chain lengths.

## PS17. Exciton-exciton annihilation in light harvesting complexes from a purple bacterium

Yuya Nagaoka<sup>A,B</sup>, Daisuke Kosumi<sup>B,C</sup>, Ritsuko Fujii<sup>B,C</sup>, Mitsuru Sugisaki<sup>A,B,C</sup>, and Hideki Hashimoto<sup>A,B,C</sup>

*Osaka City Univ.<sup>A</sup>, CREST/JST<sup>B</sup>, OCARINA<sup>C</sup>*

Both relaxation of a two-exciton state and exciton-exciton annihilation in bacteriochlorophylls of the light harvesting complexes from a photosynthetic purple bacterium have been studied by femtosecond pump-probe spectroscopy. In this study, we have targeted the B875 (bacteriochlorophyll) ring of the light harvesting complexes (LH1) from a photosynthetic purple bacterium, *Rsp. rubrum* G9. The lifetime of two-exciton state was determined to be a few ps, and exciton-exciton annihilation occurred in ~10 ps after excitation to the Q<sub>y</sub> band. A new method for analyzing the exciton-exciton annihilation in LH1 thus proposed can be a clue to clarify the excitation energy transfer between the light harvesting complexes.

## PS18. Towards Catalytic Water Oxidation: Synthesis of a Cobalt(III)-Oxon Cuban Cluster with protected-*p*-pyridylphosphonato ligand

Tomoyuki HASEGAWA, Keisuke KAWAMOTO, Isamu KINOSHITA

*Osaka City Univ., OCARINA*

Water oxidation is a very important process for artificial photosynthesis. We intend to construct a water oxidation system. A water oxidation catalyst is combined to an electrode via a semiconductor photocatalyst, which acts as a photochemical reaction center. The system will be able to directly incorporated into reducing site on an electrode. We have focused on a Cobalt(III)-Oxo Cuban Cluster [Co<sub>4</sub>O<sub>4</sub>(OAc)<sub>4</sub>(Pyridine)] as a water oxidation catalyst, because iso-structural complexes of [Co<sub>4</sub>O<sub>4</sub>(OAc)<sub>4</sub>(Pyridine)] have been synthesized by using *p*-substituted pyridine derivatives. Herein, we report the synthesis of [Co<sub>4</sub>O<sub>4</sub>(OAc)<sub>4</sub>(*p*-pyridyl-*O*-protected-phosphonato-*kN*)], which is possibly condensed on a semiconductor photocatalyst.

## PS19. Computational analysis of the electron-transfer inhibitors in Photosystem II

Ayako Tanaka<sup>1</sup>, Satoshi Suzuri<sup>1</sup>, Asada Toshio<sup>2</sup>, Keisuke Kawakami<sup>3</sup>, Yasufumi Umena<sup>3,5</sup>, Jian-Ren Shen<sup>4</sup>, Miyahara Ikuko<sup>1,3</sup>, Nobuo Kamiya<sup>3,1</sup>

<sup>1</sup>*Graduate School of Science, Osaka City University;* <sup>2</sup>*Department of Chemistry, Osaka Prefecture University;* <sup>3</sup>*The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University;* <sup>4</sup>*Division of Bioscience, Graduate School of Natural Science and Technology/Faculty of Science, Okayama University;* <sup>5</sup>*Japan Science and Technology Agency (JST), Precursory Research for Embryonic Science and Technology*

Photosystem II (PSII) is a large protein complex catalyzing water oxidation and plastoquinone reduction. PSII monomer has two plastoquinones, Q<sub>A</sub> and Q<sub>B</sub>. After light excitation and charge separation, an electron is transferred to Q<sub>A</sub>, then Q<sub>B</sub>. The key factor in this electron transfer is redox potential. Herbicides bind Q<sub>B</sub> site and inhibit the electron transfer from Q<sub>A</sub>. These herbicides have been classified into several types; phenolic-, triazine-, uracil-, and urea-types. The representatives of the four types are bromoxynil, terbutryn, bromacil, and DCMU, respectively. Using a quantum mechanical and molecular mechanical (QM/MM) method, we analyzed the redox potentials of Q<sub>B</sub> and herbicides. Based on these results, we will discuss the structure-function relationships of the herbicides in PSII.

## **PS20. Regulation of the receptor ability of Zn-porphyrin by the formation of Fe complexes**

\*Yoshikazu Ninomiya, Masatoshi Kozaki, Shuichi Suzuki, Keiji Okada

*Molecular materials Science, Graduate School of Science, Osaka City University*

We prepared Zn-porphyrin-inserted phenylene-ethynylene oligomers (**1**). Bipyridine chromophore was attached at one end of oligomer **1**, and the other end of the oligomers was diverged and attached to two other bipyridine rings through flexible alkyl chains. Addition of Fe(II) to **1** cleanly produced a Fe(bpy)<sub>3</sub>-type complex **2**. In the complex **2**, the Zn-porphyrin moiety was covered by flexible alkyl chains. Because of this geometrical change, the axial coordination on the Zn-porphyrin is thought to be suppressed. The degree of suppression was shown to be dependent on both alkyl chain length and bulkiness of axial ligands.

## **PS21. Structural study on the Mn atoms in the oxygen-evolving complex of Photosystem II by X-ray absorption techniques**

○UMENA, Yasufumi<sup>a,b</sup>, KAWAKAMI, Keisuke<sup>a</sup>, Tanka, Ayako<sup>b</sup>, SHEN, Jian-Ren<sup>c</sup>, KAMIYA, Nobuo<sup>a,d</sup>.

*<sup>a</sup>The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City Univ., <sup>b</sup>JST-PRESTO, <sup>c</sup>Graduate School of Natural Science and Technology/Faculty of Science, Okayama Univ., <sup>d</sup>Graduate School of Science, Osaka City Univ.*

Molecular oxygen on Earth is generated from photosynthesis by cyanobacteria, algae and plants, where water molecules are split by Photosystem II (PSII). PSII performs a series of light-induced electron transfer reactions to generate molecular oxygen. The catalytic center for water-splitting in PSII is composed of four Mn atoms and one Ca atom organized in a Mn<sub>4</sub>CaO<sub>5</sub>-cluster, which cycles through several different redox states to accomplish the catalytic process. In this study, we analyzed the electronic state of each Mn atom by X-ray at the wavelength on the Mn K-absorption edge. We will discuss each Mn valence of the cluster based on crystallographic analysis.

## PS22. The pH titration experiment in the crystals of ADPRase-ADPR binary complexes

°Yurie Tomita<sup>1</sup>, Yoshihiko Furuike<sup>2</sup>, Ikuko Miyahara<sup>2,3</sup>, and Nobuo Kamiya<sup>3,2</sup>

<sup>1</sup>*Faculty of Science, and* <sup>2</sup>*Graduate School of Science, Osaka City University*

<sup>3</sup>*The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University*

ADPRase is an enzyme, which hydrolyzes ADP-ribose (ADPR) into ribose-5'-phosphate and AMP in the presence of divalent metal ions. In order to identify the general acid - base catalysts in the ADPR hydrolysis reaction, we investigated the pH effect on the geometry of ADPR diphosphate in seven crystals of ADPRase-ADPR binary complexes with different pHs. The  $\alpha$ -phosphate changed its P-O bond lengths with a  $pK_a$  value of 4.2, while the  $\beta$ -phosphate didn't. This indicates the difference of environments in which  $\alpha$ - and  $\beta$ -phosphate are placed. The protonation state of the  $\beta$ -phosphate is likely controlled by the well-designed hydrogen bonding network including the acid catalyst during the ADPR hydrolysis reaction.

## PS23. Design of Polyoxometalates Aimed to Artificial Photosynthesis

Hitoshi Yoneda<sup>1,3</sup>, Keisuke Kawamoto<sup>1,3</sup>, Toshio Asada<sup>4</sup>, Isamu Kinoshita<sup>1,2,3</sup>, and Hideki Hashimoto<sup>1,2,3</sup>

<sup>1</sup>*The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University, Osaka, Japan,* <sup>2</sup>*CREST/JST,* <sup>3</sup>*Graduate School of Science, Osaka City University, Osaka, Japan,* <sup>4</sup>*Graduate School of Science, Osaka Prefecture University, Osaka, Japan.*

Polyoxometalates (POM) can manage the oxidation-reduction reaction of many-electron systems. They are expected as the potential candidates for the application of constructing artificial photosynthesis system. On the other hand, it has already been known that pyridine has the ability to catalyze the reduction of carbon dioxide into methanol [1]. Therefore, we investigated the possibility to combine these two systems *in silico*. In particular, we focus our attention to the process of reduction of carbon dioxides by pyridines as well as the possibility of incorporating pyridines into the POM system. Quantum chemical calculations have been performed using Gaussian09.

[1] E.B. Cole, P.S. Lakkaraju, D.M. Rampulla, A.J. Morris, E. Abelev, and A.B. Bocarsly. *J. Am. Chem. Soc.* **2010**, *132*, 11539-11551.

## PS24. Synthesis and Magnetic Properties of Iron and Cobalt Complexes Containing a $\pi$ -Radical Ligand with Photo-Excited High-Spin State

Koichi Katayama

*Graduate School of Science, Osaka City University*

We synthesized a new ligand,  $L^1$ , which is p-radical with a bipyridyl group. The p-radical ligand  $L^1$  has a doublet state in the ground state. The photo-excited quartet ( $S = 3/2$ ) state of  $L^1$  was detected by time-resolved ESR, which is constructed by the intramolecular ferromagnetic spin alignment between the doublet spin in the oxoverdazyl radical and  $pp^*$  excited triplet state of the phenylanthracene moiety. Fe(II) and Co complexes were synthesized using the  $\pi$ -radical ligand. The Fe(II) complex showed a spin crossover transition and a LIESST phenomenon. The Co complex showed a valence tautomerism in solution.

## PS25. Relationship of charge of heads group of lipid and photochemical activity of photosystem II in reconstituted lipid bilayer

Tomoyasu Noji<sup>1</sup>, Masaharu Kondo<sup>1</sup>, Keisuke Kawakami<sup>2</sup>, Jian-ren Shen<sup>3</sup>, Mamoru Nango<sup>2,4</sup>, Takehisa Dewa<sup>1,5</sup>

<sup>1</sup> *Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan,* <sup>2</sup> *Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan,* <sup>3</sup> *Division of Bioscience, Graduate School of Natural Science and Technology/Faculty of Science, Okayama University, Okayama 700-8530, Japan,* <sup>4</sup> *CREST/JST, Japan,* <sup>5</sup> *PRESTO/JST, Japan*

PSII can be a material for the construction of artificial photosynthetic systems that can obtain electrons from water almost infinite. Recently, immobilization of PSII to gold nano-particles or silica mesoporous materials was reported without denaturation. Thus, construction of artificial “Z-scheme” was expected by inorganic nano-structures. Therefore, reconstitution of PSI and PSII into lipid bilayers for immobilization to inorganic nano-structures would be potential approach. It is expected that control of immobilization of lipid bilayers to surface of nano-structures by control of charge of heads group of lipid. Therefore, oxygen evolution activities and durability of PSII in reconstituted various lipid bilayers were characterized.

**PS26. Construction of Carotenoid Molecularly-Oriented Film:  
A Model System of Photosynthetic Antenna**

Shouhei Kita

*Osaka City University*

Carotenoid is a pigment molecule that absorbs light energy and transfers it to nearby chlorophylls in photosynthetic antenna. The efficiency of the energy transfer depends mainly on the intermolecular distance and the molecular orientation. The aim of this research is to construct a carotenoid film where the intermolecular distance and molecular orientation of carotenoids are controlled to correlate the efficiency of the energy transfer as a function of these parameters. In this work, we prepared a barium stearate Langmuir-Blodgett film containing all-*trans*-*b*-carotene with a lipid to substrate ratio of 5 / 1 (v/v), and determined the molecular orientation of *b*-carotene by polarized optical absorption and reflection spectroscopies. We also evaluated the surface of LB films by the atomic force microscope.

**PS27. Photoinduced Electron Transfer of Platinum Bipyridine Diacetylides Linked  
by Triphenylamine and Naphthalenediimide and its application to photoelectric  
conversion system**

Shuichi Suzuki,<sup>\*a,b</sup> Yuma Matsumoto,<sup>a</sup> Mai Tsubamoto,<sup>a</sup> Masatoshi Kozaki,<sup>a</sup> Kenshi Kimoto,<sup>c</sup> Munetaka Iwamura,<sup>c</sup> Koichi Nozaki,<sup>c</sup> Naoki Senju,<sup>a</sup> Chiasa Uragami,<sup>a</sup> Hideki Hashimoto,<sup>a,b,d</sup> and Keiji Okada<sup>a,b</sup>

<sup>a</sup> Graduate School of Science, Osaka City University, <sup>b</sup> The Osaka City University Advanced Research Institute for Natural Science and Technology (OCARINA), <sup>c</sup> Graduate School of Science and Engineering, University of Toyama, <sup>d</sup> JST/CREST

The recently reported efficient charge-separated system based on bipyridine-diacetylde platinum complexes was applied to a photoelectric conversion system herein, based on MTA-Pt-NDISAc (MTA: dimethoxytriphenylamine, Pt: platinum complex, NDISAc: thioacetate derivative linked to naphthalenediimide). The charge-separated (CS) state of MTA-Pt-NDISAc was effectively generated by photo-induced electron transfer in toluene and THF. The lifetimes of the CS states were determined to be 730 ns in toluene and 61 ns (70%) and 170 ns (30%) as a double exponential decay in THF. The acetylthio group of triad MTA-Pt-NDISAc was exploited in the preparation of a self-assembled monolayer (SAM) on a gold surface. A photocurrent was detected upon irradiation of an electrochemical cell comprising Au/MTA-Pt-NDISAc /Na ascorbate/Pt, which was ascribed to the platinum complex based on the action spectrum.

**PS28. Syntheses and Properties of Nickel and Zinc Complexes  
with a Tripodal Ligand, 1-(pyridine-2-yl)-2,2-bis(pyridine-2-ylthio)ethanone**

Yu Masuda

*Osaka City University*

Tripodal ligand 1-(pyridine-2-yl)-2,2-bis(pyridine-2-ylthio)ethanone (= ppte) reacts with several first transition metal ions to form metal complexes with a metal-carbon bond. The Ni(II) complex  $[\text{Ni}(\text{m-Cl})(\text{ppte})]_2$  (**1**) has a dinuclear structure bridged by two chloride ligands. In dichloromethane, the cyclic voltammogram of **1** exhibited stepwise reversible redox waves for the dinuclear nickel species. The oxidation reaction of **1** by one equivalent of (*p*-tol)<sub>3</sub>NPF<sub>6</sub> in dichloromethane generated a rare Ni(II,III) mixed-valence complex,  $[\text{Ni}^{\text{II,III}}(\text{m-Cl})(\text{ppte})]_2$ , and by two equivalent of (*p*-tol)<sub>3</sub>NPF<sub>6</sub> generated the Ni(III) complex  $[\text{Ni}^{\text{III}}(\text{m-Cl})(\text{ppte})]_2$ . On the other hand, the Zn(II) complex  $[\text{ZnCl}(\text{ppte})]_2$  has a dimer structure containing C=O coordination to another zinc to each other, and showed keto-enolate intermediate conformation.

**PS29. A Trial for Developing the Hybrid Artificial Photosynthesis**

Yui Takemoto, Keisuke Kawakami, Isamu Kinoshita

*Osaka City University; Graduate School of Science, OCARINA*

Sunlight is the clean, sustainable only energy replaced with a fossil fuel. Artificial photosynthesis attracts much attention as a way to produce solar fuels efficiently from sunlight. Recently, Tiede and co-workers reported a new strategy for solar fuel production using hybrid of Photosystem I (PSI) and cobaloxime. We have tried to fabricate the hybrid photosynthesis system using *Thermosynechococcus vulcanus*-derived PSI and cobaloxime. Additionally, by using DCIP (= 2,6-dichloroindophenol) and PMS (= phenazine methosulfate) as a mediator instead of Cytochrome *c*<sub>6</sub>, we try to improve the system more artificially for hydrogen production.



