



THE 3RD INTERNATIONAL
CONFERENCE OF THE OCU
ADVANCED RESEARCH INSTITUTE FOR
NATURAL SCIENCE AND
TECHNOLOGY
~ KAKUNO MEMORIAL ~

7th-9th March, 2011

Osaka City University, Media Center

PREFACE

It gives us immense pleasure to invite you to the 3rd International Conference of OCU-Advanced Research Institute for Natural Science and Technology (OCARINA) to be held during March 7- 9 , 2011 at Osaka City Media Center and Library.

This annual conference follows the very successful first and second meetings held at Cultural Exchange Center in OCU (2009) and at Awaji Yumebutai in Hyogo Pref. (2010). The institute was initially planned by Late-vice president, Professor Kakuno with his enthusiastic desire for the future of Osaka City University. His basic design for the institute was nothing different from nowadays OCARINA. Without his initiation, it is impossible to find OCARINA at this time as it is. He passed away in Dec. 2009 just before OCARINA became real institute. Therefore the conference is dedicated to Late Prof. Dr. Kakuno for his great idea.

The conference will cover recent advances and new findings in OCARINA especially for the Photosynthetic research and the Urban environmental topics.

This conference also intends to find “The Novel Prize” class idea for the new project from wide ranges of the research now progressing in OCU. This session will be open for people who intend to appeal a proposal/idea for the next project of OCARINA. In the fiscal year of 2013, OCARINA will have spaces for the next projects, thus this is a good opportunity to collect ideas and two candidates will propose their plans for this.

Our institute always intends to develop the idea of equal opportunity for men and women to work together in our place. Thus one of the sessions will be dedicate to this idea.

OCARINA will intend to collaborate with Urban Plaza and related Social Science researchers to develop the outstanding idea for our future. We need to think our lives like an ancient poem “Manyo-shu” (萬葉集) that deals daily life, peace, war and especially LOVE. We need to remember the fact that every subject for university is just for us human beings. Without the collaboration, our university becomes a simple aggregation of Faculties. It is quite possible to have intimate relationship between faculties to produce fruitful result from OCU. This symposium also has a session for this purpose.

The OCU Advanced Research Institute for Natural Science and Technology (OCARINA)

Director Prof. Dr. Isamu Kinoshita

The 3rd International Conference of the OCU Advanced Research Institute for Natural Science and Technology (OCARINA)

----- KAKUNO Memorial-----

Date : 7~9th March, 2011

Venue: 10th Floor, Osaka City Univ. Media Center

Programme

Monday, 7th March, 2011

09:15~

09:30~09:40 Opening Remarks

09:40~09:50 Message from Dr. Yoshiki Nishizawa, President of Osaka City University

09:50~10:20 Annual Report from Group A

by Nobuo Kamiya(OCARINA/Osaka City University)

10:20~10:50 Annual Report from Group B

by Harue Masuda(Graduate of Science, Osaka City University)

10:50~11:00 Break

11:00~11:30 Annual Report from Group C

by Hideki Sakai(Faculty of Human Life Science, Osaka City University)

11:30~11:50 Misaki Nakai (Kansai University, JPN)

11:50~12:10 Yuriko Matsumura (Seikei University, JPN)

12:10~14:10 Poster sessions & Lunch Break

14:20~14:50 Toshio Asada (Osaka Prefecture University, JPN)

14:50~15:20 Masako Kato (Hokkaido University, JPN)

15:20~15:50 Ritsuko Fujii (OCARINA, Osaka City University, JPN)

16:50~16:10 Break

16:10~16:40 OCARINA new proposal 1

by Tetsuro Shinada (Graduate school of Science, Osaka City University)

16:40~17:10 OCARINA new proposal 2

by Makoto Miyata (Graduate school of Science, Osaka City University)

Tuesday, 8th March, 2011

- 09:00~09:30 Plenary Talk - Richard J. Cogdell (University of Glasgow, UK)
- 09:30~10:10 Kazi Matin Ahmed (University of Dhaka, Bangladesh)
- 10:10~10:50 Guoji Ding (Shanghai University, China)
- 10:50~11:05 Break
- 11:05~11:45 "Manyo-shu"(萬葉集) - by Masahiro Murata
(Graduate school of Literature and Human Science, Osaka City University)
- 11:45~12:25 Mitsuo Toda (Shizuoka University, JPN)
- 12:30~14:10 Poster sessions & Lunch Break
- 14:20~15:00 Satoshi Matsuda (Shizuoka University, JPN)
- 15:00~15:30 Sarah Henry (University of Glasgow, UK)
- 15:30~16:00 Tom Moore (Arizona State University, USA)
- 16:00~16:10 Break
- 16:10~16:40 Ana Moore (Arizona State University, USA)
- 16:40~17:10 Hideki Hashimoto (OCARINA, Osaka City University, JPN)
- 17:10~17:40 Dario Polli (Politecnico di Milano, Italy)
- 18:00~ Conference Party

Wednesday, 9th March, 2011

- KAKUNO Memorial Ceremony ～角野メモリアル～
- 10:00~10:10 セレモニー開催の辞 「角野メモリアルセレモニー開催意義について」
複合先端研究機構 機構長 木下 勇
- 10:10~10:40 角野先生を偲んで「複合先端研究機構設立の経緯とその後」
元・複合先端研究機構 機構長／大学院理学研究科・教授 畑 徹
- 10:40~11:10 角野先生を偲んで「角野さんの思い出」
大阪市立大学名誉教授 小田一紀
- 11:10~11:40 角野先生を偲んで「角野先生のご研究の歩み」
大阪市立大学大学院工学研究科・教授 重松孝昌
- 11:40~11:50 閉会の辞 複合先端研究機構 機構長 木下 勇

OCARINA annual report

A group Photosynthesis

B group Urban environment and disaster prevention

C group Urban functionality



Structure of Mn_4CaO_5 Cluster of Photosystem II; The heart of Oxygen-Evolving Photosynthesis

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

Under the flag of “Artificial Leaf”, Professors Hashimoto and Kamiya, and other researchers are organized in the Group-A of OCARINA. A total report covering all valuable results achieved in 2010 F.Y. by all members of the Group-A is out of my ability, and hereafter, I will present only results according to the title of this abstract, which will be published soon [1]. Photosystem II (PSII) performs light-induced electron transfer and water-splitting reactions, which lead to the formation of molecular oxygen essential for almost all of the life on the earth. PSII from thermophilic cyanobacteria consists 17 membrane-spanning subunits, 3 hydrophilic, peripheral subunits, and many cofactors with a total molecular mass of 350 kDa for a monomer. The X-ray crystal structures of PSII have been reported at 3.8-2.9 Å resolution for PSII isolated from *Thermosynechococcus elongatus* or *T. vulcanus*, which provided the arrangement of protein subunits and most of the cofactors involved in the electron transfer reactions. However, the detailed structure of the Mn_4Ca -cluster, the catalytic center of light-induced oxygen evolution, has not been resolved due to the limited resolution and radiation damage induced during the X-ray experiments. We have improved the resolution and diffraction quality of PSII crystals significantly, and succeeded in solving the crystal structure of PSII from *T. vulcanus* at 1.9 Å resolution [1]. In order to reduce the X-ray radiation damage to the Mn_4Ca -cluster, we employed a slide-oscillation method to collect a low-dose X-ray diffraction data set at BL44XU, SPring-8, using large PSII crystals. In the crystal structure obtained at 1.9 Å resolution, the electron density distributions for each of the 5 metal ions in the Mn_4Ca -cluster were clearly separated, allowing us to locate the individual metal atoms and all of the ligands to the metal cluster unambiguously. Five oxygen atoms forming the oxo-bridges between the metal ions were identified by difference Fourier map, and four water molecules were found to be associated with the metal cluster, some of which may serve as substrates in the oxygen-evolving reaction. Two chloride-binding sites were identified in the anomalous D-Fourier map calculated with a data set of 1.75 Å wavelength, which were located in the same position as in Br^- or I^- substituted PSII reported previously. In addition, more than three thousands of water molecules were found in the structure of PSII dimer in a crystallographic asymmetric unit. Some of the water molecules form hydrogen-bond networks linking the catalytic site and the bulk phase. We will discuss the detailed structure of PSII at the atomic resolution.

[1] Umena, U., Kawakami, K., Shen, J.-R., Kamiya, N., *nature* (2011), in press.

Groundwater and its potential and risk as a water resource in Osaka Basin –for planning the integrated management system

Harue MASUDA¹, Muneki MITAMURA¹, Akihiko OHSHIMA²,
Yoshinori KANJO², and Sadakazu NISHIKAWA³

1: Graduate School of Science, Osaka City University, 2: Graduate School of Engineering, Osaka City University, 3: Graduate School of Human Life Sciences, Osaka City University

Abstract:

Groundwater is excellent fresh water resource, however, it would cause natural disasters if not properly controlled to use. Thus, we should understand the hydrological cycle of the whole basin to construct the management plan of water resources. Osaka basin is one of the largest Quaternary sedimentary basins, in which rich groundwater is hosted. We have figured out the whole groundwater system, summarized potential problems and those solutions in the Osaka basin to propose ideal management plan of local water resources.

Groundwater in the Osaka basin is categorized according to the depth of aquifers and scale of water cycle; 1) the shallow aquifer including unconfined and uppermost confined groundwater, which is in a few to 100 m depths beneath the center of the Osaka Plain. 2) Deep aquifers including the groundwater between 100 and 600 m depths, where unconfined marine clay layers are intercalated in fresh water sandy aquifer sediments. 3) Deepest aquifers below 600 m depth to 1500 m depth at the maximum. The shallowest aquifers are recharged by local meteoric water, and have excess hydropressure due to less withdrawal and cutting groundwater flow by underground constructions such as subways and buildings, potentially causing liquefaction when earthquake occurs. Thus, the groundwater must be properly used to decrease the hydropressure. Groundwater in 100 to 500 m depths is recharged in the surrounding terraces of the plain at the center of the basin, and flowing rate is slow. Withdrawal of the groundwater from this depth interval, especially <300 m depth, is increasing to use by many hospitals, industries, buildings, etc., instead of the public supplied water to save the cost. Since intercalated marine clay layers of this depth interval have not been consolidated enough at present, subsidence would be a serious problem to cause unequal settling of buildings, storm surge, etc. Groundwaters below 600 m depth to the basement rocks are mostly used for hot spas in Osaka. Such deepest groundwaters are principally fossil water, and it will be depleted due to excessive use. The groundwaters below 100 m depth in the Osaka basin must be used under proper management for highly public purposes to prohibit hydrogeological disasters and give priority to the public interests.

Two Next-Generation Retroreflective Materials: A Countermeasure to Urban Heat Islands

Hideki Sakai

Faculty of Human Life Science, Osaka City University

Abstract:

Making a building reflective reduces the amount of solar heat it absorbs. These "cool roof" products have been widely used to mitigate the urban heat island effects. In closely-packed building areas, however, heat reflected by one building may be absorbed by the other (Fig.1, Left). To prevent this opposite effect of high-reflective materials, retroreflective materials come into use (Fig.1, Right). In retroreflection the incident light is returned back in the direction of the source (i.e., the sun), with a very small spread in the light around this particular direction[1].

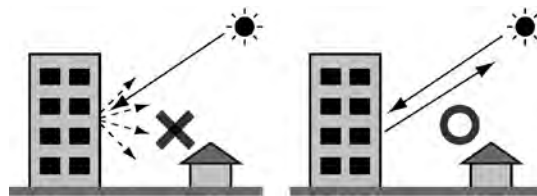


Figure 1 High reflective (Left) and retroreflective (Right) materials

Technically, computer-controlled mirrors can also reflect sunlight upward and prevent the opposite effect in much the same way as retroreflective materials. However, mechanical moving parts are complicated and need constant maintenance. Thus, it is a distant idea that we cover wide areas of the building exterior with movable mirrors. In contrast, retroreflective materials have no moving parts, thus, no breakdown; they require little maintenance. This is a great advantage for building materials.

Retroreflective materials are usually used as the road markings and signs to enhance night-time visibility [1]. Thus, they were already carefully evaluated with respect to visibility. From the viewpoint of heat transfer, however, their characteristics were unknown. Therefore, in the first stage of the study, we showed experimentally that retroreflective materials reduce the reflected heat of the sun[1]. In Fig.2, when a high reflective paint was used as a sample, its surface temperature (T_1) was kept low under infrared light irradiation (E); however, the road (T_2) and the neighboring wall (T_3) temperatures were increased by reflected light. When a retroreflective material was used as a sample, not only its surface temperature (T_1) but also the road (T_2) and the neighboring wall (T_3) temperatures were kept low. Therefore, they can be used as the building materials to reduce urban heat island effect.

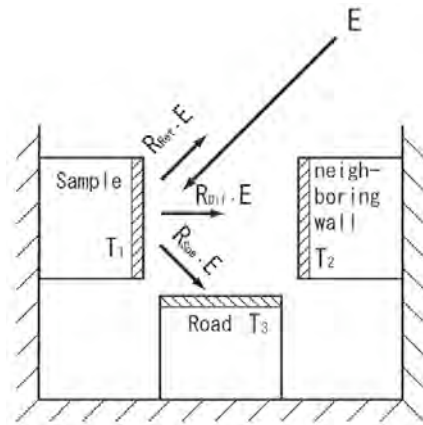


Figure 2 Experimental setup (miniature model)

R_{Spe} : specular reflectance, R_{Dif} : diffuse reflectance, R_{Ret} : retroreflectance

In the next stage, we have evaluated the solar retroreflectances of several retroreflective materials, which cannot be measured directly by a spectrophotometer. The procedures were as follows: First, the reflectance without retroreflection was measured by using a spectrophotometer with the integrating sphere. Then, the total reflectance was deduced from the amount of temperature rise by solar irradiation. Finally, the retroreflective component was calculated by subtracting the former from the latter. The measured retroreflectances are 20 to 30 percent for the prism-array type, about 20 percent for the capsule-lens type, and about 10 percent for the bead-embedded type.

Our study is now in the third stage. We are proposing two new-type retroreflective materials: high-spec directional retroreflective ones and low-cost, simplified ones.

References:

- [1] CIE Publ.180. Road Transport Lighting For Developing Countries. Vienna: CIE Central Bureau, 2007
- [2] H. Sakai, K.Emura, N.Igawa, H.Iyota, Reduction of Reflected Heat of the Sun by Retroreflective Materials, Proc. the Second International Conference on Countermeasures to Urban Heat Islands (SICCUHI), CD-ROM 211450, pp.1-6, 2009

**Equal Opportunity
for All Researchers
related to OCARINA project**

**Active Female Researchers
related to Photo Science**



Syntheses of Sugar Linked Indium Porphyrin As a Dual Drug and their Photodynamic Activities

Misaki Nakai^a, Tomohiro Maeda^a, Shigenobu Yano^b, Shiho Sakuma^c, Eriko Otake^c, Akira Maeda^c, Akimichi Morita^c, Yasuo Nakabayashi^a

^aMaterials and Bioengineering, Kansai University, 3-3-35, Yamate cho, Suita city, OSAKA, 564-8680, ^bInnovative Collaboration Center, Kyoto University, ^cGraduate School of Medical Sciences and Medical School, Nagoya City University,

Abstract: The development of photosensitizers for photodynamic therapy (PDT) is a very important for cancer treatment. Therefore, sugar-linked porphyrins and fullerene derivatives were synthesized and investigated for phototoxic properties. When diagnostic metals such as ¹¹¹In, ⁶⁷Ga, ^{99m}Tc, and Gd are complexed to these porphyrin derivatives, the resulting compounds are expected to be bifunctional, exhibiting diagnostic imaging and the PDT effects. Therefore, towards our aim of developing a dual function drug, the sugar linked free base porphyrin 5-{4-(2-*O*-tetraacetyl-β-D-gluconopyranosyl)ethoxy}-10,15,20-triphenylporphyrin (**1**), Indium porphyrin derivative (**2**), and Zinc porphyrin derivative (**5**) were synthesized. The deacetylated sugar linked free base (**3**) and Indium porphyrins (**4**) were also synthesized from **1** and **2** (Fig. 1).

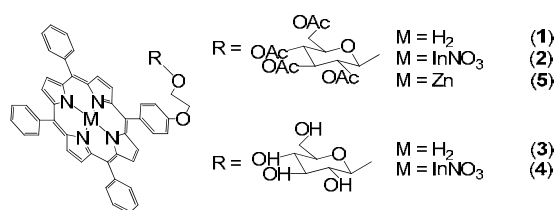


Fig.1 structures of sugar linked porphyrins

The photocytotoxic efficiency for Colo679 was investigated with **1**, **2**, **3**, **4** and **5** after 24 h of incubation and irradiation with a light dose of 16 J/cm² (Table 1). Laserphyrin was used as a standard. The PDT effect of **4** was most efficient of all compounds. Compared with **2**, Indium porphyrin **4** was higher photocytotoxicity. The metalation of porphyrin was effective for increasing PDT activity. It is due to the deference of singlet oxygen production activity. The photocytotoxicity of **4** is higher than that of compound **3**. It indicated that the sugar moiety was also effective for PDT activity. The confocal microscopic images of Colo 679 exposed to compound **1** and **2**, suggested that uptake of **1** is greater than **2**. The deference of IC₅₀ between **3** and **4** was results in the amount of uptaken in the cell.

Table 1. IC₅₀ values against Colo679

compound	(a) IC ₅₀ / μM	(b) IC ₅₀ / μM	(a) / (b)
	in dark condition	with light irradiation	
H ₂ TPPOAcGlc (1)	160	> 47	< 3.4
[InTPPOAcGlc]NO ₃ (2)	0.90	0.35	2.6
H ₂ TTPPGlc (3)	1.5	0.50	3.0
[InTTPPGlc]NO ₃ (4)	4.6 × 10 ⁻²	1.2 × 10 ⁻²	3.8
ZnTPPOAcGlc (5)	81	27	3.0
Laserphyrin	31	14	2.2



Preparation of gold nanoparticles using thermo-responsive copolymers having a fluorescent quinoxaline derivative

Yuriko Matsumura¹, Takayuki Onodera¹, Takanori Nishioka², and Keisuke Kurita¹

¹Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan

²Division of Molecular Materials Science, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Abstract: It is well known that localized surface plasmon (LSP) generated in gold nanoparticles upon visible light irradiation produces a strong electric field in the near field of the gold nanoparticles. This phenomenon can be used for modifications of both absorption and emission processes of the molecular fluorescence. When the distance between gold nanoparticles and a fluorophore is more than several tens of nanometers, there is no interaction between them. On the other hand, when it is less than 10 nm, fluorescence can be enhanced by LSP. However, quenching occurs when they are located too close to each other. We have been focusing our attention on the switchable strong photon-molecule coupling field based on the interaction between gold nanoparticles and fluorophores labeled with a thermo-responsive polymer. In this study, gold nanoparticles were prepared by using thermo-responsive poly(*N*-*n*-propylacrylamide) (PNNPAM) having a pyrazole-fused quinoxaline (DEDPQx) as a fluorophore and *N,N*-dimethyl-aminoethylmethacrylate(DMAEMA) as a stabilizer of gold nanoparticles (**Fig. 1**). The SPR absorption band at 522 nm gradually appeared when poly(DEDPQx-*co*-NNPAM-*co*-DMAEMA) (70/30) was used in the molar ratio of tertiary amino groups (DMAEMA) to HAuCl₄ of 8 under pH 8 (**Fig. 2**). Gold nanoparticles obtained were stable in water at least for a month at room temperature and their diameters were 7.1 ± 0.8 nm. These results suggest that the gold nanoparticles formed by autoreduction of tetrachloroauric acid were stabilized by the copolymer having tertiary amino groups. The fluorescence property of the copolymer with gold nanoparticles upon heating is also discussed.

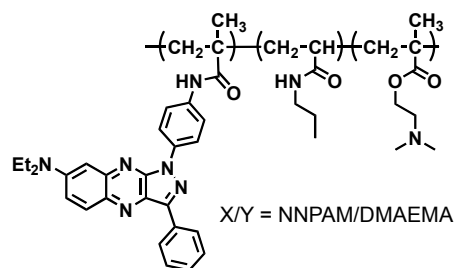


Fig. 1. Structure of poly(DEDPQx-*co*-NNPAM-*co*-DMAEMA)(X/Y).

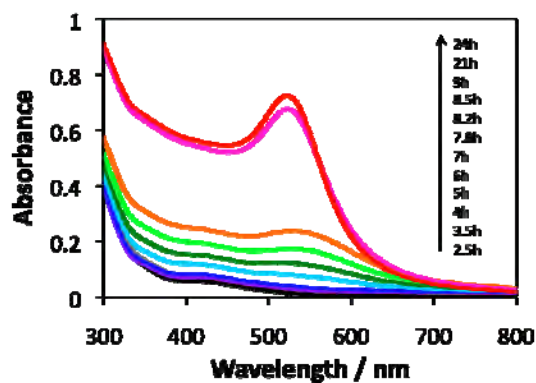


Fig. 2. Time-dependent UV-vis absorption spectra of the poly(DEDPQx-*co*-NNPAM-*co*-DMAEMA)(70/30)-coated gold nanoparticles (DMAEMA / Au = 8) synthesized at pH 8.



Computational Approach for Enzymatic Reaction using QM/MM Method

Toshio Asada

Department of Chemistry, Osaka Prefecture University, Gakuen-cho,
Naka-ku, Sakai-city 599-8531, Japan

Chemical reactions in a large molecular assembly usually proceed on the free energy surface. In recent computation approaches, the combined quantum mechanical and molecular mechanical (QM/MM) calculation [1] can provide reliable physical properties for a given structure. However, it is still difficult to predict reaction paths and free energy barriers, because acceptable conformational entropies can only be evaluated from long time simulation such as Monte Carlo or molecular dynamics (MD) simulations.

To obtain reaction paths on the free energy surface, our Amber-Gaussian interface [2] can be applied to employ both the free energy gradient (FEG) and the nudged elastic band (NEB) methods. Using FEG-NEB method, the reaction path can be optimized as a series of chain of conformations on the free energy surface automatically. It is applied to the isomerization reaction of the simple glycine molecule in an aqueous solution and the enzymatic reaction in the trypsin-BPTI complex.

For the glycine molecule, the zwitter ion form (ZW) is known to be more stable than the neutral form (NF) in an aqueous solution, while NF is stable in the gas phase. The calculated free energy barrier of 16.4 kcal/mol is reasonably agreement with the experimental one as shown in Fig.1. The calculated results for the acylation reaction in trypsin-BPTI will also be discussed (see Fig.2)

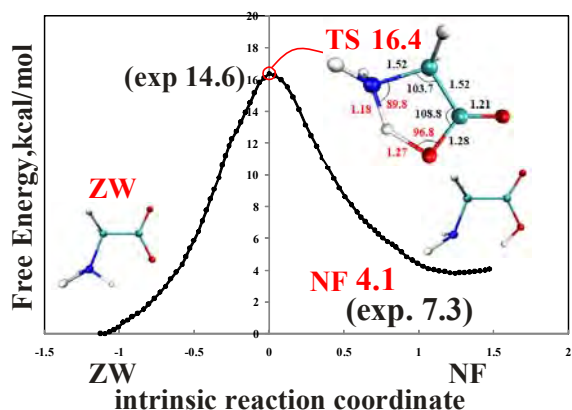


Fig.1 Calculated free energy curves by FEG-NEB method

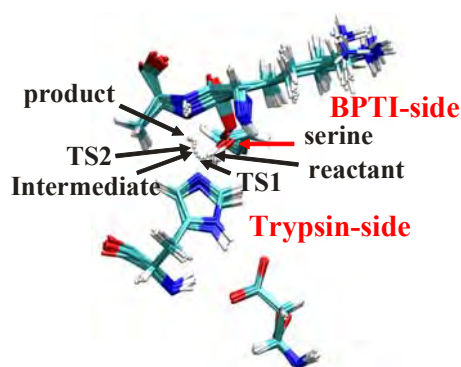


Fig.2 Optimized acylation reaction path in trypsin-BPTI complex

References:

- [1] Asada, T.; Koseki, S.; Nagaoka, M. *Phys. Chem. Chem. Phys.* **2011**, 13, 1590-1596.
- [2] Okamoto, T.; Yamada, K.; Koyano, Y.; Asada, T.; Koga, N.; Nagaoka, M. *J. Comp. Chem.*, **2011**, 32, 932-942.



Vapor-induced Multichromic Luminescence of Platinum(II) Complexes with Dicarboxybipyridine

Masako Kato

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

Luminescent metal complexes exhibiting vapor-induced chromic behavior (*i.e.* vapochromism) have recently drawn much attention as promising chemical sensing materials. In this context, we have developed various luminescent metal complexes with sensing functionalities [1]. Herein, our recent progress regarding vapochromic behavior of platinum(II) complexes bearing carboxy groups which can act as a good supramolecular synthon (Fig. 1) is introduced.

The platinum(II) complex, $[\text{Pt}(\text{CN})_2(\text{H}_2\text{dcbpy})]$ (H_2dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) was found to exhibit diverse color changes in the solid state under different atmospheres of organic vapors [2]. The complex can form a porous three-dimensional network structure by the hydrogen bonds and $\text{Pt}\cdots\text{Pt}$ interactions. It exhibits red luminescence originated from the $^3\text{MMLCT}$ state as is well known for the platinum(II) complexes with short $\text{Pt}\cdots\text{Pt}$ distances. When the dried sample of the complex is exposed to various organic vapors, the luminescence spectrum shifts more than 200 nm in the visible region depending on the kind of vapors. The color changes are attributed to the changes in the $\text{Pt}\cdots\text{Pt}$ interactions. On the basis of the powder X-ray diffraction (PXRD), it was clarified that the color changes in the complex occur by two-step structural transformation (Fig. 2). It

is noteworthy that the three-dimensional structure is reconstructed spontaneously from the amorphous solid in the atmosphere of particular vapors. The details of the interesting phenomena of these complexes as well as other related systems will be discussed [3].

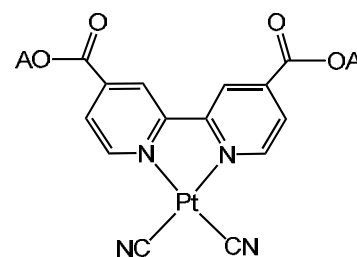


Fig. 1.

A = H^+ : $[\text{Pt}(\text{CN})_2(\text{H}_2\text{dcbpy})]$
A = Na^+ : $\text{Na}_2[\text{Pt}(\text{CN})_2(\text{dcbpy})]$

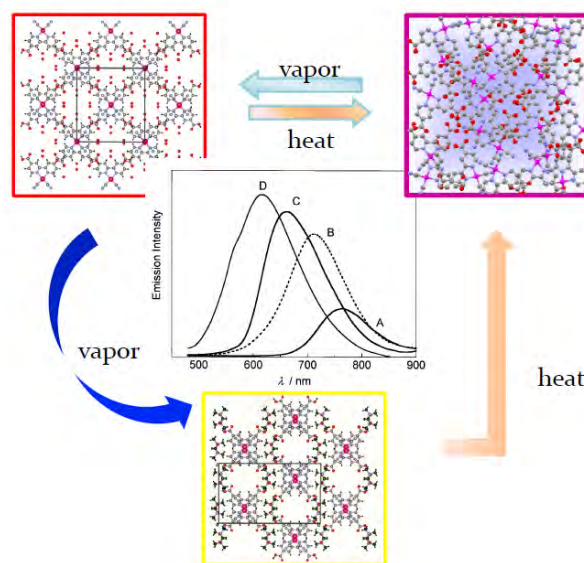


Fig. 2. Luminescence spectral changes and the two-step structural transformation of $[\text{Pt}(\text{CN})_2(\text{H}_2\text{dcbpy})]$ induced by DMF vapor.

- [1] Kato, M. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 287; Kato, M. *et al.*, *Chem. Lett.* **2008**, *37*, 16; Kobayashi, A. *et al.*, *Chem. Lett.* **2009**, *38*, 998; *Dalton Trans.*, **2010**, *39*, 3400; *J. Am. Chem. Soc.*, **2010**, *132*, 15286.
- [2] Kato, M.; Kishi, S. *et al.*, *Chem. Lett.*, **2005**, *34*, 1368.
- [3] Kobayashi, A.; Yonemura, T.; Kato, M. *Eur. J. Inorg. Chem.*, **2010**, 2465.



Pigments and Function of the Oceanic Photosynthetic Antenna from Japanese Brown Alga, “Okinawa Mozuku”

**Ritsuko Fujii^{1,2}, Mamiko Kita^{2,3}, Naoki Senju³, Daisuke Kosumi^{2,3},
Matsumi Doe¹, Masahiko Iha⁴, Tadashi Mizoguchi⁵
and Hideki Hashimoto^{1,2,3}**

¹ *The OCU Advanced Research Institute for Natural Science and Technology (OCARINA),*
² *CREST/JST and* ³ *Dept. of Physics, Graduate School of Science, Osaka City University,*
3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan; ⁴ *South Product Co. Ltd., 12-75*
Suzaki, Uruma-shi, Okinawa 904-2234, Japan; ⁵ *Dept. of Bioscience and Biotechnology,*
Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Oceanic photosynthetic organisms contribute almost one quarter of global primary production [1]. In adapting to the fluctuated light conditions of their habitat, they are evolving a variety of light-harvesting antennae. They widely possess the membrane-intrinsic antenna contains a unique porphyrin type chlorophyll (Chl), Chl *c* in addition to the general Chl *a* [2]. The aminoacid sequences of the Chl *a/c* type antennae are similar to that of the well-known peripheral Chl *a/b* type antenna in higher plants, LHCII, although the X-ray structure was not clarified yet [2]. One of the major Chl *a/c* type antennae is “fucoxanthin-Chl *a/c* protein” (FCP) found mainly in brown algae and diatoms. In the FCP, both fucoxanthin and Chl *c* collect the light energy and transfer it to Chl *a*, followed by the energy transfer to the oxygenic reaction centers (both photosystems I and II) where charge separation occurs. To elucidate the mechanisms of the energy transduction, excited-state properties of the pigments should be investigated. The study on the excited-state properties of Chl *c* left behind [2].

Cladosiphon okamuranus, “Okinawa Mozuku” in Japanese, is an original strain of a brown alga in Okinawa, Japan. Super large-scale culture of the strain has been established in the “discoid germiling” form. The discoid germiling is a beneficial source of photosynthetic apparatus because it is a micron-size without tough lipids and polysaccharides. Therefore by using this strain, we are targeted to clarify the structure and function of the FCP. We have already established the purification of the “Mozuku FCP”. Subunit analyses and amino acid sequencings by using TOF-MS/MS spectrometry are on going to determine the proteomics of the “Mozuku FCP”. In this presentation, we focused on our recent progress on the pigments bound to the “Mozuku FCP”. Pigment composition and temperature tolerance of the pigment-binding were determined. Large scale purification of Chl *c* was established. Binding properties of the pigments in the FCP were discussed based on a FCP-model structure.

References: [1] Jeffrey, S. W. et al. (Eds.), “Phytoplankton Pigments in Oceanography”, UNESCO, Madrid, 2nd Ed., **2005** [2] Macpherson, A. N. and Hiller, R., In: Green, B. R., Parson, W. W. (Eds.) “Light-Harvesting Antennas in Phosotynshesis”, Kluwer Academic Publishers, Netherlands, **2003**

**Proposals for
the OCARINA project**

Advance Molecular Science Research Program

Tetsuro Shinada

Graduate School of Science, Osaka City University

Abstract:

The molecular science research covering fundamental research areas of organic, inorganic, analytical, and physical chemistries has been contributed to human prosperity because chemical reactions and transformations are the key to the innovation of useful materials and understanding biological processes in the levels of molecular structures.

Herein, “Advanced Molecular Science Research Program” toward contribution to prosperity of Osaka City is proposed. The experts of chemical and biological researches in OCU are collected into “the agora of molecular science” a field of the collective intelligence. Their idea and knowledge are exchanged to encourage the progress of the research proposals to create various advanced materials for human health, energy accumulation and transformations, electronics device, molecular sensor devices, and green chemistry.

The outline and details of this proposal will be presented on behalf of the project members.

Project outline



The agora of molecular science for technological innovation



Collaboration Network

OCARINA PROJECTS, Other OCU Research Programs

Paris University, University of St Andrews, Scotland, Harvard University, Kyoto University - Osaka University, Osaka Prefecture University - The University of Electro-Communications - Suntory Institute for bioorganic research, Iwate University, NAIST, Chemistry Promotion Platform Kansai.

知識発見手段としての競争の議論、競争を調整し知識の有効利用を実現する自制的秩序に基づく分子科学ネットワーク

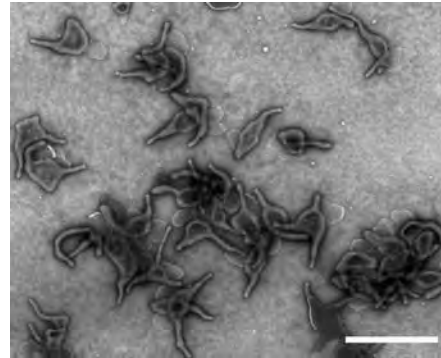
A novel biomotility, *Mycoplasma* gliding

Makoto Miyata

Department of Biology, Graduate School of Science, Osaka City University

Sumiyoshi-ku, Osaka 558-8585 Japan

Mycoplasma, a group of pathogenic bacteria is the cause of “walking pneumonia”, which is very epidemic this year in Japan. They form a membrane protrusion at a cell pole as presented in the figure, bind to animal cells with the protrusion, and glide. Although the gliding is fast and smooth, the mechanism is not related at all to the known bacterial motility systems such as flagella or pili, or conventional motor proteins including myosin. The gliding motility is essential for their pathogenicity, but the mechanism had not been studied, before we started our study.



We have studied mainly on the fastest species, *Mycoplasma mobile*, which glides with 4 micron per s, i.e. 7 times of cell length on glass, focusing on the following subjects: (i) Gliding machinery including supporting structure, (ii) Component proteins of machinery, (iii) Measurements of force and steps, (iv) Direct energy source and its coupling to cycle, and (v) binding target as the rail. Based on these observations, we proposed a working model. “The gliding machinery is composed of four huge proteins at the base of membrane protrusion and supported by a cytoskeletal architecture from the cell inside. Many flexible legs about 50 nm long are sticking out from the machinery. The movements generated by ATP hydrolysis cell inside transmits to “leg” protein through “gear” protein, resulting in the repeated catching, pulling, and releasing of the sialic acids fixed on the surface by the legs.”

- [1] Uenoyama, A.; Miyata, M. *Proceedings of the National Academy of Sciences of the United States of America* **2005**, 102, 12754.
- [2] Hiratsuka, Y.; Miyata, M.; Tada, T.; Uyeda, T. Q. *Proceedings of the National Academy of Sciences of the United States of America* **2006**, 103, 13618.
- [3] Nakane, D.; Miyata, M. *Proceedings of the National Academy of Sciences of the United States of America* **2007**, 104, 19518.
- [4] Miyata, M. *Trends in Microbiology* **2008**, 16, 6.
- [5] Miyata, M. *Annual Review of Microbiology* **2010**, 64, 519.

Invited Lectures



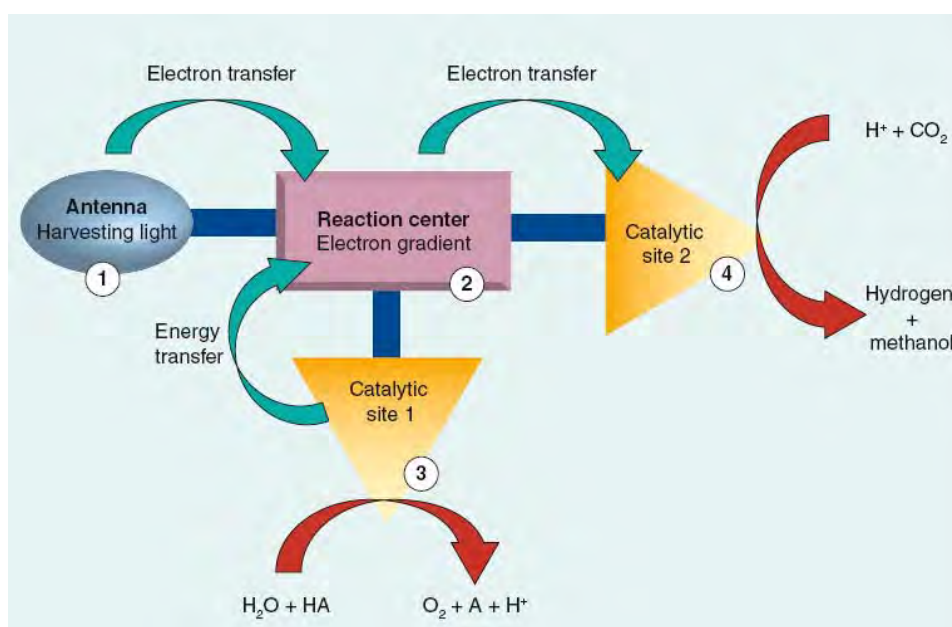
An Overview of the Human Frontiers of Science Program: Report on the Grant

Richard Cogdell

*Microbial Photosynthesis Lab, Glasgow Biomedical Research Centre,
120 University Place, University of Glasgow, G12 8TA, UK*

Abstract:

One of the grand challenges facing mankind is to develop ways to convert solar energy into dense portable fuels. There is one global scale biological/chemical process that does this, namely photosynthesis. The essence of photosynthesis can be broken down into four key steps.



Our research program is focussed on steps one and two. We are trying to determine the design flexibility in organising light harvesting modules and reaction analogues onto surfaces to efficiently harvest solar energy and use it to separate charge. This requires two challenging problems to be overcome. Firstly to be able to order these modules on a surface with nanoscale precision and secondly to be able to image and measure light harvesting processes on the same nanoscale. Both these aims are very challenging.

Our approaches to solving these problems will be described. Then in the following talks each of the groups involved in this program will give progress reports.



Groundwater Development Constraints in Urban and Rural Bangladesh: Options for Sustainable Management

Kazi Matin Ahmed

Department of Geology, University of Dhaka, Dhaka 1000, Bangladesh

Abstract:

Bangladesh depends heavily on groundwater for all uses in urban and rural areas. Potable water supply in urban and rural areas mostly provided by groundwater abstracted from shallow and deep aquifers. Municipal water supplies exists around 100 urban centers whereas rural water supply is mainly through more than 10 million domestic hand tube wells. Apart from shallow hand tube wells there are thousands of deep hand tube wells, mostly in the coastal region.

Irrigation is the main consumer of groundwater which uses more than 90% of the abstracted water. Irrigation water is provided by thousands of shallow tube wells fitted with centrifugal pumps and few thousand of deep tube wells fitted with turbine pumps. Of the current irrigated areas more than 70% comes from groundwater sources.

Groundwater has been the backbone of providing access to safe water and providing security for a national with a population of more than 150 millions. However, there have been recent problems both in terms of quantity and quality of groundwater. High abstractions for irrigation cause domestic wells to dry up and results into water shortage in certain areas during dry season. Also high abstractions in urban areas like Dhaka cause water level to decline and dewatering parts of the aquifer. Wells have to drilled into deeper and deeper levels to provide water supply to the megacity dwellers.

Most severe problems related to groundwater development in Bangladesh are related to water quality. Arsenic occurs over a vast part of the country at shallow aquifers exposing over 22 million people to arsenic at allowable limit. Apart from arsenic Manganese is also wide spread in the country. Chloride is a quality constraint in coastal areas and certain pockets inland.

Though the country is heavily dependent on groundwater there is no groundwater management in place. As a result of unregulated use, groundwater is becoming an endangered resource. A proper management strategy is needed to protect the vital natural resources of the country.



EXCESS SLUDGE REDUCTION BY COMBINED PROCESS OF PHYSICAL PRETREATMENT AND MICROFAUNA OF PREDATION ACTIVITY

Guoji Ding, Fei Yu, Li Mu, Yanjing Yu, Haihua Shen, Huiqing Qiu

Shanghai University, Shanghai, China, gjding@shu.edu.cn

Excess sludge treatment is a big challenging problem in wastewater treatment plants due to economic and environmental factors. Excess sludge reduction by predatory activity of microfauna may be an ecological method with low energy consumption. The ingestion efficiency of sludge by microfauna is restricted by the size of sludge, which can be improved by physico-chemical treatment. Based on study of various physico-chemical methods, effects of sludge crushing were investigated. The result indicated that on the premise of low energy consumption, ozone oxidation or microwave radiation had little effects on sludge size to satisfy the requirement of predation by *Aeolosoma hemprichii*. While ultrasonic treatment or mechanical shearing could efficiently reduce the particle size and improve the percentage of sludge which can be ingested by *A. hemprichii*. Compared with other physico-chemical treatments, mechanical shearing was more suitable for the new technology, since it just required simple equipments and was easy to implement. In addition, some of biologically active substances were studied for promoting the growth of *A. hemprichii* in a reactor of biological wastewater treatment. It is clear that honey residue and rice bran had a significant role on promoting the growth of *A. hemprichii*. The population density can be doubled and population growth increased by 10.2% with the addition of honey residue and rice bran.

Acknowledgement:

Authors sincerely thank the National Hi-Tech Research and Development Program of China (No. 2007AA06Z347), the Key Special Program on the S&T for the Pollution Control and Treatment of Water Bodies (No. 2008ZX07421-004), and the Shanghai Leading Academic Discipline (No. S30109).

References:

- [1] Low, E.W., Chase, H.A., 1999, Reducing production of excess biomass during wastewater treatment [J]. *Water Research*, 33(5):1119-1132
- [2] Song, B.Y., Chen, X.F., 2009, Effect of *Aeolosoma hemprichii* on excess activated sludge reduction [J]. *Journal of Hazardous Materials*, 162(1):300-304
- [3] Zhang, G., He, J., Zhang P, et al., 2009, Ultrasonic reduction of excess sludge from activated sludge system II: Urban sewage treatment. *Hazard. Mater*, 164:1105-1109

Keywords: excess sludge reduction, particle size, physico-chemical treatment, microfauna, predation



**The Works of Sights in *Manyō-shū*,
The Anthology of Ancient Japanese Poems**

Masahiro Murata

Department of Literature, Osaka City University

要旨

知覚や表現の多層性について、古典和歌を通して考えてみたい。その一例として、『萬葉集』に伝わる「国見歌」を取りあげる。

『萬葉集』冒頭部に、大和盆地中の小山「天の香具山」に^{あめ かぐやま}登り立って「国原は^{くにのはら}けぶり立ち立つ ^{うなはら}海原はかまめ(海鳥)立ち立つ」と全国土を眺望することをうたう舒明天皇作の国見歌が収められている(巻一 - 2)。その表現は、私たちの認識からすると、幻視をうたったものとも言わなければならない。しかし、それは、当時にとっては、まさしき視覚だったのであり、そのまさしき視覚を可能にするものとして言葉が機能し、その視覚をしるしとどめるものとして言葉があったと理解するべきであろう。

こうした言葉のありように、和歌というものの本質が求められるのであり、現代の私たちが古典和歌に学ぶところがあるとすれば、その大いなるものが、すなわちこれかと思案される。



Environment of Lake SANARU: A small urban watershed

Mitsuo TODA

*Faculty of Engineering, Shizuoka University
3-5-1 johoku, Hamamatsu, Shizuoka, 432-8561 JAPAN*

Abstract:

introduction

Lake Sanaru known as a small eutrophic lake is located in Hamamatsu city. Population of the city is over 800,000 and population density of watershed is 2800/km². One of the main pollution loading is human waste because of high population density, though the sewerage is build up to over 90%. In addition, nonpoint source pollution (synthetic fertilizer, natural loading from precipitation and ecosystem) especially inorganic nitrogen is serious. It had been the most polluted lake by COD-Mn from 2001 to 2006 in Japan. Profiles of the lake are shown in Table 1. The lake has two rivers and there branches in upstream and connects to Pacific Ocean via Lake Hamanako. To decrease the pollution, Shizuoka University established the team “amenity SANARUKO project”. This work is one of the outputs of the project. The presentation consists of two topics based on the stable isotope analysis. One is for hydrology, and another is for food web of the lake.

In 2009, COD-Mn decreased to 7.6 ppm and pollution rank was 10th. It is the result of the steady control measures. In addition, we believe understanding of mass balance and mass transfer must be important for restoration of the environment in next step.

Hydrology of lake Sanaru

We collected the water samples from lake, rivers, ground waters and precipitations. After filtration, salinity and stable isotopes ratio (δD and $\delta^{18}O$) were measured. Mixing ratio of seawater and freshwater was calculated by salinity. Mixing ratio of seawater varied in the range of 3 % - 26 %. On the other hand, $\delta^{18}O$ value of ground water (-7 ‰) and running water (-10.2 ‰) vary in only narrow range. (Fig.2) So, the proportion of freshwater from different sources is able to calculate using $\delta^{18}O$ value. In some case, calculation is difficult because of fluctuation in $\delta^{18}O$ of precipitation. So we collected the samples of precipitation at 30 min intervals during period of hard rainfall. This time, we will estimate the proportion using $\delta^{18}O$ value.

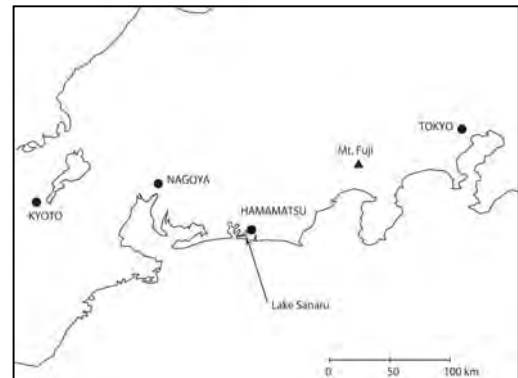


Fig.1 Location of lake SANARU

Table 1 Profile of lake SANARU

Lake size	2.2 km×0.6 km×2 m
Lake volume	2.4×10 ⁶ m ³
Lake area	1.2 km ²
Watershed area	up:18.3 km ² , down:40.0 km ²
Population	1.6×10 ⁵ km ²
Population density	2822 km ⁻²
COD-Mn (average)	~ 9 ppm
Hydraulic residence time	~ 46 days
Salinity (average)	5‰
Tidal flow	~ 1×10 ⁶ m ³ day ⁻¹

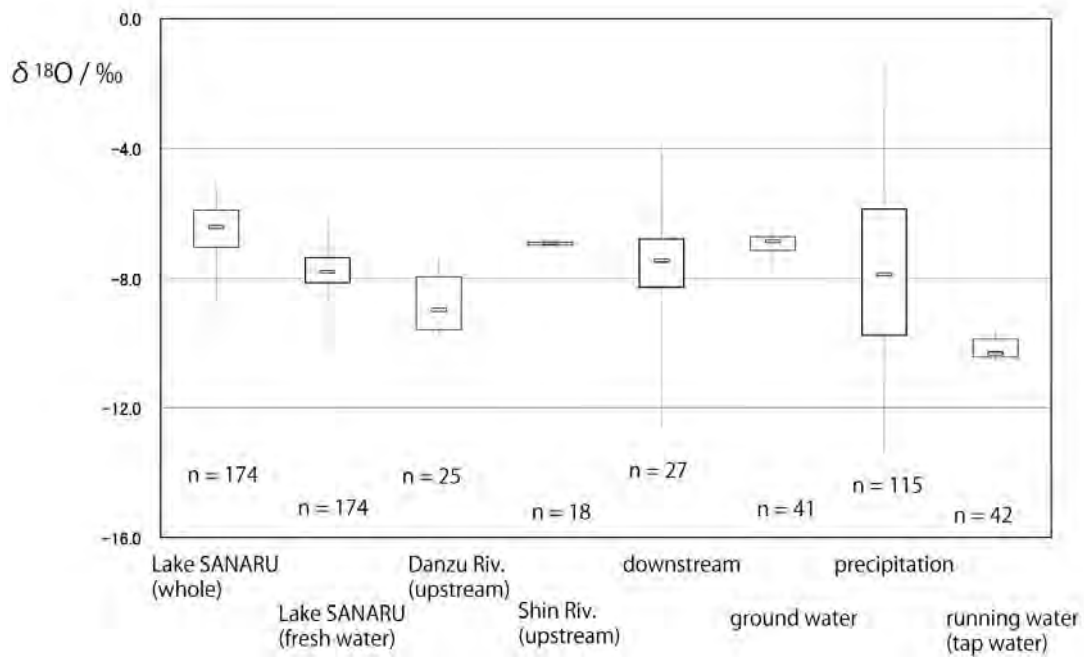


Fig.2 Distribution of $\delta^{18}\text{O}$ value in the watershed

Food web of lake Sanaru

The lake connects to the Pacific Ocean via lake Hamanako. Therefore the water is brackish and normal salinity of the lake is around 5‰. There are over 50 fishes includes freshwater, seawater and amphidromous species. Eutrophic water and flat shallow structure (average depth 2m, max. 2.5 m) enable the high production of organic matter by phytoplankton. Almost all days of the year, water is muddy and transparency is under than 30 cm. In order to find any key to the settlement of the environmental problem, we were interested in food web and mass balance of lake Sanaru. We collected many fishes, other animals and SS. In Fig.3, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ value of each samples were shown. Fig.4 represents the outline of the unexpected simple food web consist of only three trophic levels.

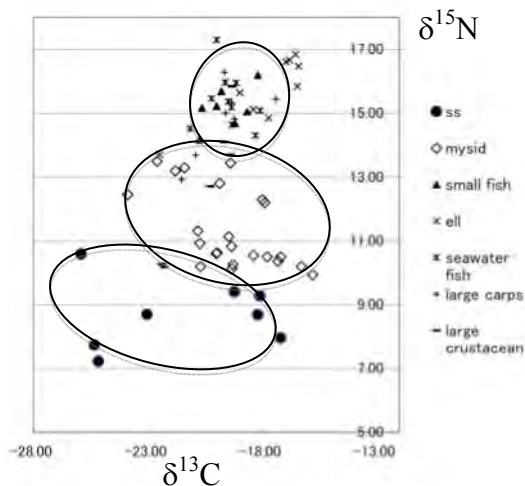


Fig.3 Food web analysis of lake SANARU

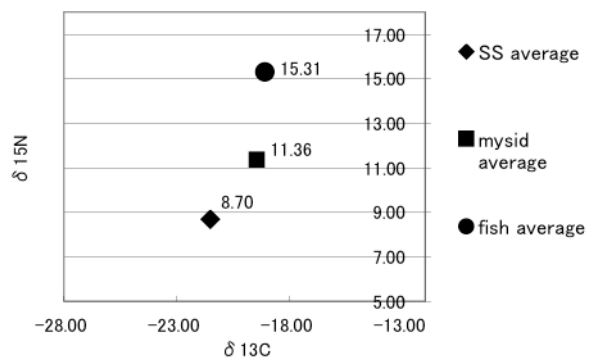


Fig.4 Three trophic levels of lake SANARU



What is the Most Environmentally Friendly Utilization of Biomass?

Satoshi MATSUDA

*Department of Materials Science and Chemical Engineering, Shizuoka University,
3-5-1 Johoku, Naka-ku, Hamamatsu, 432-8561 Japan*

Abstract:

Recently the liquid fuel production from crops and other biomass resources ('biofuel') has attracted much attention in the world as the prevention of global warming is becoming an urgent issue, because the biofuel is perceived to be 'carbon neutral' and useful as a countermeasure against global warming. In fact, the production of biofuel has been put into practical use not only in the US, EU, Brazil and other countries but also in Japan. As for its impact on the environment, however, evaluations still vary including those on the influence of biofuel on the global economy, for example the food price crisis that might have been caused by competition with food. In the previous study [1], the author pointed out that 'bio-ethanol' from crops is never 'carbon neutral', which means the production and use of the fuel does not lead to a net increase in atmospheric CO₂ concentration, nor is useful as a countermeasure against global warming.

Since the shortage of food crops affected by the expansion of biofuel production became a critical issue, the 'second-generation' of biofuel made from non-food biomass has attracted much attention all over the world. In particular, the following statement in the Hokkaido Toyako G8 summit held in Nov. 2008 accelerated this trend which made 'use of biofuels with food security and accelerated the development and commercialization of sustainable second-generation biofuels from non-food plant materials and inedible biomass' (in 'G8 Leaders Statement on Global Food Security' [2]).

The target biomass has a wide variety of kinds; cellulosic materials such as woody biomass and paddy straw, algae and some kinds of oil producing plants, which are considered as sustainable. Research on the kinds of the target biomass is in progress. Among them 'Jatropha' has emerged as one of the best candidates for future biodiesel production [3], partially because the production of bio-ethanol from cellulosic materials has encountered many difficulties in practice. For example in Indonesia, there is a national program for biofuels development in which 20% of diesel consumption will be supplied with biodiesel utilization mainly by Jatropha oil (equiv. 10.22 million kL) by the year 2016 to 2025. But a positive result of an assessment on the validity of Jatropha production was not obtained from research by the author, in which a feasibility study was tried as quantitatively as possible using the data obtained from a field survey in Indonesia conducted by the author in January and March of 2009 [4].

The situation regarding the utilization of biomass is rather complicated: There are many problems in the liquid biofuel production pointed out from various points of view, and the author has considered the liquid biofuel to be not environmentally friendly. The estimation of the real amount of utilizable biomass resources is also a very difficult task. However, the fact remains true that biomass should be utilized effectively as one of the most valuable renewable resources in our society which should be sustainable and independent of petroleum, because biomass is the main source of food, timber, paper and also fuel. In this presentation, the real and effective estimation of biomass use was discussed, concrete examples of the quantitative evaluation of biomass utilization were exhibited, and a concrete plan for increasing the production of domestic forest biomass was proposed, because the largest biomass resource in Japan is undoubtedly forest biomass whereas domestic forestry has been following a course of decline.

The emphasized points in this presentation are as follows:

- 1) In order to quantitatively estimate the contribution of biofuel to the reduction of CO₂ emission, a new index of CO₂ emission reduction as well as its calculation method should be proposed.
- 2) The validity of biomass utilization should be assessed from the standpoint of both resources (=the amount and distribution of really utilizable biomass resources and a comparison of the amount with their demand, and also environmental impacts) and technology with the utilization system (=how to utilize the biomass resources).
- 3) The priority of biomass use should be as follows according to its economical value: human food > animal feed > industrial material > fuel (energy), thus the cascade type of the biomass utilization system should be sought.
- 4) Automobiles should be driven with electricity rather than an internal combustion engine using bio-ethanol or bio-diesel because the former is highly efficient in energy utilization.
- 5) If the purpose is to obtain electricity from solar energy, solar cell is a much better option than the power generation with biomass combustion due to the difference in conversion efficiency.
- 6) The absolute amount of really utilizable biomass in the energy equivalent value compared with fossil fuel is rather small; only a small percent of the world's primary energy can be supplied with biomass, meaning that biomass should be only used as one of the local energy sources.

References:

- [1] Matsuda, S.; *J. Environ. Information Sci.* **2009**, 37(5), 1.
- [2] http://www.mofa.go.jp/policy/economy/summit/2008/doc/doc080709_04_en.html
- [3] Fairless, D.; *Nature* **2007**, 449, 652.
- [4] Matsuda, S. et.al. ; *J. Automation, Mobile Robotics & Intelligent Systems* **2009**, 3(4), 18.



HFSP 'Team Glasgow' Progress Report

Sarah Henry, Richard Cogdell

*Microbial Photosynthesis Lab, Glasgow Biomedical Research
Centre,*

120 University Place, University of Glasgow, G12 8TA, UK

Abstract: The work in Glasgow consists of two main themes; (1) to understand energy transfer within native purple bacterial photosynthetic membranes and (2) to use this knowledge to help us understand the requirements necessary to obtain directed energy transfer on surfaces.

Photosynthetic bacteria are able to alter the architecture of their photosynthetic membranes in response to different light conditions. Many spectroscopic studies have been performed on individual, purified complexes, whereas in Glasgow we wish to understand energy transfer within the intact membrane and how the complexes work together. To this end we are able to produce membranes from a variety of different species and from cells grown under different environmental conditions [1], which can then be investigated using time resolved spectroscopy [2]. The second part of the work is to understand all the parameters necessary for energy transfer between photosynthetic complexes attached to fixed surfaces. Photosynthetic complexes with specific tags should allow complexes to be attached in a defined orientation and so facilitate energy transfer along the surface. We have access to a state of the art nanotechnology facility to produce gold patterns on fixed substrates. To overcome any quenching of the fluorescence from the gold, work is underway to produce tagged and linkered light harvesting proteins with variable height and orientation.

The understanding of energy transfer within the intact native membrane and the application of these principles to energy transfer along fixed surfaces should allow the basic principles to be established from which an artificial light-harvesting device can be designed.

References:

1. Gardiner, A. T.; Cogdell, R. J.; Takaichi, S., The Effect of Growth-Conditions on the Light-Harvesting Apparatus in *Rhodospseudomonas-Acidophila*. *Photosynthesis Research* **1993**, 38, (2), 159-167.
2. Moulisova, V.; Luer, L.; Hoseinkhani, S.; Brotsudarmo, T. H. P.; Collins, A. M.; Lanzani, G.; Blankenship, R. E.; Cogdell, R. J., Low Light Adaptation: Energy Transfer Processes in Different Types of Light Harvesting Complexes from *Rhodospseudomonas palustris*. *Biophysical Journal* **2009**, 97, (11), 3019-3028.



Optimizing Light Absorption and Controlling Energy Flow in Artificial and Natural Photosynthesis

Thomas A. Moore, Devens Gust and Ana L. Moore

Center for Bioenergy and Photosynthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA 85287-1604

*Corresponding author, e-mail: tmoore@asu.edu

Even though photosynthesis powers the planet, its global rate of energy flow of ~120 TW is currently totally reserved for biosphere service and food and bioenergy production for human use. There are no reserves of photosynthetic capacity to provide increasing amounts of biofuel for growing the human GDP and food for the ever-increasing human population. Indeed, when such demands are made, the capacity comes at the peril of biosphere service. Fortunately for us, photosynthesis can be dramatically improved to meet human needs. The theoretical limit to solar energy conversion efficiency is set by fundamental thermodynamic principles that apply to the isothermal conversion of light into chemical and/or electrical potential. While human ingenuity in photovoltaic technology uses these principles to achieve record efficiencies of solar to electrical power conversion today, photosynthesis, having been optimized by Darwinian selection to push genes forward, is not optimal for providing the solar-derived fuel to support human activities. Measured against maximum conversion efficiency, the less-than-optimal efficiency of photosynthesis starts with a poor match of the absorption of light by photosynthetic organisms to the solar spectrum. In selected photosynthetic systems, rational design based on the principles demonstrated in artificial systems and the techniques of molecular and synthetic biology, can be used to optimize solar-to-biofuel conversion efficiencies to meet particular needs. Key biological parts necessary to initiate this research are found in photosynthetic organisms; I will present our progress on using fundamental design principles and existing technology to inspire the design of high efficiency artificial and natural photosynthesis. This combination of technology with biology can be a step towards achieving sustainable energy production based on efficient solar-driven water oxidation and carbon reduction. Indeed, along these lines, I plan to also bring up work from other labs in which new hybrid systems using PV cells to drive geobacteria growth with remarkable faradaic efficiency and energy conversion efficiency have been reported. I will also present our latest work on the photonic control of energy transfer in multichromophoric model antenna systems done in collaboration with the Fleming group based on a pH sensor and an actinic light intensity sensor. Model systems have also been recently developed in collaboration with the Kennis and van Grondelle groups to define a new exciton-based coupling mechanism between carotenoid pigments and tetrapyrroles.



Design of Photoelectrochemical Cells for the Splitting of Water and Production of Fuel

*Ana L. Moore**, Thomas A. Moore and Devens Gust

Center for Bioenergy and Photosynthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, 85287-1604, USA

*Corresponding author, e-mail: amoore@asu.edu

The design of bioinspired schemes that couple solar energy conversion to the oxidation of water and the subsequent use of the reducing equivalents to synthesize energy-rich compounds, such as hydrogen or fuels based on reduced carbon is the main objective of our present research.¹ In order to establish the design principles for a tandem, two junction (or threshold) photochemical cell, we are assembling Grätzel-type photoelectrodes that model photosystems I and II (PSI and PSII) of plants. The photoanode model of PSII will contain a mimic of the donor side (water oxidizing side) of PSII reaction centers. In PSII, tyrosine Z (Tyr_Z) mediates charge transport between the photo-oxidized primary donor (P680⁺) and the oxygen-evolving complex (OEC). The oxidation of Tyr_Z by P680⁺ likely occurs with the transfer of the phenolic proton to a hydrogen-bonded histidine residue (His190). This coupling of proton and redox chemistry is thought to poise the Tyr_Z oxidation potential between those of P680⁺ and the OEC. We have prepared a bioinspired system (BiP-PF₁₀) consisting of a high oxidation potential porphyrin (PF₁₀, 1.59 V vs. NHE, a model of P680) that is covalently attached to a benzimidazole-phenol pair (BiP) that mimics the Tyr_Z-His190 pair in PSII. Electrochemical studies show that the phenoxyl radical/phenol couple of the model system is chemically reversible with a midpoint potential of 1.24 V vs. NHE and is therefore thermodynamically capable of water oxidation. When the BiP-PF₁₀ construct is attached to TiO₂ nanoparticles and excited with visible light, it undergoes photoinduced electron transfer. Electrons are injected into the semiconductor and the corresponding holes are localized on either the porphyrin (BiPPF₁₀⁺-TiO₂⁻) or the phenol (BiP⁺-PF₁₀-TiO₂⁻). EPR provides a clear spectroscopic picture of these processes.² The photoelectrode model of PSI will be sensitized by low potential naphthalocyanines or phthalocyanines, which absorb light in the near IR region of the spectrum. Upon photoexcitation, these dyes are designed to inject electrons into semiconductors having sufficiently negative conduction bands to effectively drive the reduction of protons to hydrogen at a cathode. The semiconductor will be electrically wired to a cathode suitable for hydrogen production: either a metal electrode (Pt or Ni) or a hydrogenase-modified carbon electrode.³

References:

1. Hambourger M. et al. *Chem. Soc. Rev.*, 2009, 38, 25–35.
2. Moore, G. F. et al. *J. Am. Chem. Soc.* 2008, 130, 10466–10467.
3. Hambourger M. et al. *J. Am. Chem. Soc.* 2008, 130, 2015–2022.



Energy-transfer dynamics between carotenoid and bacteriochlorophyll in the light-harvesting system of purple photosynthetic bacteria as visualized by sub-picosecond pump-and-probe and sub-20 fs four-wave mixing spectroscopies

Hideki Hashimoto^{1,2,3}, Daisuke Kosumi^{2,3}, Satoshi Maruta^{2,3}, Tomoko Horibe^{2,3}, Ritsuko Fujii^{1,2}, Mitsuru Sugisaki^{1,2,3}, Mamoru Nango^{2,3} and R.J. Cogdell⁴

¹ The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585 Japan

² CREST/JST, 4-1-8 Hon-cho Kawaguchi, Saitama 332-0012, Japan

³ Department of Physics, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

⁴ Glasgow Biomedical Research Centre, University of Glasgow, 126 University Place, Glasgow, G12 8QQ, Scotland, UK

E-mail: hassy@sci.osaka-cu.ac.jp

In purple bacterial photosynthesis, carotenoids play the crucial roles of light-harvesting and photoprotection. These functions reflect singlet-singlet and triplet-triplet excitation energy transfer between carotenoid and bacteriochlorophyll [1]. Singlet-singlet excitation energy transfer from chlorophyll to carotenoid have been discussed in terms of non-photochemical quenching of the chlorophyll Q_y fluorescence (NPQ) that plays a key role of dissipation of excess light energy in oxygenic photosynthesis [2,3]. On the other hand, the photoprotection of purple bacterial photosynthetic organisms from excess light energy has been discussed in terms of triplet-triplet excitation energy transfer from bacteriochlorophyll to carotenoid. Here, singlet-singlet energy transfer from bacteriochlorophyll to carotenoid has not been considered to be active in bacterial photosynthesis even though it is energetically possible, *e.g.* the excitation energy transfer from the bacteriochlorophyll Q_x excited state to the carotenoid S_1 excited state. In this lecture, we report a discovery of this new singlet-singlet excitation energy transfer pathway in purple bacterial photosynthetic light-harvesting complexes [4].

Another devotion of the present lecture is the development of new aspect for time-resolved experiments. In order to achieve this objective we have focused our attention on sub-20 fs four-wave mixing experiments. We have successfully developed the methods to understand complicated relaxation dynamics of carotenoids free in solution and those bound to LH2 antenna pigment-protein complexes. The concurrent dynamics of the electronic excitation and vibronic oscillations of carotenoids have been investigated by means of the transient grating spectroscopy. The experimental results have been compared with the theoretical calculations that are based on a Brownian oscillator model. The excitation energy-transfer processes as well as the internal conversion are modeled within the framework of Liouville space pathways. We demonstrated a general framework to use the Feynman-diagrammatic approach that can be readily extended for including some additional electronic states. The results have been reported in five publications of *Physical Review B* [5].

- 1) Frank, H.A. and Cogdell, R.J. (1996) *Photochem. Photobiol.* **63**, 257-264.
- 2) Ruban, A.V. *et al.* (2007) *Nature* **450**, 575-578.
- 3) Ma, Y.-Z., *et al.* (2003) *PNAS* **100**, 4377-4382.
- 4) Kosumi, D. *et al.* (2011) *Angew. Chem. Int. Ed.* **50**, 1097-1100; Maruta, S. *et al.* (2011) *Phys. Status Solidi B* **248**, 403-407.
- 5) Sugisaki, M. *et al.* (2007) *Phys. Rev. B* **75**, 155110 ; Fujiwara, M. *et al.* (2008) *Phys. Rev. B* **77**, 205118 ; Fujiwara, M. *et al.* (2008) *Phys. Rev. B* **78**, 161101(R) ; Sugisaki, M. *et al.* (2009) *Phys. Rev. B* **80**, 035118 ; Sugisaki, M. *et al.* (2010) *Phys. Rev. B* **81**, 245112.



Femtosecond Pump-Probe Confocal Microscopy for the Study of Excited-State Dynamics with High Temporal and Spatial Resolution

Dario Polli

Dipartimento di Fisica – Politecnico di Milano (Italy)
Piazza L. da Vinci, 32 – 20133 Milano



Femtosecond pump-probe spectroscopy is a powerful technique for investigating excited state dynamics in molecules, providing access to both radiative and non-radiative deactivation processes. This technique has the potential to unravel photophysical processes, but in standard implementations it has limited spatial resolution: the probed sample area has diameter of about 100 micrometers. We have developed an instrument combining broadband femtosecond pump-probe spectroscopy and confocal microscopy, delivering simultaneously high temporal and spatial resolution.

Composites are at the heart of polymer applications in photonics and optoelectronics, and are indispensable in devices ranging from solar cells to all-optical modulators. In such samples, phenomena occurring at interfaces between two materials are of fundamental importance but are extremely complex and poorly understood. Blending different semiconducting polymers leads to samples with enhanced or new properties. Engineering such composites in order to obtain the desired functionalities is one of the major challenges in polymer technology, but it also raises fundamental questions about the physics and chemistry at the interfaces between different domains. Phenomena occurring at these interfaces often determine device performances, but are poorly understood due to the variety of possible electronic states (excitons, excimers, charge transfer states) and processes (energy transfer and charge separation) and to their complicated dynamics.

We have applied our newly developed tool to study the properties of polymer blends by directly accessing the dynamics at the interfaces between different materials, which are of fundamental importance to understand the fate of the excited states and the relaxation paths which dictate the ultimate device performance. We will report on pump-probe measurements of phase-separated conjugated-polymer thin films with ≈ 150 -fs temporal resolution and ≈ 300 -nm spatial resolution. Our results provide new insight into their complex structure and single out “dynamical” interfaces, i.e. border regions at the phase separated islands that behave differently in terms of transient absorption and relaxation dynamics.