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**Bio-inspired assembly of artificial photosynthetic antenna complexes  
for development of nanobiodevices**

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## Contents

I . Abstract of the project results .....	3 p
II . Result of the project. ....	3 p
1. Introduction .....	3 p
2. Experiment .....	5 p
3. Results & Discussion .....	6 p
4. List of Publications .....	11p
A. Journal paper publications	11p
B. Conference presentations	12p
C. Representative abstracts	

## I . Abstract of the project results

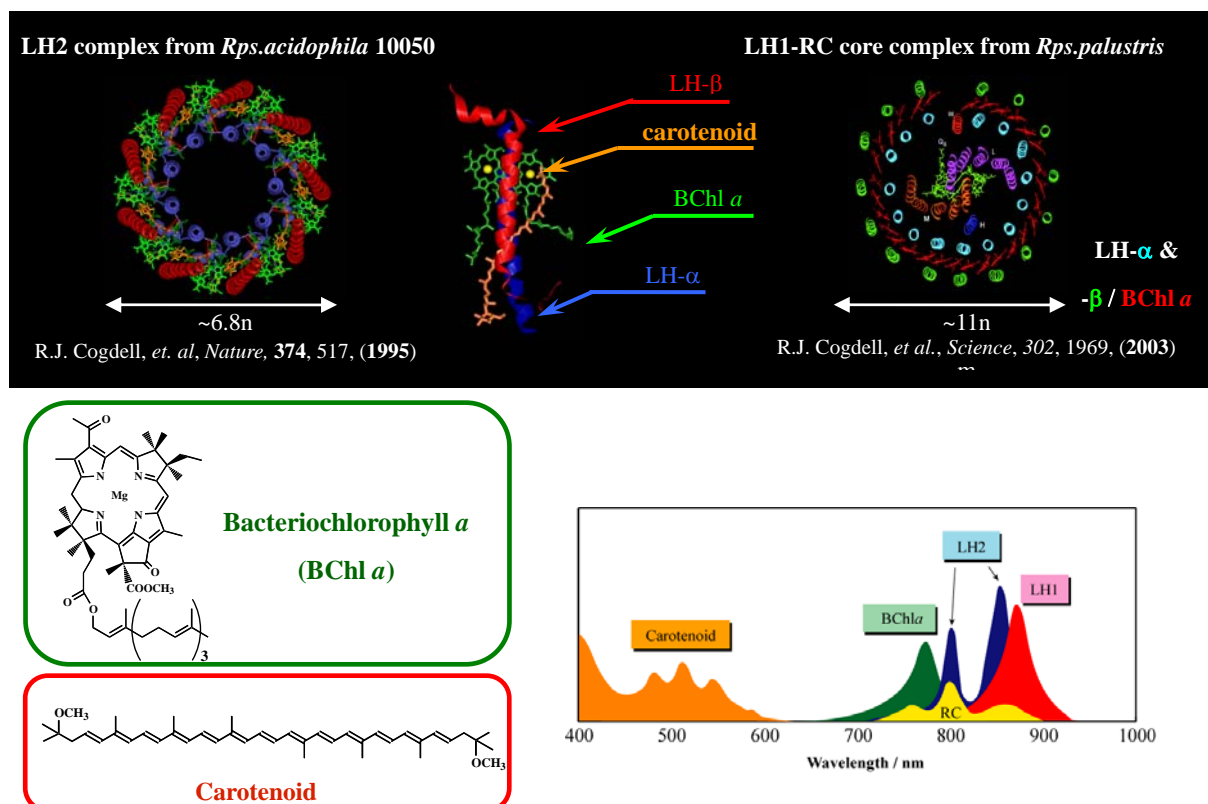
The purpose of this proposal is to use photosynthetic antenna pigment complexes of purple photosynthetic bacteria in order to control the direction and orientation of the complex on electrodes with pattern for developing nanobiodevices ([nanobiophotonics](#)). The advantage of the pigment complex is its high efficiency of light-energy conversion throughout the near UV to near IR region and much higher durability using these methods than ordinary light-harvesting (LH) complex isolated from photosynthetic bacteria. The present generations of [sensor and semiconductor devices with an integrated circuit](#) for developing nano-level size are too expensive to be cost-effective compared to other existing technologies. Expanding existing silicon device technologies and nanofabrication technics by incorporation of modified photosynthetic protein / pigments complexes or their protein-mimic materials to perform tasks of light-harvesting and charge separation, is currently explored as a novel concept, which makes use of natural protein environments to create a directional flow of light energy and electronic charge separation, meanwhile reducing the cost aspect by the use of bio-materials and their synthetic protein-mimic materials. The majority of the aim is construction of the array of artificial photosynthetic antenna system with nano-patterning substrate using modified photosynthetic protein materials prepared from [modern biosynthetic manufacturing methods](#) and photosynthetic pigments for developing nanobiophotonics.

## II . Result of the project.

### Introduction

Nature provides a number of examples, in which processes of energy conversion, storage and transport are combined and optimized through 'smart matrices' at various levels, going from molecular to cellular or higher organisms. Based on biological design principles, future biology-based photonics or their synthetic organic photonics could form clean and inexpensive future alternatives [for productions of nanosensors and nanosemiconductors](#).

The past 10 years have seen tremendous progress in our understanding of the structure and function of the pigment-protein complexes involved in the primary reactions of bacterial photosynthesis. The structure of the reaction center (RC, the first membrane protein to have its structure determined to high resolution) revealed the nearly  $C_2$  symmetrical arrangement of the redox centers and this system has now been extensively studied by ultrafast laser spectroscopy. More recently the structures of the LH2 complexes has revealed the nonameric and octameric arrangement of repeating units consisting of two apoproteins and one or two carotenoids and three BChls while the recent crystal structure of the LH1-RC core complex reveals that the LH1 complex surrounds the contours of the RC although a high-resolution structure has not yet been determined for the LH1 complex (Scheme 1).



### Scheme 1. Compartmentalization of light harvesting and charge separation.

The antenna complexes(LH2,LH1-RC) efficiently realize various photosynthetic functions using cofactors (BChl *a* and carotenoid) assembled into the apoproteins (LH1 and LH2).

The light-harvesting mechanisms in these light-harvesting complexes have been studied both spectroscopically and theoretically. These advances put us in a unique position of being able to exploit this information to design artificial photosynthetic antenna systems based on 'biological blueprint'. Our aim is to see if we could produce an antenna module, which acts as a 'sensitizer', and a light-induced redox component for nanobiophotonics. As well as using LH2 complexes this summary also propose to use LH1-RC complexes. One of its unique features is that it works over a large dynamic range of incident light intensities. It has a remarkable ability to capture efficiently photons even at very low light fluxes, yet at the same time to withstand very high light fluxes by efficiently dissipating the excess photons. Thereby protecting itself against the potential harmful effects of over-excitation.

It is important to understand not only the mechanisms of efficient light-harvesting but also those of photo-protection. In order to understand these reactions both structural and functional information is required. The data on how the energy levels and intermolecular interactions of the pigments affect their energy-transfer properties, and how the 'durability' of the complexes is required for rational design of novel biophotonics. Based on the experiments using the native photosynthetic antenna complexes, a variety of

modified complexes will be synthesized and tested for their usefulness in [artificial nanobiophotonics](#). After elucidation of the mechanisms of harvesting, transferring, usage and dissipation of light energy, our aim is to optimize under a given light intensity the energy-conversion efficiency and the durability of the core and the antenna complexes by modifying the pigment Car and BChl or chlorophyll as well as the supporting peptides. These modified photosynthetic protein-mimic complexes will be introduced into a membrane system on electrodes [with pattern as a light-induced redox component, and the antenna complexes will be attached to electrodes modified with or without lipid bilayers](#) as a UV and Vis light harvester modules to produce [a new type of nanobiophotonics](#). These approaches will provide a foundation for using the artificial domains of photosynthetic core-antenna and antenna complexes with patterning substrate and the development of new type of nanosensors and nanosemiconductors.

### Approach

The present generations of [sensor and semiconductor devices with an integrated circuit](#) for developing nano-level size are too expensive to be cost-effective compared to other existing technologies. Hence there is a need for productions of sensors and semiconductors using novel-low-cost, systems with the inherently high photon-capturing and charge separation efficiency of natural photosynthetic systems. Integration of photosynthetic proteins or its pigments complexes with nanopatterned devices for tasks of light-harvesting and charge separation will expand existing silicon device technologies and nanofabrication techniques using [novel and inexpensive bio-components](#). Design principles of natural photosynthetic units will form the guideposts for the design and development of native light-harvesting and photoconversion matrix modules as described in the section of a plan of work below. A critical step is creating functional supramolecular nanoassembly of small organic building blocks that co-operate to create a directional flow of energy and electron using the operational principles of the natural systems. Properties of the building-block molecules intrinsically have the capacities to direct their co-operative assembly into structures with specific orientation and alignment. The advantages of the large scale of modern biosynthetic manufacturing methods offers a promising route to economically viable devices.

[Our goal is to use photosynthetic pigment complex or its model complex as a light harvester of the well-established cell to convert light energy in the ultraviolet and visible region into that in the near infrared region for development of new type of nanosensors and nanosemiconductors \(nanobiophotonics\).](#) The advantage of the light-harvesting complex is its efficient capture of photons throughout the near UV to near IR region and much higher durability than ordinary isolated dyes supported by its inherent photo-protective function. Thus, [the results of the above grounds can be directly applied to the development of nanosensors and nanosemiconductors using modified photosynthetic pigments or their model light-harvesting materials with nanopatterning substrate.](#)

## Experiment

More details are presented in our papers in the list of publication and in the abstracts of some representative papers attached.

## Results and Discussion

### **1. Artificial domains of LH2 & LH1-RC with nanopatterning substrate for development of antenna-mimics nanosensors**

Molecular self-assembly of LH1-RC core complexes and LH2 complex (as shown in Scheme 1 ) and its model complexes onto various electrodes were used to develop new types of antenna-mimics nanosensors.

#### **1): Preparation of modified photosynthetic antenna core complex (LH1-RC) with His-tag and modifiers at the LH 2 polypeptide with SH using molecular biological methods to control the orientation and direction of the complex on electrodes**

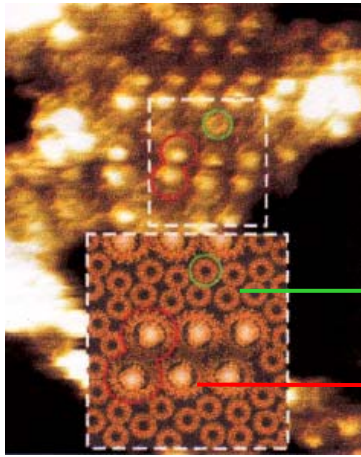
In the current of our previous study, we used modified photosynthetic antenna complex with His-tag or modifiers at the LH polypeptide with SH using molecular biological methods to control the orientation and direction of the complex onto electrodes as shown in Scheme 2.

The pigment-protein complexes of modified LH1-RC and LH2 were laid down onto functionalized electrodes, such as ITO, Au and SiO<sub>2</sub> electrode modified with or without lipid bilayers (M. Kondo, M.Nango, to be submitted (as shown in Scheme 2b and in the attached abstract), A. Sumino , M. Nango, et al., *Langmuir*, **27**, 1092-11099 (2011) and in the attached abstract, S. Yajima, M. Nango, et al., to be submitted (as shown in Scheme 2a-2 and in the attached abstract). Upon illumination photocurrents were successfully measured. Excitation spectra confirmed that these photocurrents were produced by light absorbed by the pigment-protein complexes as shown in our previous data (M. Ogawa, M. Nango, et.al., *Chem. Lett.*, 772-773 (2004) and M. Kondo, M. Nango, *Biomacromolecules*, **8**, 2457-2463 (2007) ) .

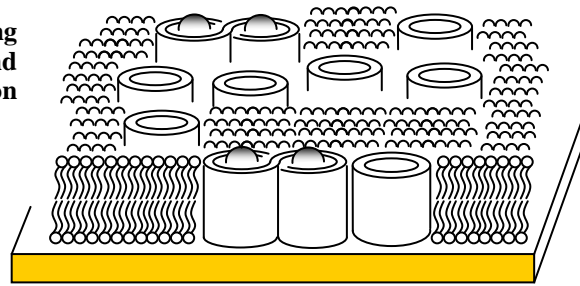
It proved critical in these studies to capitalize on our knowledge of the behavior of these complexes to select those that are the most stable and well organized. The best results were only obtained with the subset of the most stable complexes which the orientation and direction are controlled. These studies were examined to correlate the supramolecular organization of the complexes on the electrodes with an efficient capture of photons.

AFM studies resolved the organization of antenna complexes both in reconstituted lipid bilayers and in native photosynthetic membranes (A. Sumino , M. Nango, et al., *Surface Science and Nanotechnology*, **9**, 15-20(2011), *Langmuir*, **27**, 1092-11099 (2011) and in the attached abstract, and *Biomacromolecules*, in press and in the attached abstract). These techniques were applied to investigate the organization of the antenna complexes and their synthetic model complexes on the electrodes. This work required very careful attention to detail and the current pictures were very exciting.

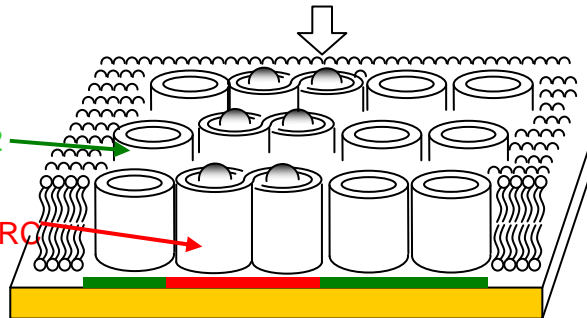
Modern biosynthetic manufacturing methods to control the direction and orientation of the complexes on electrodes



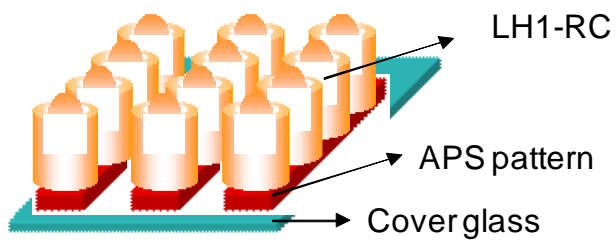
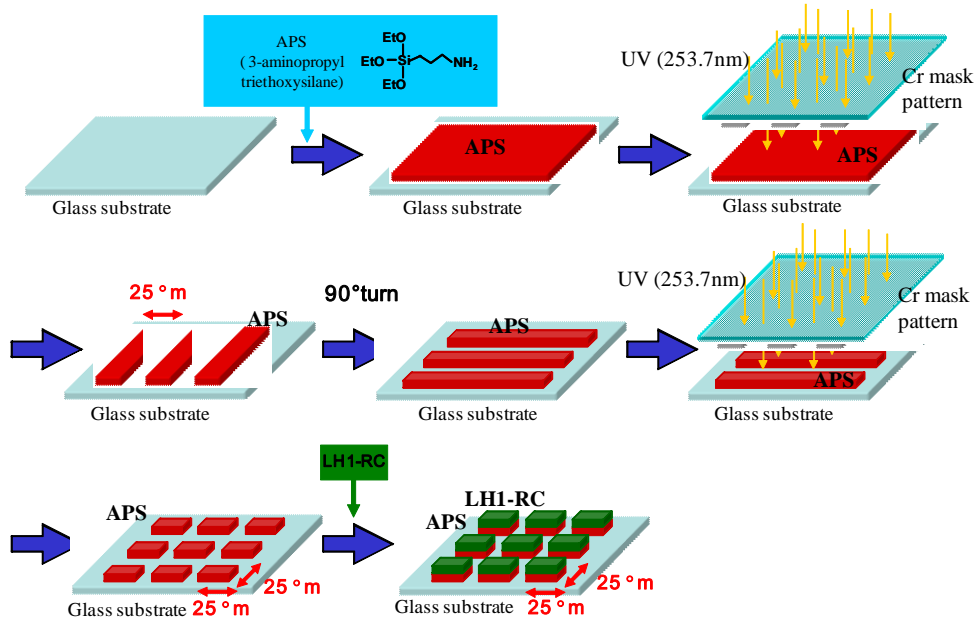
AFM image of a bacterial photosynthetic membrane



Random immobilization

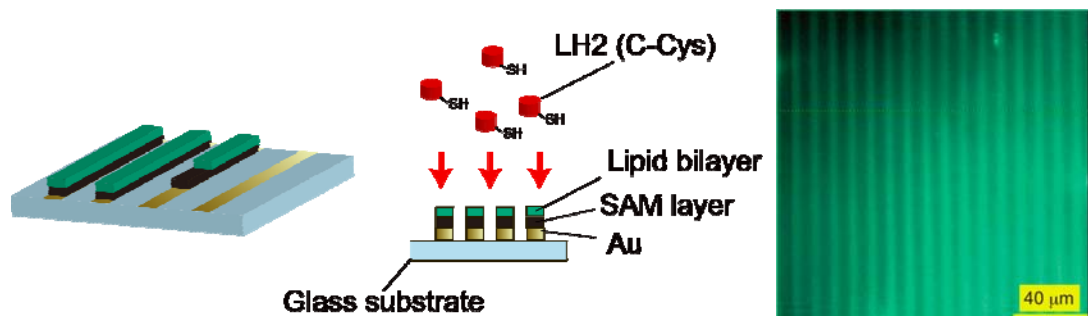


Artificial domains of LH2 & LH1-RC with patterning substrate

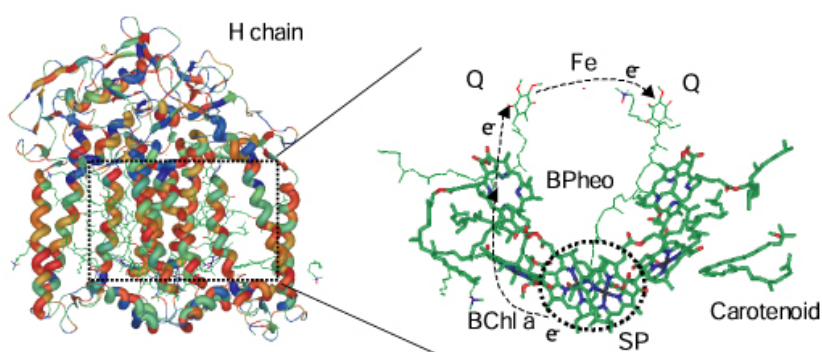


(a)-1

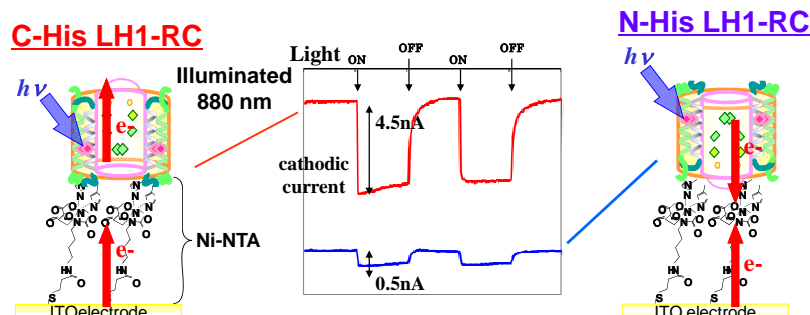




(a)-2



Immobilization of His-tagged LH1-RC on an ITO electrode with a defined orientation



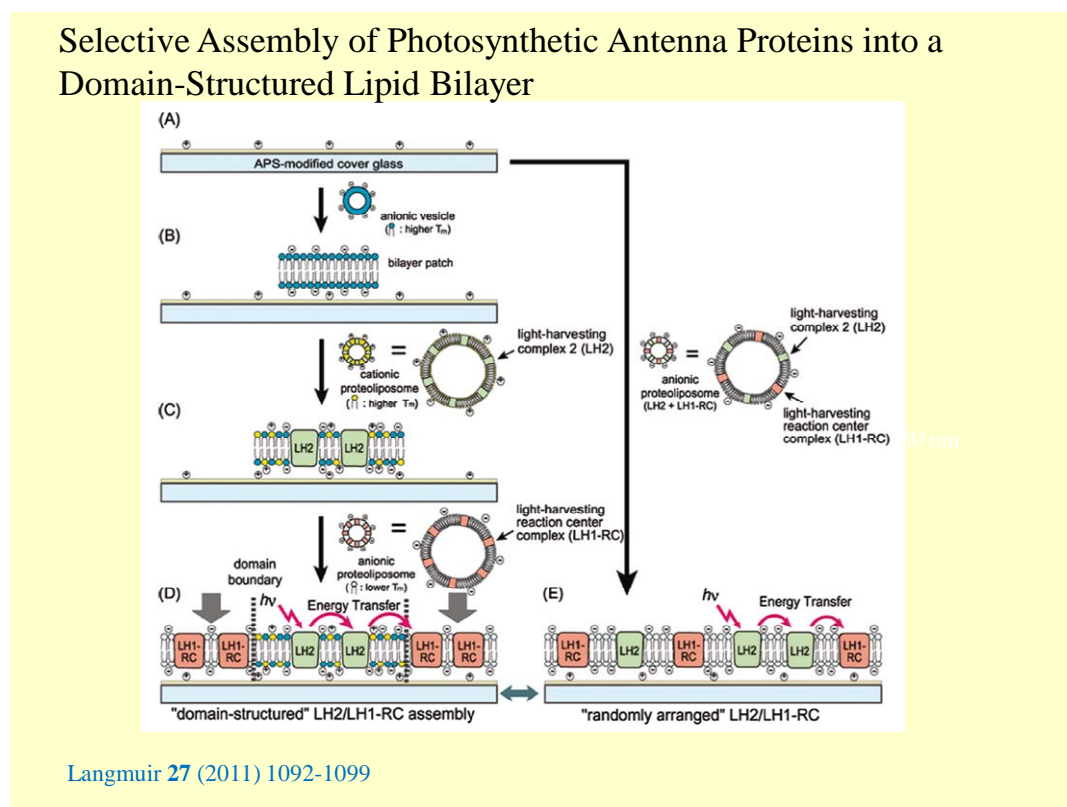
The cathodic photocurrent response were corresponded to RC orientation on C-His LH1-RC.

(b)

**Scheme 2. Artificial domains of LH2 & LH1-RC with patterning substrate:** Schematic model of the assembly of LH1-RC complex with His-tag(a-1) and LH2 with SH(a-2) on an electrode with pattern and electron flow pathway of RC (b). (a) LH1-RC complex and SP side of RC is oriented to hydrophilic SAMs on the electrode and the H-chain is oriented to aqueous phase (a-1). LH2 with SH is selectively assembly onto the electrode modified with thiol groups or lipid bilayers (a-2). 5 μm-scale fluorescence patterning of LH2 complex with SH was observed (a-2)

(b) Electrons are transferred along the pigments associated with the L-subunit of the RC i.e. from SP to BChl *a* (0.47 nm transfer distance), to Bpheo (0.38 nm transfer distance) and finally to Q (0.9 nm transfer distance). The intensity of the photocurrent depended on the orientation of the LH1-RC with His-tag attached at the C-terminal or the N-terminal.

**2 ): Artificial domains of LH2 & LH1-RC with nanopatterning substrate to construct an efficient energy and electron transfer systems in lipid bilayers analogous to the photosynthetic antenna complexes.**



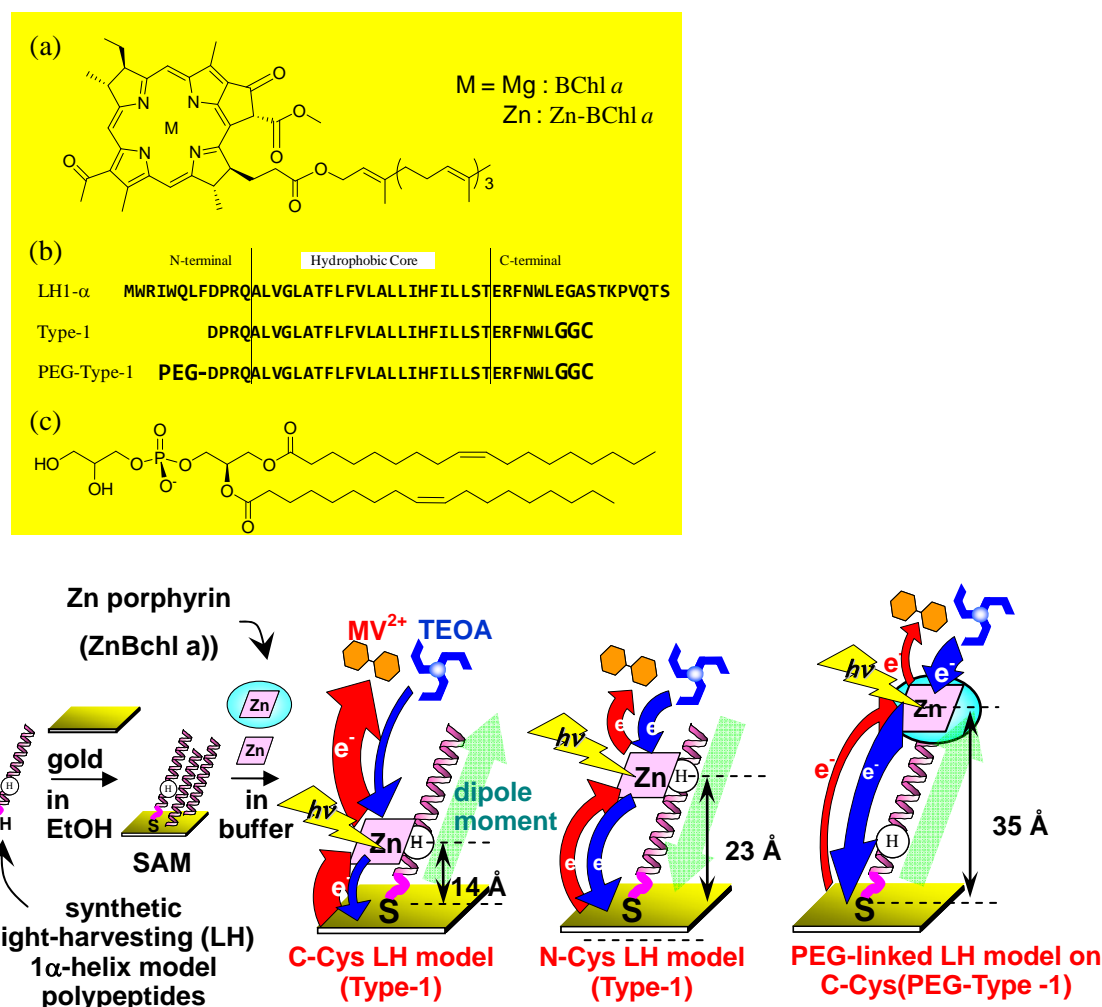
**Scheme 3**

Assembly of LH2 & LH1-RC on the supported lipid bilayer membrane was observed by the AMF image and energy transfer from LH2 to LH1-RC in lipid bilayer was clearly observed as shown in Scheme 3 (A. Sumino, M. Nango, et al., *Langmuir*, **27**, 1092-11099 (2011) and in the attached abstract ). Further, photocurrent generation by reconstituted LH1-RC was observed. Combination of the structural and function analyses of these LH complexes can reveal the relationship between the supramolecular structure and its function as well as for developing nanobiophotonics and energy harvesting materials.

**3) Molecular assembly of photosynthetic pigments using chemically synthesized LH model polypeptides on electrodes with a defined distance and orientation for developing nanobiophotonics**

In the current of our previous study, LH1 synthetic model polypeptides with cysteine group at the C-

terminal, analogous to the native LH 1- $\alpha$  or - $\beta$  polypeptide were assembled on Au or ITO electrode (T. Ochiai, M.Nango, et al., *Langmuir* **26**, 14419-14422 (2010) and *Langmuir*, accepted and in the attached abstract ). Then pigments such as native and chlorophyll derivatives were further selected and assembled on the specific site of the LH1 synthetic model polypeptides to control the organization of the LH1-RC model complex on electrodes modified with or without lipid bilayers as shown in Scheme 4. The structural effects of the pigments and the synthetic polypeptides on the production of the efficient electron flows were further examined (T. Ochiai, M.Nango, et al., *Langmuir*, accepted).



**Scheme 4.** Schematic model of the assembly of synthetic LH model polypeptides (b) with pigments (a) on Au electrode with or without lipid bilayers (c).

Molecular assembly of Zn porphyrin pigments on a gold electrode using synthetic 1 $\alpha$ -helix hydrophobic polypeptide which have similar amino acid sequences to the hydrophobic core in the native photosynthetic light-harvesting (LH) LH 1- $\alpha$  or - $\beta$  polypeptide from photosynthetic bacteria, has been achieved. This method was clearly successful in allowing assembly of porphyrins together with LH1 type functional complexes with a defined distance and orientation on the electrode. In this case, the switching

of photocurrent direction by changing the applied potential was successfully demonstrated. This method was useful for the self-assembly of these complexes in order to study the energy transfer and electron transfer reactions (capture of photons) between individual pigments in the supramolecular complexes on the electrode with pattern as well as to provide insight into the effect of the structure of 1 $\alpha$ -helix hydrophobic polypeptide on the energy transfer and capture of photons.

### Pay-off

**Effects of dissemination of research results are as follows,**

**1) Assembly of photosynthetic antennas and their protein-mimic complexes on electrodes with nanopattern.** This proposal aims to incorporate modified core complex (LH1-RC) and the antenna (LH2) complexes, and their model complexes onto Au, ITO, SiO<sub>2</sub> and polymer matrix with pattern. If this trial becomes successful, it can trigger the development of a new information technology, IT industry as well as development of a new type of nanosensors and nanosemiconductors..

**2) Efficient usage of light. Photosynthetic antennas can collect light in the entire region from ultraviolet to near infrared.** It has a unique property to harvest a small number of photons from all the different directions and to concentrate them for usage. This mechanism to enable high sensitivity in a wide spectral region can be used as a guiding principle in designing photo-electronic materials.

### Summary

The present generations of sensor and semiconductor devices with an integrated circuit for developing nano-level size are too expensive to be cost-effective compared to other existing technologies. Expanding existing silicon device technologies and nanofabrication technics by incorporation of modified photosynthetic protein / pigments complexes or their protein-mimic materials to perform tasks of light-harvesting and charge separation, is currently explored as a novel concept, which makes use of natural protein environments to create a directional flow of light energy and electronic charge separation, meanwhile reducing the cost aspect by the use of bio-materials and their synthetic protein-mimic materials. Based on biological design principles, future biology-based photonics or their synthetic organic photonics could form clean and inexpensive future alternatives for productions of nanosensors and nanosemiconductors.

We propose a scenario where construction of artificial photosynthetic systems with patterning substrate is expected to start from molecular and supramolecular entities in a variety of smart matrices that collect light energy and separate charge, leading to an electrochemical potential that can be used to produce current for developing new types of nanobiophotonics

### 4) List of Publications:

#### Publication

- 1) T. Ochiai, M. Nagata, K. Shimoyama, M. Amano, M. Kondo, T. Dewa, H. Hashimoto, and M. Nango, "Immobilization of Porphyrin Derivatives with a Defined Distance and Orientation

- onto a Gold Electrode Using Synthetic Light-Harvesting  $\alpha$ -Helix Hydrophobic Polypeptides”, *Langmuir* **26**, 14419-14422 (2010).
- 2) K. Nakagawa, S. Sakai, M. Kondo, T. Dewa, T. Horibe, H. Hashimoto, M. Nango, “Structural Forming of Photosynthetic Polypeptide Supramolecular Complexes and Functional Analysis of Carotenoids in These Complexes” *Kobunshi Ronbunshu*, **67**, 574-583 (2010).
  - 3) I.Oda, M. Iwaki, D. Fujita, Y. Tsutsui, S. Ishizuka, M. Dewa, M. Nango, T. Kajino, Y. Fukushima, and S. Ito Photosynthetic Electron Transfer from Reaction center Pigment-Protein Complex in Silica Nanopore, *Langmuir* **26**, 13399–13406 (2010).
  - 4) A. Sumino, T. Takeuchi, M. Kondo, T. Dewa, N. Sasaki, N. Watanabe, T. Morii, H. Hashimoto, and M. Nango, “Reconstitution and AFM Observation of Photosynthetic Membrane Protein Assembly in Planar Lipid Bilayers”, *Surface Science and Nanotechnology*, **9**, 15-20(2011).
  - 5) A. Sumino, T. Dewa, M. Kondo, T. Morii, H. Hashimoto, A. Gardiner, R. Cogdell, and M. Nango, “Selective Assembly of Photosynthetic Antenna Proteins into a Domain-Structured Lipid Bilayer for the Construction of Artificial Photosynthetic Antenna Systems: Structural Analysis of the Assembly using Surface Plasmon Resonance and Atomic Force Microscopy”, *Langmuir*, **27**, 1092-11099 (2011).
  - 6) R. Nakamura, K. Nakagawa, M. Nango, H. Hashimoto, and M. Yoshizawa, “Dark Excited States of Carotenoid Regulated by Bacteriochlorophyll in Photosynthetic Light Harvesting”, *J. Phys. Chem. B*, **115**, 3233-3239 (2011).
  - 7) D. Uchiyama, H. Oikawa, K. Otomo, M. Nango, T. Dewa, S. Fujiyoshi, and M. Matsushita, “Reconstitution of bacterial photosynthetic unit in a lipid bilayer studied by single-molecule spectroscopy at 5 K”, *Phys. Chem. Chem. Phys.*, **13**, 11615–11619(2011).
  - 8) A. Sumino, T. Dewa, T. Takeuchi, R. Sugiura, N. Sasaki, N. Misawa, R. Tero, T. Urisu, A. T. Gardiner, R. J. Cogdell, H. Hashimoto, and Mamoru Nango, “Construction and Structural Analysis of Tethered Lipid Bilayer Containing Photosynthetic Antenna Proteins for Functional Analysis”, *Biomacromolecules*, in press.
  - 9) T. Ochiai, M. Nagata, K. Shimoyama, T. Kato, T. Asaoka, M. Kondo, T. Dewa,<sup>†</sup> K. Yamashita,<sup>†</sup> A. Kashiwada, S. Futaki, H. Hashimoto, and M. Nango, “Two-Dimensional Molecular Assembly of Bacteriochlorophyll a Derivatives Using Synthetic Poly(Ethylene Glycol)-Linked Light-Harvesting Model Polypeptides on a Gold Electrode Modified with Supported Lipid Bilayers”, *Langmuir*, accepted.
  - 10) M. Kondo, K. Iida, T. Dewa, H. Tanaka, T. Ogawa, S. Nagashima, K. V. P. Nagashima, K. Shimada, H. Hashimoto, A. T. Gardiner, R. J. Cogdell, and M. Nango, “Photocurrent and Electronic Activities of Oriented-His-tagged Photosynthetic Light-Harvesting/Reaction Centre Core Complexes Assembled onto a Gold Electrode”, to be submitted.

11) S.Yajima, R.A. Furukawa, M. Nagata, S. Sakai, M. Kondo, K. Iida, T. Dewa and M. Nango, "Fluorescence Observation of a Patterned Bacterial Light-harvesting Protein Complex 2 Immobilized to a Lipid-Modified Gold Substrate", to be submitted.

#### **Conference presentations:**

1. Nobuaki Sasaki, Ayumi Sumino, Natsuko Watanabe, Kaori Harada, Masaharu Kondo, Toshihisa Mizuno, Takashi Morii, Hideki Hashimoto, Takehisa Dewa, and Mamoru Nango "Organization of photosynthetic antenna-reaction center complex into supported lipid bilayer and its functional analysis" Symposium on Biorelevant Chemistry CSJ Osaka University, Toyonaka-Campus (2010.9.24-26)
2. M. Nango and H. Hashimoto, "Artificial photosynthetic antenna: Self-assembly of light-harvesting complexes onto and its synthetic model complex on electrodes for developing nanobiodevices " "The 70<sup>th</sup> Okazaki Conference, Molecular mechanism of photosynthetic energy conversion: The present research and future prospects, Okazaki, Dec 24-6, 2010.
3. Mizuki.Amano, Morio Nagata, Masaharu Kondo, Hideki Hashimoto, Yutaka Amao, Takehisa Dewa, Mamoru Nango, "Photocurrent Measurement of photosynthetic complex including the dye associated with porphyrin on electrodes" The 37<sup>th</sup> Porphyrin Society Science Symposium, Tokyo Insutitute of Technology, Ookayama Campas (2011.5. 7)

#### **Representative abstracts in the publication**

- 1) T. Ochiai, M. Nagata, K. Shimoyama, M. Amano, M. Kondo, T. Dewa, H. Hashimoto, and M. Nango, "Immobilization of Porphyrin Derivatives with a Defined Distance and Orientation onto a Gold Electrode Using Synthetic Light-Harvesting  $\alpha$ -Helix Hydrophobic Polypeptides", *Langmuir* **26**, 14419-14422 (2010).

#### **Abstract**

Molecular assembly of Zn porphyrin pigments on a gold electrode using synthetic 1  $\alpha$ -helix hydrophobic polypeptide which have similar amino acid sequences to the hydrophobic core in the native photosynthetic light-harvesting (LH) 1  $\alpha$ -polypeptide from *Rhodobacter sphaeroides*, has been achieved. This method is clearly successful in allowing assembly of porphyrins together with LH1 type functional complexes with a defined distance and orientation on the electrode. In this case, the photocurrent direction and the distance of electron transfer of pigments could be controlled by these synthetic LH1 model polypeptides. This method will be useful for the self-assembly of these pigment and protein complexes in order to study the energy transfer and electron transfer reactions between individual pigments in the supramolecular complexes on the electrode as well as to provide insight into the effect of the distance and orientation of pigments and the effect of the structure of 1  $\alpha$  -helix hydrophobic polypeptide on the energy transfer and electron transfer reactions.

- 5) A. Sumino, T. Dewa, M. Kondo, T. Morii, H. Hashimoto, A. Gardiner, R. Cogdell, and M. Nango, "Selective Assembly of Photosynthetic Antenna Proteins into a Domain-Structured Lipid Bilayer for the Construction of Artificial Photosynthetic Antenna Systems: Structural Analysis of the Assembly using Surface Plasmon Resonance and Atomic Force Microscopy", *Langmuir*, **27**, 1092-11099 (2011).

### **Abstract**

Two types of photosynthetic membrane proteins, the peripheral antenna complex (LH2) and the core antenna-reaction center complex (LH1-RC), play an essential role in the primary process of purple bacterial photosynthesis that is, capturing light energy, transferring it to the RC where it is used in subsequent charge separation. Establishment of experimental platforms is required to understand the function of the supramolecular assembly of LH2 and LH1-RC molecules in to arrays. In this study, we assembled LH2 and LH1-RC arrays into domain-structured planar lipid bilayers placed on a cover glass using stepwise combinations of vesicle-to-planar membrane formation and vesicle fusion methods. First, it was shown that assembly of LH2 and LH1-RC in planar lipid bilayers, through vesicle-to-planar membrane formation, could be confirmed by absorption spectroscopy and high resolution atomic force microscopy (AFM). Second, formation of a planar membrane incorporating LH2 molecules made by the vesicle fusion method was corroborated by AFM together with quantitative analysis by surface plasmon resonance (SPR). By combining planar membrane formation and vesicle fusion, in a stepwise manner, LH2 and LH1-RC were successfully organized in the domain-structured planar lipid membrane. This methodology for construction of LH2/LH1-RC assemblies will be a useful experimental platform with which to investigate energy transfer from LH2 to LH1-RC where the relative arrangement of these two complexes can be controlled.

- 8) A. Sumino, T. Dewa, T. Takeuchi, R. Sugiura, N. Sasaki, N. Misawa, R. Tero, T. Urisu, A.T. Gardiner, R.J. Cogdell, H. Hashimoto, and Mamoru Nango, "Construction and Structural Analysis of Tethered Lipid Bilayer Containing Photosynthetic Antenna Proteins for Functional Analysis", *Biomacromolecules* in press.

### **Abstract**

The construction and structural analysis of a tethered planar lipid bilayer containing bacterial photosynthetic membrane proteins, light-harvesting complex 2 (LH2) and light-harvesting core complex (LH1-RC), is described and establishes this system as an experimental platform for their functional analysis. The planar lipid bilayer containing LH2 and/or LH1-RC complexes was successfully formed on an avidin-immobilized coverglass via an avidin-biotin linkage. Atomic force microscopy (AFM) showed that a smooth continuous membrane was formed there. Lateral diffusion of these membrane proteins, observed by a fluorescence recovery after photobleaching

(FRAP), is discussed in terms of the membrane architecture. Energy transfer from LH2 to LH1-RC within the tethered membrane was observed by steady-state fluorescence spectroscopy, indicating that the tethered membrane can mimic the natural situation.

9) T.Ochiai, M. Nagata, K. Shimoyama, T. Kato, T. Asaoka, M. Kondo, T. Dewa,<sup>†</sup> K. Yamashita,<sup>†</sup> A.Kashiwada, S. Futaki, H. Hashimoto, and M. Nango, “Two-Dimensional Molecular Assembly of Bacteriochlorophyll *a* Derivatives Using Synthetic Poly(Ethylene Glycol)-Linked Light-Harvesting Model Polypeptides on a Gold Electrode Modified with Supported Lipid Bilayers”, *Langmuir* accepted.

### Abstract

In this study, the two-dimensional molecular assembly of bacteriochlorophyll *a* (BChl *a*) and zinc-substituted BChl *a* (Zn-BChl *a*) together with synthetic poly(ethylene glycol)(PEG)-linked light-harvesting (LH) model polypeptides on a gold Au(111) electrode modified with supported lipid bilayers was accomplished. The LH model polypeptides from *Rhodospirillum rubrum* (*Rs. rubrum*) LH1- $\alpha$  were successfully synthesized and stably assembled with Zn-BChl *a* in 1,2-dioleoyl-*sn*-glycero-3-[phospho-*rac*-(1'-glycerol)] (DOPG) lipid bilayers on an electrode at room temperature, as well as in liposomal solution, in which the Zn-BChl *a* complex was stably assembled when compared to BChl *a*. The PEG moiety of the model polypeptide assisted the stable assembly with an  $\alpha$ -helical conformation of the LH1- $\alpha$  model peptides together with these pigments onto the gold electrode with a defined orientation. The photocurrent response depended on the combinations of the pigments and synthetic LH model polypeptides. The results presented herein will be useful for the self-assembly of these complexes on electrodes to construct efficient energy-transfer and electron-transfer reactions between individual pigments in lipid bilayers.

10) M. Kondo, K. Iida, T. Dewa, H. Tanaka, T. Ogawa, S. Nagashima, K. V. P. Nagashima, K. Shimada, H. Hashimoto, A. T. Gardiner, R. J. Cogdell, and M. Nango, “Photocurrent and Electronic Activities of Oriented-His-tagged Photosynthetic Light-Harvesting/Reaction Centre Core Complexes Assembled onto a Gold Electrode” to be submitted.

### Abstract

A poly-histidine (His) tag was fused to the C- or N-terminus of the light-harvesting (LH1)- $\alpha$  chain of the photosynthetic antenna core complex (LH1-RC) from *Rhodobacter sphaeroides* to allow immobilization of the complex on a solid substrate with defined orientation. His-tagged LH1-RCs were adsorbed onto a gold Au (111) electrode modified with Ni-NTA (3,3'-Dithiobis [*N*-(5-amino-5-carboxypentyl) propionamido-*N,N*-7-diacetic acid]). The presence of the characteristic near-IR absorption peaks of LH1-RC indicated that the LH1-RCs were assembled



and that they retained their native conformation on the modified electrode. The LH1-RC with the C-terminal His-tag (C-His LH1-RC) in self-assembled monolayers (SAMs) produced a photovoltaic response upon illumination. Electron transfer is unidirectional within the RC, and starts when the bacteriochlorophyll *a* dimer (special pair, SP) in the RC is activated by light absorbed by LH1. The LH1-RC with the N-terminal His-tag (N-His LH1-RC) produced very little or no photocurrent upon illumination at any wavelength. The conductivity of the His-tagged LH1-RC was measured with point-contact current imaging atomic force microscopy, indicating that 60% of the C-His LH1-RC are correctly oriented. A similar degree of order also occurs with N-His (63%). The rest of the C-His LH1-RC or N-His LH1-RC (35% or 37%, respectively) showed semiconductive behavior i.e. had the opposite orientation. These results indicate that the His-tag successfully controlled the orientation of the RC on the solid substrate, and that the RC produced photocurrent depending upon the orientation on the electrode.

11) S.Yajima, R.A. Furukawa, M. Nagata, S. Sakai, M. Kondo, K. Iida, T. Dewa and M. Nango, "Fluorescence Observation of a Patterned Bacterial Light-harvesting Protein Complex 2 Immobilized to a Lipid-Modified Gold Substrate", to be submitted.

## **Abstract**

Photosynthetic membrane proteins convert solar light into chemical energy in a significantly high efficiency. Up-to-date reports of the photosynthetic bacterium suggest that such effective light conversion is due to the energy transfer between two light-harvesting (LH) protein complexes that are patterned in two dimensions. In this report, LH complex isolated from *Rb. sphaeroides* was immobilized onto a patterned gold surface with self-assembled monolayers (SAMs) and lipid bilayers at two main objectives: (1) micron-scale patterning of LH complex, and (2) prevention of quenching for pattern observation.