VIII-DD Macromolecular Self-Assembly Opens the Way for Development of Novel Materials that Have Characteristics of Cellular Systems

Self-assembly is a principle to integrate molecular devices into a cellular supramolecular system. Exchangeability of the components, characteristic of assembled structures, allows the system to be repairable, reusable and modifiable on demand, and enables metabolism, adaptation, and evolution of the system. This insight may open new perspective for artificial photoelectronic apparatuses at the nano scale. Development and integration of molecular devices have been focuses for downsizing and energy-saving in the field of photoelectronics. For global, sustainable development, in our opinion, the future materials should also be "entropy-saving" (reusable, repairable, and bio-degradable) that has not been considered to date. We thus aimed at development of an artificial photosynthetic system that allows on-demand reuse (Figure 1); for their basis, we also study on molecular mechanisms of photosynthesis. Our study should serve a new design concept for nano- and molecular-scale intelligent materials (see also Special Research Project (c)).

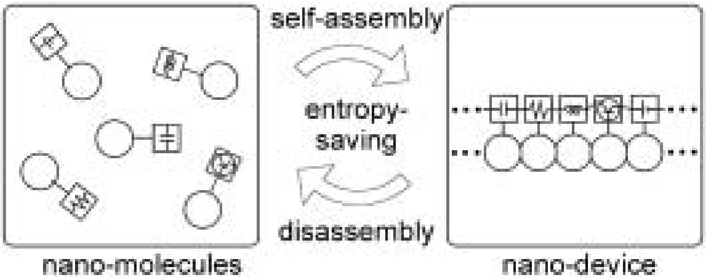

Figure 1. A concept of the "entropy-saving" nano-devices. The device does not function until on-demand self-assembly of nano functional blocks, and the device can easily be decomposed into the reusable components on demand.

VIII-DD-1 Engineering of Tobacco Mosaic Virus

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Green photosynthetic bacteria possess rod-shaped nano-elements (4 ~ 5 nmϕ × 200 ~ 300 nm) as cores of light-harvesting antenna function. The rod-element is thought to be a self-assembled chlorophylls whose details remain yet unclear. Such a supramolecule may be useful as unique devices for future photoelectronics and biotechnology, but (1) it is impossible to obtain intact rod-elements from the cell and (2) it is quite difficult to build artificial tubule supramolecules by self-assembly of chlorophylls. We aimed at construction of nano-tubule of self-assembled chlorophylls by using tobacco mosaic virus (TMV) as a template. TMV possesses a tubule structure with an outer diameter of 15 nm, inner diameter of 4 nm, and length of 300 nm: the size of the channel matches that of the chlorosomal rod-element. We synthesized novel hydrophilic chlorophyll derivatives, and examined their affinities for the inner surface of TMV and their self-assemblies in the channel.

VIII-DD-2 Synthesis and Properties of Novel Biotin Derivatives

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Arrangement and connection of functional molecules in desired sequences and shapes are basic techniques for future fabrication of elaborate molecular systems including nano-devices and nano-computers. We aimed at development of a new method to arrange functional molecules sequentially in a desired order by utilizing specific interaction between avidin and biotin. Avidin is a 6.8 kDa protein (*ca.* 5 × 5 × 6 nm in size) that can bind four biotin molecules. The topology of the biotin binding sites is appropriate to link avidin molecules linearly when using a linear molecule that possesses two biotin moieties at both ends. Syntheses of novel bitoin derivatives and examination of their abilities to control the assembly of avidin molecules are now under way.

VIII-DD-3 Physicochemical Studies on the Molecular Mechanism of Photosynthesis

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Since chlorophylls (Chls) and bacteriochlorophylls (BChls) are highly asymmetric molecules, an external ligand can coordinate to the central Mg atom of (B)Chls either from the chlorin macrocycle side where the C13^2-methoxycarbonyl moiety protrudes (denoting as the "back" side) or from the other side (the "face" side, Figure 2). We found that the "back" side is favored for the ligand coordination, by survey of the highly resolved crystal structures of photosynthetic proteins and by theoretical calculations of model molecules. The calculations reveal that stability of the (B)Chl-ligand complex is sensitive to distortion of the macrocycle, and the distortion is affected by steric repulsion between particular peripheral substituents as well as flexibility of the macrocycle. We note that not only the static pigment-protein (pigment-pigment) interactions but also dynamics of the pigment-protein (pigment-pigment) assembly should be clarified for better understanding of the role of the planar chirality of (B)Chls *in vivo*.

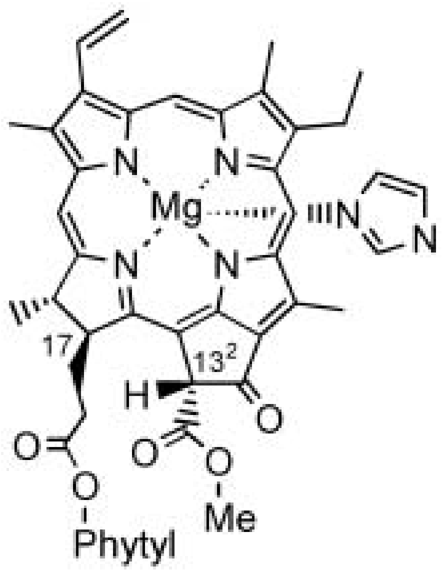

Figure 1. Molecular structure of the “back” type chlorophyll *a*-imidazole complex.