VIII-S Macromolecular Self-Assembly Opens a Way to the Development of Novel Materials that Have Characteristics of Cellular Systems

In cellular systems, assembly of devices (*e.g.* enzymes) into complexes is a principle to construct supramolecular apparatuses and ensure the specificity, fidelity, and efficiency of intracellular events. Exchangeability of the components of the complex is also advantageous for adaptation to the environment and metabolism of the apparatus. For global, sustainable development, in our opinion, readiness for the adaptation and decomposition is required for any future materials and systems such as highly integrated device arrays. Utilizing elaborate macromolecular self-assemblies, we thus aimed at development of artificial systems endowed with energy- and entropy-saving properties: the system can be formed and function on demand, and are readily reusable, repairable, and bio-degradable. We attempt to fabricate the nano-systems for energy conversion and computing; for their basis, we also study on molecular mechanisms of photosynthesis and signal transduction. Our study should serve a new design concept for nano- and molecular-scale intelligent materials (see also Special Research Project (c)).

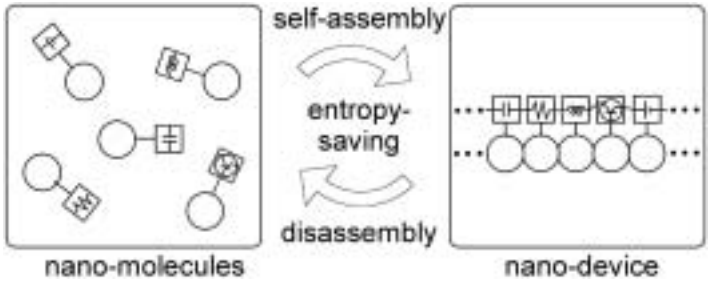

Figure 1. A concept of the "entropy-saving" nano-materials.

VIII-S-1 Fabrication of "Entropy-Saving" Nano-Solar-Cells

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Photosynthetic apparatuses in living organisms are, in common, assemblies of light-harvesting antenna parts and reaction centers (RCs) where energy conversion occur. Nano-scale order in the assembled supramolecular structure contributes efficient function. The assembly is advantageous to light adaptation and metabolism. These facts suggest that elaborate self-assembly of macromolecular components can provide solar-cells that can be formed and function on demand. We developed such device utilizing cytoskeletal nano-tubes, "microtubules" (MTs). The component protein "tubulin" (Tub) molecules assemble to form MTs at 37 ˚C in the presence of nucleotide, and MTs disassemble to Tubs at 0 ˚C. We prepared Tubs conjugated with a fluorophore for the antenna part and a photosensitizer-labeled hemoprotein for the RC, respectively. The modified Tubs were mixed and the temperature of the solution was switched simply. Only in the Tub-assembled state (MTs), solar energy absorbed by the antenna parts migrated to the sensitizer, leading to charge separation in the RC, as occurs in photosynthesis. The device reversibly functioned at each Tub-assembled state in the course of the Tub-assembly / MT-disassembly cycles.

VIII-S-2 Model Study on Signaling Behaviors of Scaffold Proteins—Toward its Application to Novel Computing Devices—

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Scaffold proteins, found in postsynaptic termini, can bind several members of a signaling cascade to form a supramolecular complex, which may contribute to rapidity, fidelity, and selectivity of signal transduction.[1)] Such a mechanism can correlate to learning and memory formation. Due to the limitation of the experiments, however, no detailed model of scaffold action has been reported except for numerical simulations. We utilized a eukaryotic cytoskeleton 'microtubule' (MT) for fabrication of a model of the signaling complexes. We conjugated both glucose oxidase (GOx) and horseradish peroxidase (HRP) on the surface of an MT by use of the avidin-biotin interaction. The upstream effector (GOx) converted an input signal (*D*-glucose) into a second messenger (H_2O_2) that was diffusely supplied to the downstream effector (HRP) and converted into an output signal (Dye). It was found that sensitivity of the system to the stimulus increased with increasing density of the effectors on a MT. Further examinations of this model system may contribute to development of novel computing devises.

Reference

1) U. Thomas, "Modulation of synaptic signalling complexes by Homer proteins," *J. Neurochem.* **81**, 407 (2002).

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

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[*Photosynth. Res.* in press]

Since chlorophyll *a* and bacteriochlorophyll *a* are asymmetric molecules (Figure 1), an external ligand can coordinate to the central Mg atom 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). We investigated which side of the macrocycle is favored for the ligand coordination, by survey of the highly resolved crystal structures of various photosynthetic proteins and theoretical model calculations. It is found that chlorophyll *a* as well as bacteriochlorophylls *a* and *b* in the photosynthetic proteins mostly bind their ligands on the 'back' sides. This finding was confirmed by the theoretical calculations for methyl chlorophyllide *a* and methyl bacteriochlorophyllide *a* as models: the 'back' type ligand-(bacterio)chlorophyll complex was more stable than the 'face' type one. The calculations predicted influence of the $C13^2$-stereochemistry on the choice of the side of the ligand coordination, which may be correlated to the presence of the $C13^2$-epimer of chlorophyll *a* in photosystem I reaction center.[1)]

Reference

1) P. Jordan, P. Fromme, H. T. Witt, O. Klukas, W. Saenger and N. Krauß, "Three-dimensional structure of cyanobacterial photosystem I at 2.5 Å resolution," *Nature* **411**, 909 (2001).

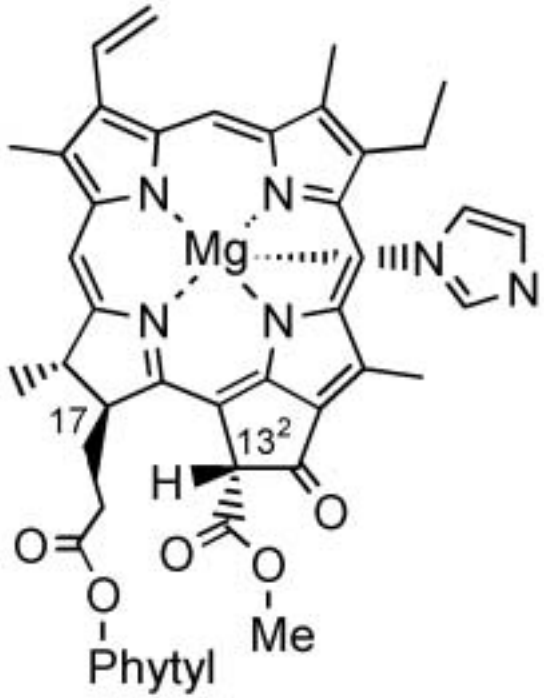

Figure 1. Molecular structure of the 'back' type chlorophyll *a*-imidazole complex.