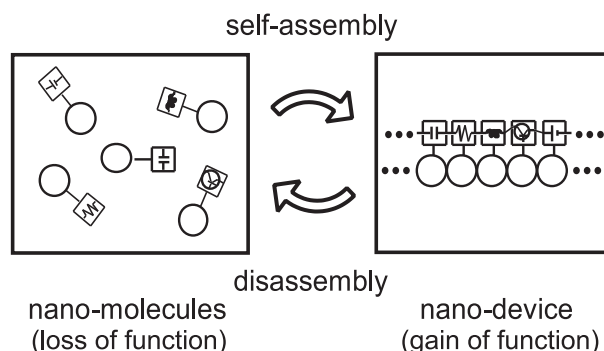


IX-Z Macromolecular Self-Assembly Opens the Way for Development of Novel Materials That Have Characteristics of Cellular Systems

Methods to integrate functional molecules into well-defined nano structures is a key for fabrication of future materials. Nano-integrated circuits may be afforded by elaborate arrangements of various molecular- and nano-devices. Self-assembly is a strong tool for integration of molecules into various nano structures. Self-assembly, however, tends to give polymorphism and structural defects in the assembled structures. Furthermore, functions of elaborate molecular systems should be sensitive to small structural damages and heat dissipation. For development of the future materials, thus, one should employ a self-assembly process that selectively affords a single, well-defined supramolecular structure to suppress polymorphism. It is also necessary that the formed device is repairable to be robust to damages and defects. We examine such a design strategy that has not yet been examined to date (Figure 1; see also Special Research Project (c)).

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



IX-Z-1 Fabrication of Nano-Devices on the Principle of Cellular Supramolecular System

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[*Photosynthesis: Fundamental Aspects to Global Perspectives in press*]

Development of molecular devices has attracted much attention in the field of electronics and photo-electronics. For global, sustainable development, molecular devices and nano-devices should be reusable, repairable, and bio-degradable, which has not been considered to date. We thus aimed at development of an artificial photosynthetic device as a prototype of the flexible (supra)molecular system that functioned on demand (Figure 1). We employed naturally occurring nano-tube, 'microtubule' (MT), to integrate functional molecules into a nano ordered structure. We prepared tubulins (Tubs), component proteins of MT, conjugated with a fluorophore for light-harvesting and with a photosensitizer-labeled hemoprotein for charge separation, respectively, and mixed them simply. Each time these functional blocks self-assembled to form MTs in the assembly/disassembly cycle, solar energy absorbed by the antenna fluorophore migrated to the sensitizer, leading to charge separation between the sensitizer and the heme. The nano-device can easily be decomposed into the components on demand, and the components can readily reassemble on demand to recover the function again.

IX-Z-2 Synthesis and Properties of Novel Cationic Chlorophyll Derivatives

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[*Photosynthesis: Fundamental Aspects to Global Perspectives in press*]

Not only metal nano particles but also biomolecules such as DNA, phospholipids, proteins and their supramolecules have been studied for development of molecular devices. It is of much interest to conjugate chlorophylls (Chls), quite abundant photofunctional molecules in nature, with these biomolecules in water for fabrication of novel photofunctional materials such as artificial photosynthetic devices. Chl derivatives that carry cationic charges may be advantageous for interaction with anionic surfaces of the biomolecules and their supramolecules. The conjugation is, however, quite difficult, because, in general, Chls are insoluble in water, resulting in facile formation of higher aggregates. We prepared Chl derivatives that had cationic polymer moiety. Condensation of cationic polymer improved water-solubility, lowered the aggregation number, and enabled conjugation with proteins. The cationic, water-soluble Chl derivative is thus a useful tool for various investigations and applications.

IX-Z-3 Physicochemical Studies on the Molecular Mechanism of Photosynthesis

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[*Photosynthesis: Fundamental Aspects to Global Perspectives* in press]

Since chlorophylls (Chls) and bacteriochlorophylls (BChls) are highly asymmetric molecules, an external ligand can coordinate to the central Mg atom of (B)Chls from either of the two sides of the chlorin macrocycle. We found that the 'back' side (Figure 1) is favored for the ligand coordination, by survey of the highly resolved crystal structures of photosynthetic proteins and by theoretical calculations of model molecules. We have recently found that the 'back' type complex is also the major isomer in two newly resolved photosynthetic proteins. In light-harvesting complex II, 6 of 8 Chl *a* and 4 of 6 Chl *b* are the 'back'-type complexes, respectively. Among 28 ligand-identified Chls in the photosystem 2 core complex, 22 are the 'back' stereoisomers. Further calculations on the virtual chlorin molecules revealed the origin of the energy gap between the 'back' and the 'face' stereoisomers. We also discuss yet undetermined nomenclatures for the macrocycle faces of (B)Chls.

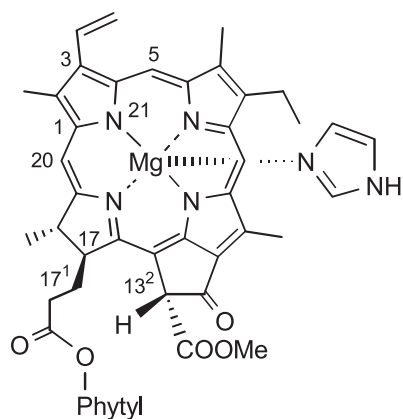


Figure 1. Molecular structure of the 'back' type chlorophyll *a*-imidazole complex.