1-11-2. Light-Harvesting Systems

Overview

All phototrophs possess light-harvesting (LH) systems where sunlight with a low photon energy density in their culturing environments is absorbed by a large amount of pigments and the excitation energy is migrated efficiently. Although most of the their supramolecular structures have been revealed, the energy transfer processes in their up-hill type and strongly interacted LH systems have not been confirmed. Artificial LH systems with a high efficiency and their connection with chemical energy conversion systems have not been achieved yet. In addition, metabolisms of composite pigments and dynamic formation processes of LH systems are highly required to be clarified.

Current State and Recent Advances

Analyses of (supra)molecular structures of natural light-harvesting (LH) systems, mechanisms of their light absorption and excitation energy processes, and their artificial models have been extensively investigated by Japanese (photo)scientists for the last two decades. Here some related topics are briefly introduced.

1. Structural analysis of natural LH systems: Cryo-electronic microscopy as well as X-ray crystallographic analysis are useful for the determination of natural LH structures at an atomic level, and supramolecular structures of their pigment–protein complexes have been revealed. The structures of LHs in chromophytes producing chlorophyll-*c* (Chl-*c*, see Fig. 1) with a porphyrin π-system in its core which absorbed a blue light more efficiently than Chl-*a* were confirmed.[1] The other LH structures with Chls-*d*/*f* absorbing a far-red light which could not be utilized by Chl-*a* were determined.[2]

2. (Bio)synthesis of LH pigments: Although the biosynthetic processes of Chls-*c*/*f* were almost found,[3] *in vivo* production of Chl-*d* has not been revealed yet. Treatment of Chl-*a* with some natural enzymes (Kobayashi et al.) and organic reagents (Oba, Tamiaki et al.) afforded Chl-*d* *in vitro*. BChl-*f* which had not been found in natural photosynthetic bacteria was prepared through organic synthetic reactions (Tamiaki et al.). Later, BChl-*f* was found from the genetic variant of a BChl-*e* producing bacterium.[4] The photosynthetically active BChl-*f* was the seventh bacterial chlorophyllous pigment.

3. Excitation energy transferring mechanisms: In contrast to the well-known down-hill (exergonic) excitation energy transferring mechanism from photoexcited states of Chls-*b*/*c* as accessory pigments to Chl-*a* through Förster type, up-hill (endergonic)

mechanisms from far-red light absorbing Chls-*d*/*f* to Chl-*a* were not confirmed.[3] For the small energy gap, the up-hill energy transfer is possible by use of thermal excitation, and the other mechanisms for the systems with large energy gaps were postulated including the presence of specific excitation states and the utilization of special intermediates (Hashimoto, Fujii et al. and Shibata et al.).

4. Artificial LH system: Modification of a large amount of synthetic pigments and a small amount of energy-accepting species on flat clay surfaces[5] or on/in mesoporous organic silica (Inagaki et al.) provided artificial LH systems. Connection of self-aggregates of semi-synthetic BChl-*d* analogs with energy acceptable molecules produced self-assembling LH (chlorosome) models (Tamiaki et al.).

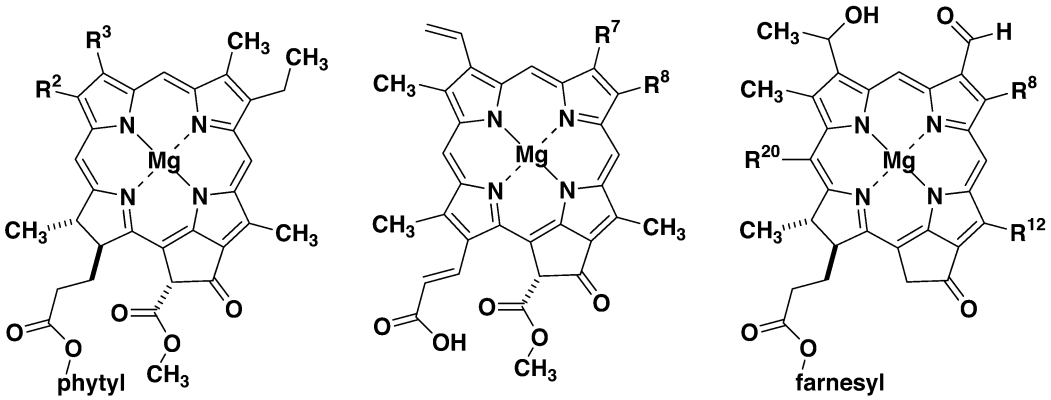

Figure 1. Molecular structures of naturally occurring (B)Chls.

References

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Future Perspectives and Directions

Elucidation of dynamic formation mechanism of LH systems. Determination of metabolic processes of minor LH pigments. Elucidation of excitation energy mechanisms in up-hill type and strongly correlated LH systems. Development of artificial LH systems and their connection with chemical energy conversion systems (artificial photosynthesis).

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