

主 論 文 要 旨

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論文題名

Synthesis and Physical Properties of Metallochlorophylls

ふりがな 　まさあき 　あまかわ
学位申請者 　Masaaki Amakawa

主論文要旨

Green photosynthetic bacteria have unique, extramembranous light-harvesting antennas, called chlorosomes, the core part of which is formed by self-aggregation of specific bacteriochlorophylls without any support of proteins. Here, a variety of metal complexes of a 3-hydroxymethylated chlorophyll derivative were synthesized as a model of the chlorosomal chlorophylls and their self-aggregativities in non-polar organic solvents and solid film states were examined using various spectroscopic methods.

Methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-*a* was prepared by modifying chlorophyll-*a* and metallated to give desired complexes possessing Mg, Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, and Cd at the central position.

In THF, all the synthetic metal complexes gave sharp electronic absorption peaks at Soret and Q_y regions, indicating that they were monomeric in a polar solvent. Visible spectra showed that Ni, Cu, Pd, and Ag complexes were still monomeric in hexane as one of non-polar organic solvents. Mn and Fe complexes in hexane afforded broad visible peaks and red-shifted Q_y peaks, showing that they were dimeric in the solution. In hexane, Mg, Co, Zn, and Cd complexes gave more broadened and red-shifted peaks with large, exciton-coupled CD signals, indicating that they readily formed large oligomers, similar to chlorosomal J-type self-aggregates.

In the thin solid films of such oligomers, intramolecular coordination of a 3^l-hydroxy group with a central metal and hydrogen bond of the 3^l-hydroxy with 13-keto-carbonyl group were observed from the FT-IR spectroscopy, to give their ordered, self-aggregated supramolecules. Moreover, the coordination chemistry of the present metallochlorophylls was revealed from FT-IR analysis.