Chlorosomal self-aggregation of synthetic fluorinated chlorophyll derivatives

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In photosynthesis, absorption of sunlight by light-harvesting antennae is the initial event. Extramembranous light-harvesting antennae of green photosynthetic bacteria, chlorosomes, are unique, where the main pigments, bacteriochlorophyll(=BChl)s-*c, d* and *e* densely self-aggregate to form large oligomers with no assistance of protein. In a chlorosome, the composite BChl molecules specifically interacted with each other through the 3^1-hydroxy, 13-keto carbonyl groups and the central magnesium to form highly ordered self-aggregates. In contrast, BChls-*c, d* and *e* have a variety of long hydrocarbon chains at the 17-position, for example, farnesyl, stearyl, phytyl and others. Their roles in the self-aggregates have not been unraveled.

In chapter 2, I synthesized 3^1-hydroxy-13^1-oxo-chlorin possessing a perfluoroheptyl group on the 17-propionate. The synthetic compound self-aggregated in a flon solvent to give similar large oligomers as in natural chlorosomes. Visible absorption, circular dichroism and fluorescence emission spectra showed that F-F interaction between the perfluoroheptyl side chain and the flon solvent stabilized the supramolecular structure.

In chapter 3, I synthesized zinc zinc 3^1-hydroxy-13^1-oxo-chlorins possessing two, three, four and six perfluorooctyl chains. Only the synthetic zinc chlorin possessing six perfluorooctyl chains was directly dissolved in perfluorinated solvents due to its high fluorine content in molecular weight (over 50%). In this solution, visible absorption spectra gave a red-shifted Q_Y band and showed the formation of well-ordered self-aggregates. These showed that the supramoleculer structure was stabilized by F-F interaction among the perfluorooctyl chains on the 17-position and perfluorinated solvents.