Synthesis of Bacteriochlorins by Modifying Natural Chlorophylls and Their Optical Properties in Monomeric and Oligomeric States

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Bacteriochlorin, one of cyclic tetrapyrrole derivatives, is utilized in natural photosynthesis as photoactive pigments. Since a bacteriochlorin π-conjugate system is a double reduced porphyrin derivative, it is sensitive to be oxidized and decomposed even under ambient conditions.

In chapter 2, I synthesized stable bacteriochlorin derivatives by use of Diels-Alder reactions of 8-vinyl-chlorins with tetracyanoethylene. Such synthetic bacteriochlorins possessing the 8-alkylidene group resembled with natural bacteriochlorophyll(BChl)*s*-*b*/*g* possessing the 8-ethylidene group and were chemically more stable than the natural pigments due to no hydrogen atoms at the 7,8-positions. Furthermore a series of 3-substituted bacteriochlorins were available. The electronic absorption properties of 3-substituted bacteriochlorins showed that their Qy maxima were controlled by the 3-substituents to be red-shifted in the order of ethyl, hydroxyethyl, vinyl, acetyl and formyl group, which was consistent with that in 3-substituted chlorins.

In chapters 3 and 4, I investigated oligomeric properties of synthetic bacteriochlorin molecules. Bacteriochlorins are generally utilized in purple bacterial light-harvesting antenna system (LH1) by assistance of protein scaffold to make exciton coupling among the molecules, whereas chlorins in green bacterial antenna make exciton coupling only by their self-aggregation. In chapter 3, I synthesized self-aggregative magnesium 3-(1-hydroxyethyl)-bacteriochlorin and separated its 3^1-epimers. Their self-aggregation was strongly dependent on the 3^1-stereochemistry; red-shift value by self-aggregation of the 3^1R -epimer was 2170 cm^{-1} while that of 3^1S -epimer was 1280 cm^{-1}. Especially, self-aggregation of the 3^1R -epimer showed similar electronic absorption property with LH1.

In chapter 4, I synthesized chemically stable self-aggregative 7- or 8-oxo-bacteriochlorins. As compared with the above self-aggregative bacteriochlorins modified from natural BChl-*a*, the present oxo-bacteriochlorins were chemically stable because they had no hydrogen atoms at the 7,8-positions. The self-aggregation behaviors of 7- or 8-oxo-bacteriochlorins were controlled by the situation of 8- or 7-dialkyl groups. Molecular modelings of their dodecamers showed that 7-oxo-8-dialkyl-bacteriochlorin self-aggregated with less hindered motif than 8-oxo-7-dialkyl-bacteriochlorin did.