Journal of Photoscience (2002), Vol. 9(2), pp. 347–349

Self-assembly of Amphiphilic Zinc Chlorins in an Aqueous Medium as a Model for Chlorosome of Green Photosynthetic Bacteria

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Synthetic zinc chlorins possessing a hydrophylic polyoxyethylene chain at the 17 -position were prepared. An amphiphilic zinc chlorin possessing a single chlorin moiety showed absorption maxima at 675 nm in an aqueous medium, indicating that the zinc chlorin did not form large aggregates but a dimeric structure. In contrast, amphiphilic zinc chlorin dyads in which two zinc chlorin moieties were connected with a hydrophilic polyoxyethylene linkage showed red-shifted absorption band around 720–740 nm in an aqueous medium. The result indicated that the amphiphilic zinc chlorin dyad self-aggregated to form chlorosome-like oligomer.

Key words: antenna, chlorophyll, photosynthesis, self-assembly

INTRODUCTION

Self-assembled aggregates of chlorophyllous pigments are found in chlorosome of green photosynthetic bacteria [1]. A number of bacteriochlorophylls(BChls) *-c*, *d* and *e* molecules self-aggregated to produce rod-like oligomers. Interestingly, the isolated BChls and synthetic model compounds similarly self-aggregated to give chlorosome-type oligomer *in vitro* [2]. The spectroscopic studies on the self-aggregated BChls showed the C=O···H–O···Mg bondings among BChl molecules are important in self-aggregation [3]. However, the precise supramolecular structure of the unique antenna aggregate was not known. One possible structural model was provided by molecular modeling study, in which the esterified alkyl chain at the 17-position is oriented to the outside of rod structure [4].

Here we report that the self-assembly of synthetic zinc chlorins possessing a hydrophilic oligo-oxyethylene chain at the 17-position. The amphiphilic zinc chlorin **1**

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possessing a single chlorin moiety and zinc chlorin dyads **2a–e** in which two chlorin moieties were connected with a hydrophilic (oligo)oxyethylene chain were self-organized in an aqueous medium.

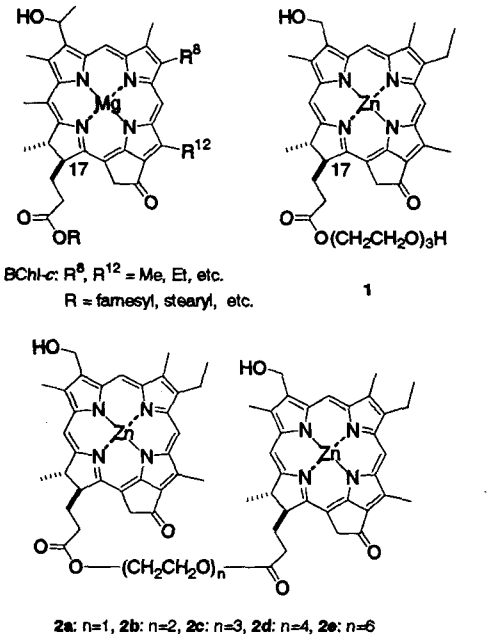

Figure 1. Structure of BChl-*c* and amphiphilic zinc chlorins **1** and **2a–e**.

MATERIALS AND METHODS

The monoesterified zinc chlorin **1** and the zinc chlorin dyads **2a–e** were prepared by esterification of (oligo)ethylene glycol with a propionic acid side chain of a chlorin. The obtained amphiphilic zinc chlorins were purified with a reversed-phase HPLC run and characterized with both ^{1}H-NMR and FAB-MS spectra. Visible absorption and circular dichroism spectra were recorded with Shimadzu UV-3100 spectrophotometer and Jasco J-720W spectropolarimeter, respectively.

RESULTS AND DISCUSSION

Visible absorption spectra of the amphiphilic zinc chlorins **1** and **2** showed Qy maxima at 647 nm in THF, indicating that the amphiphilic pigments were monomeric in the polar organic solvent (Table 1). When the monomeric solution of **1** possessing a single chlorin moiety was diluted with 99-fold volume of water, the Qy band was red-shifted to 675 nm. The spectral change suggested that the zinc chlorin **1** aggregated to form dimer in an aqueous medium. Thus the hydrophilic trioxyethylene group disturbed the further aggregation of zinc chlorin.

Table 1. Qy absorption maxima (nm) of amphiphilic zinc chlorins **1** and **2**.

zinc chlorins	in THF	in 1% THF / water*
1	647	675
2a	647	738
2b	647	656(sh), 725
2c	647	663, 723
2d	647	657(sh), 722
2e	647	656(sh), 723

* after standing for 2 days.

In contrast, the zinc chlorin dyads **2a–e** gave red-shifted absorption band around 720–740 nm, indicating that the

amphiphilic dyads self-aggregated to give large aggregates in an aqueous medium (Table 1). Although the aqueous aggregates of dyad **2a** (n=1) gave precipitate in an aqueous medium, the dyads **2b–e** (n=2, 3, 4 and 6) did not form any precipitate. These results indicated that a hydrophilic oxyethylene linkage of **2b–e** was oriented to outside of the oligomeric structure to stabilize the aqueous large aggregates.

CD spectra of aggregated zinc chlorin dyads **2a–e** showed the intense signals around Qy absorption region (Table 2). The dyad **2a** gave a positive band at 753 nm and a negative band at 719 nm, respectively. In contrast, the dyads **2b–e** gave only a negative peak at 742 nm, indicating that the suprastructure of the aggregated **2b–e** was different from that of **2a**. In addition, the intensity of the negative peak at 742 nm increased with the length of oxyethylene chain. This result suggested that the basic suprastructure of the aggregated **2b–e** were similar, but the long oxyethylene linkage stabilized the aqueous aggregates and provided a well-aligned supramolecular arrangement.

Table 2. CD spectral maxima of zinc chlorin dyads **2a–e** in 1% THF / water.

Zinc chlorin dyads	Wavelength / nm (intensity / mdeg)
2a	719 (–35), 753 (+128)
2b	742 (–2)
2c	741 (–4)
2d	741 (–23)
2e	743 (–20)

ACKNOWLEDGEMENTS

This work was partially supported by Izumi Science and Technology Foundation, Grant-in-Aid for Scientific Research (No.14780465) and a grant based on High-Tech Research Center Program for private Universities from the Japan Ministry of Education, Culture, Sports, Science and Technology.

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