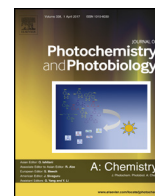




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Invited feature article

## Temperature-dependent self-assemblies of zinc $3^1$ -hydroxy-chlorins in polydimethylsiloxane oil

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### ABSTRACT

Self-aggregates of zinc  $3^1$ -hydroxy-chlorins were prepared in a polydimethylsiloxane (PDMS) oil. The artificial self-aggregates provided a similar chlorophyllous aggregate found in light-harvesting antennas of green photosynthetic bacteria. The zinc chlorin aggregates showed a red-shifted Qy absorption band as well as intense circular dichroism signals at room temperature due to strong exciton coupling among the pigment molecules along their molecular y-axes. Disaggregation studies of the zinc chlorin aggregates were successfully performed in PDMS at a high temperature, which indicated that the aggregate of the  $3^1R$ -stereoisomer of zinc 3-(1-hydroxyethyl)-chlorin was more stable than that of the corresponding  $3^1S$ -isomer. In addition, mixed aggregates of the  $3^1R$ - and  $3^1S$ -epimers prepared in PDMS provided a good structural model of the natural light-harvesting system.

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### 1. Introduction

Self-aggregate of  $\pi$ -conjugated compounds would provide unique optical properties due to strong interactions among the pigment molecules. In nature, extra-membranous light-harvesting antennas of green photosynthetic bacteria consist of self-aggregates of specific chlorophylls (Chls). The supramolecular photosynthetic apparatus is called “chlorosome” in which a large number of bacteriochlorophyll (BChl) *c/d/e* molecules self-aggregate to form oligomers in a J-aggregate fashion [1,2]. The chlorosomal Chls have a hydroxy group at the  $3^1$ -position of a chlorin (17,18-dihydroporphyrin) macrocycle (Fig. 1), and the OH group contributes intermolecular interactions with neighboring molecules with forming hydrogen bond with the 13-carbonyl group and coordination bond with the central magnesium [3,4]. These intermolecular interactions as well as  $\pi$ - $\pi$  stacking give excitonically coupled J-aggregates showing red-shifted visible absorption bands, intense circular dichroism (CD) signals and efficient exciton migration among the chlorophyllous molecules [5,6].

Chlorosomal Chls isolated from green bacteria self-aggregate and reproduce the supramolecular light-harvesting systems *in*

*vitro*. Generally, Chls and their derivatives are well soluble in polar organic solvents such as acetone, methanol, dichloromethane (DCM), and tetrahydrofuran (THF), but less soluble in non-polar organic solvents. When a concentrated Chl solution in the former solvents is dispersed into an excess amount of hexane or cyclohexane, the Chl pigments self-organized to reproduce the natural J-aggregate showing similar red-shifted absorption bands and intense CD signals as in natural chlorosomes [7]. The good *in vitro* reproducibility of the chlorosomal antenna system enabled us to make a supramolecular light-harvesting antenna with synthetic chlorosomal Chl models. Zinc Chl derivatives possessing a  $3^1$ -hydroxy group have been prepared from isolated Chl *a*, which is the most abundant Chl in nature. The 3-vinyl group of Chl *a* is readily transformed to a 1-hydroxyethyl group by hydration or a hydroxymethyl group by oxidative cleavage followed by reduction of the resulting formyl group [8,9]. Zinc complexes of the Chl analogues are easily prepared, and zinc chlorins normally show similar optical properties as those of the corresponding magnesium chlorins and accommodate one axial ligand to form 5-coordinated complexes. Self-aggregates of the semi-synthetic zinc  $3^1$ -hydroxy-chlorins (Fig. 1) were prepared in non-polar organic solvents as well as in micro-hydrophobic environments prepared with aqueous surfactant assemblies [8–10]. These artificial Chl aggregates provide good structural and functional models of chlorosomal antennas showing efficient energy migration to an energy acceptor molecule [11]. Relatively stable zinc  $3^1$ -hydroxy-chlorins would be potential photofunctional

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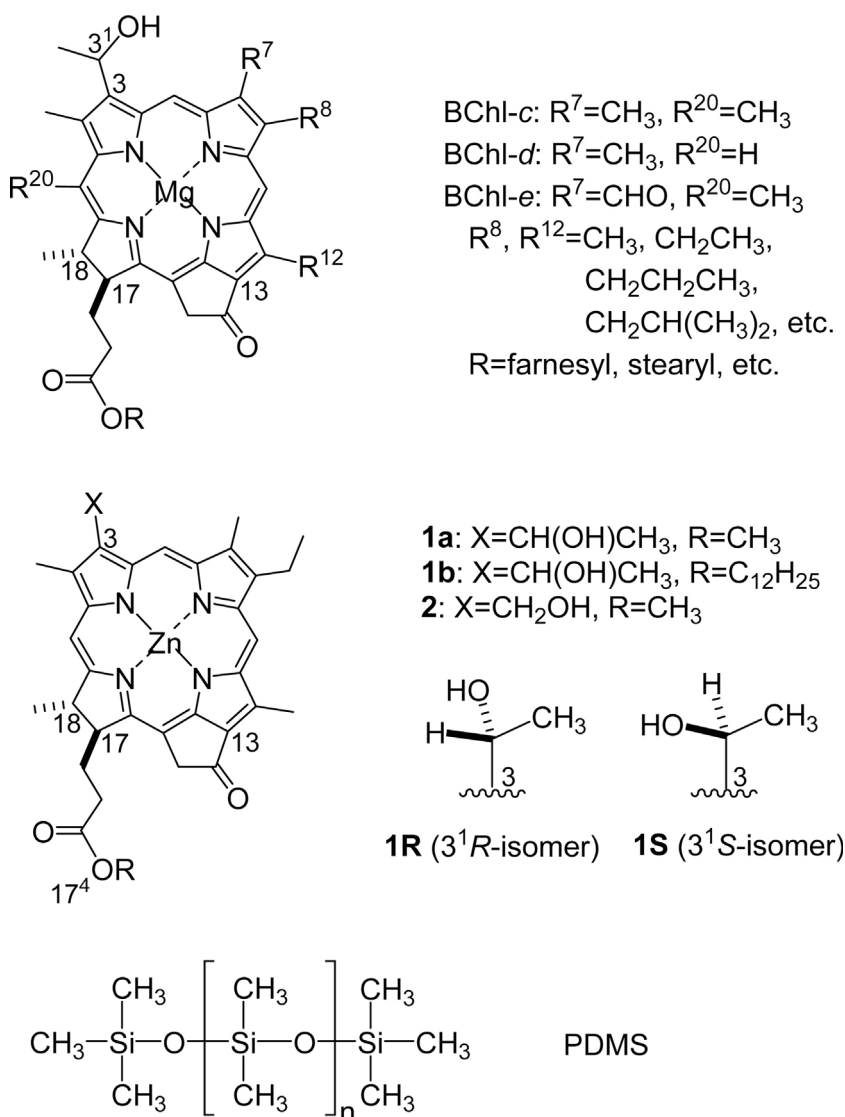


Fig. 1. Structures of chlorosomal Chls (top), zinc 3<sup>1</sup>-hydroxy-chlorins 1–2 (middle), and polydimethylsiloxane (bottom).

pigments for fabricating effective artificial light-harvesting antennas.

Here we prepared self-aggregates of zinc 3<sup>1</sup>-hydroxy-chlorins in a polysiloxane oil. Polysiloxanes are organosilicon compounds and commonly referred to as “silicone” which are chemically stable heat-resistant materials. One of the common forms of polysiloxanes is a silicone oil which is used as lubricants, electrical insulators, etc. Especially, polydimethylsiloxane (PDMS, Fig. 1) is the most widely used silicone. PDMS is generally non-flammable viscous liquid and its viscosity is depended on the number of dimethylsiloxane (—O—Si(CH<sub>3</sub>)<sub>2</sub>—) units in a macromolecule. PDMS shows relatively a low dielectric constant (2.3–2.8), and therefore the silicone oil would be a potential non-polar medium for self-aggregation of chlorosomal Chls and their analogues. Self-aggregates of zinc 3<sup>1</sup>-hydroxy-chlorins were successfully prepared by diluting a small volume of the DCM or THF solution of the chlorophyllous pigments with a large volume of a PDMS oil, and optical properties and temperature effects of the artificial aggregates were examined.

The chlorosomal Chls have a chiral 1-hydroxyethyl group at the 3-position, and interestingly, natural chlorosome consists of both 3<sup>1</sup>R- and 3<sup>1</sup>S-stereoisomers. These stereoisomers are diastereomers because the chlorin macrocycle in the natural Chls

has additional chiral centers at the 17- and 18-positions with the S-configurations. The supramolecular structure of the naturally occurring mixed aggregates of the epimers is of great interest, and artificial self-aggregates have been prepared with epimerically pure or mixed synthetic zinc 3-(1-hydroxyethyl)-chlorins [9]. The previous studies indicated that the absolute configuration at the 3<sup>1</sup>-position of the chlorin influences the molecular arrangement of the chlorophyllous aggregates. The stabilities of the aggregated zinc 3-(1-hydroxyethyl)-chlorins have been examined by using some additives to disaggregate the oligomers; for example, self-aggregates of Chls prepared in hexane gradually changed to their monomers by sequential titration of a polar organic solvent. In this paper, disaggregation of the self-aggregated zinc chlorins were achieved by applying high temperature, and the stabilities of zinc chlorins possessing a chiral 1-hydroxyethyl group were examined.

## 2. Experimental

Visible absorption and CD spectra were recorded by using a Shimadzu UV-2700 spectrometer and a Jasco J-820 spectropolarimeter, respectively. High-performance liquid chromatography (HPLC) was performed on a packed

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