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Aqueous self-aggregates of amphiphilic zinc 3^1-hydroxy- and 3^1-methoxy-chlorins for supramolecular light-harvesting systems

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Abstract—Aqueous aggregates of zinc 3^1-hydroxy- and 3^1-methoxy-13^1-oxo-chlorins possessing a hydrophilic tetraoxyethylene chain were prepared. Zinc 3^1-methoxy-chlorin formed a well-ordered aggregate without intermolecular hydrogen bonding which has been widely accepted in most structural models for BChl-*c*, *d*, *e* aggregates in a major light-harvesting antenna of green photosynthetic bacteria, chlorosome.

Generally, a photosynthetic light-harvesting (LH) antenna consists of pigment—protein complexes in which many chlorophyll molecules are adequately organized for efficient intermolecular energy transfer.[1] In contrast, in the main LH (chlorosome) of green photosynthetic bacteria, a large number of bacteriochlorophyll(BChl)-*c*, *d*, and *e* molecules (Fig. 1) self-organized to form supramolecular LH antenna systems without any assistance of protein.[2] Although many in vivo and in vitro studies of chlorosomal aggregates have been carried out, the precise supramolecular structure of the natural aggregates has not been clarified yet, and some structural models have been proposed.[3,4] Spectroscopic measurements as well as molecular modeling studies suggest that the specific interactions among BChl molecules afford a chlorosomal aggregate.[2,5] Most structural models are based on the 3^1-hydroxy group of a BChl molecule making both a hydrogen bonding with the 13^1-oxo group of the second molecule and an axial coordination bonding with central Mg of the third molecule.[2,3] Additionally, π–π interactions among chlorin macrocycles assist the self-aggregation. The esterified chain at the 17-position of BChls would surround the stacked metallochlorin core to stabilize the antenna.[6]

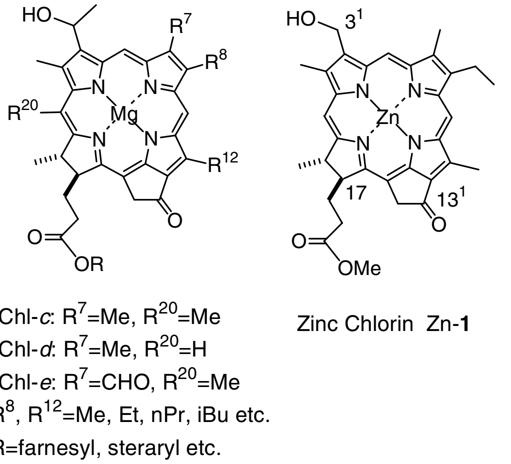

Figure 1. Structures of BChls-*c*, *d*, *e* in chlorosome and semi-synthetic zinc chlorin Zn-**1**.

In order to make a structural model for the natural supramolecular LH system, zinc analogues of BChls-*c*, *d*, and *e* were prepared by a semi-synthetic process.[7] Zinc chlorin possessing a 3^1-hydroxy group (Zn-**1** in Fig. 1) formed a self-aggregate in a nonpolar organic solvent in a similar manner as BChl-*c*, *d*, and *e* aggregates in a chlorosome. In addition, efficient energy transfer was observed when an energy acceptor molecule co-aggregated with the artificial aggregate.[8] Therefore,

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Keywords: Chlorophyll; Chlorosome; *J*-Aggregate; Photosynthetic antenna; Self-assembly.

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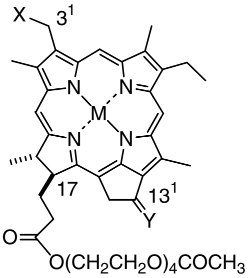
the zinc chlorin aggregate actually acts as an artificial LH antenna. In this Letter, we report novel artificial aggregates of zinc 3^1-hydroxy- and 3^1-methoxy-13^1-oxo-chlorins (Zn-**2** and Zn-**3**[9]) possessing a hydrophilic tetraoxyethylene chain (Table 1). The amphiphilic chlorophyll derivatives formed stable aqueous aggregates with a red-shifted Qy absorption band. The oligooxyethylene chain at the 17-position would be oriented toward the outside of the aqueous aggregate to stabilize the micelle-like assemblies.[10] Specifically, Zn-**3** afforded a highly ordered *J*-aggregate without intermolecular hydrogen bonding.

Amphiphilic zinc chlorins Zn-**2** and Zn-**3** were prepared from methyl pyropheophorbide-*d* (**7**), which is readily accessible from naturally occurring chlorophyll-*a* (Scheme 1).[7] The formyl group at the 3-position of **7** was reduced to the hydroxymethyl group followed by acid-catalyzed etherification with methanol to give 3-methoxymethyl-chlorin. The 17-propionic acid side chain of the resulting chlorin was esterified with tetraethylene glycol. Afterwards, the hydroxy group at the terminal position of the glycol chain was end-capped with acetyl group by treatment of acetic anhydride. Successive zinc metallation of **3** gave the corresponding zinc chlorin Zn-**3**. Other (zinc) chlorins were prepared similarly.

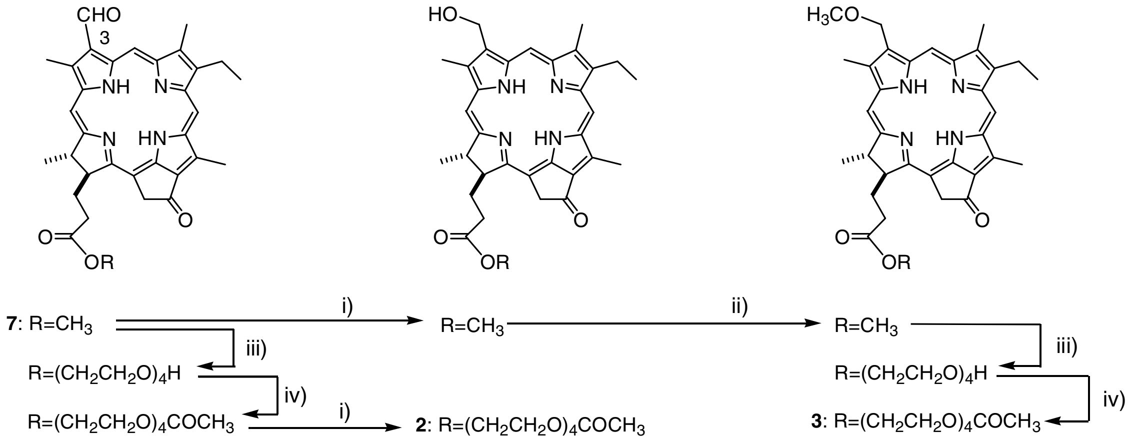
Table 1. Qy maxima of (zinc) chlorins (ca. 10^{-5} mol dm^{-3})



	M	X	Y	λ_{max} (nm)	
				MeOH	1% (v/v) MeOH–water
Zn-2	Zn	OH	O	652	729
Zn-3	Zn	OCH_3	O	652	729
Zn-4	Zn	OH	H_2	617	623
Zn-5	Zn	OCH_3	H_2	617	620
Zn-6	Zn	CH_3	O	652	660
2	H_2	OH	O	661	673
3	H_2	OCH_3	O	661	664

Aqueous aggregates of zinc chlorins were prepared by dilution of their methanol or THF solutions with a 99-fold volume of water. The aqueous methanolic solution of amphiphilic zinc 3^1-hydroxy-chlorin Zn-**2** was green-colored and showed a broad Qy absorption band at 729 nm, which was red-shifted from that of monomeric Zn-**2** in methanol, 652 nm (the dashed line in Fig. 2a and Table 1). This suggests that amphiphilic Zn-**2** gave micelle-like assemblies in the aqueous medium and the hydrophobic zinc chlorin moiety in Zn-**2** self-aggregated to give its chlorosome-type *J*-aggregate. A similar absorption spectrum was obtained in Zn-**2** aggregate prepared in 1% THF–water; therefore, a trace amount of organic solvent was not included in the aggregates of the amphiphilic zinc chlorin. Under the same conditions, zinc 3^1-methoxy-chlorin Zn-**3** gave aqueous aggregate with a red-shifted Qy band at 729 nm (the solid line in Fig. 2a) and a small amount of the monomeric species at 656 nm. Circular dichroism (CD) spectra of aqueous Zn-**2** and Zn-**3** aggregates showed inverse-S shaped signals at around the red-shifted Qy band region. Such an inverse-S shaped CD spectrum is often observed in natural chlorosomes.[11] Therefore, in the aqueous aggregates, both Zn-**2** and Zn-**3** molecules aligned along the *y*-axis of the chlorin macrocycle (N(21)–N(23) axis as in Fig. 1) as BChl-*c*, *d*, and *e* molecules do in their chlorosomal aggregates. However, spectral properties of Zn-**2** and Zn-**3** aggregates were obviously different. The full width at half maxima of the Qy absorption band of Zn-**3** aggregate (380 cm^{-1}) was smaller than that of Zn-**2** aggregate (1140 cm^{-1}), and the intensity of CD signals of Zn-**3** aggregate was about 6-times larger than that of Zn-**2** aggregate. These spectral results suggest that Zn-**3** molecules would be more highly aligned.

Other amphiphilic (zinc) chlorins lacking 3^1-oxygen atom (Zn-**6**), 13^1-oxo group (Zn-**4** and **-5**) or central zinc



Scheme 1. Synthesis of amphiphilic chlorins. Reagents and conditions: (i) $tBuNH_2{\cdot}BH_3$, CH_2Cl_2, rt, 2 h; (ii) H_2SO_4, MeOH, 50 °C, 2 d; (iii) concd HCl, rt, 2 h/tetraethylene glycol, EDC·HCl, DMAP, CH_2Cl_2, rt, 10 h; (iv) $(CH_3CO)_2O$, $(C_2H_5)_3N$, CH_2Cl_2, rt, 12 h.

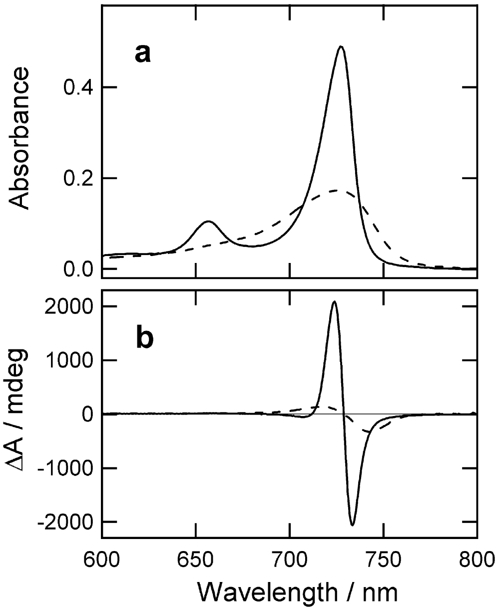


Figure 2. Visible absorption (a) and CD (b) spectra of aqueous aggregates of Zn-**2** (dashed lines) and Zn-**3** (solid lines) prepared in 1% MeOH–water. CD spectra are normalized to the Qy maximum, $\Delta A = (A_L - A_R)/A_{max}$.

(**2** and **3**) did not give red-shifted absorption bands at around 730 nm which are characteristic in the formation of *J*-aggregates (Table 1). Consequently, formation of a chlorosome-like aggregate requires all of the three components in a molecule, 3^1-oxygen atom, 13^1-oxo group and central zinc. In most cases structural models for chlorosomal aggregate employed the coordination bonding between the 3^1-oxygen atom and central metal, which might be one of the essential driving forces for self-aggregation of both Zn-**2** and Zn-**3** (Fig. 3). Investigation of functionalized chlorophyll derivatives showed that the axial coordination to the central zinc was assisted by the electron withdrawing 13^1-oxo group of a chlorin.[12] Therefore, the 13^1-oxo group might be required for the self-aggregation, and the zinc chlorins lacking 13^1-oxo group Zn-**4** and Zn-**5** were monomeric in 1% MeOH–water (Table 1).

The aggregate of zinc 3^1-methoxy-chlorin Zn-**3** must be formed without the intermolecular hydrogen bonding accepted in most structural models for natural chlorosome as shown in Figure 3b. The lack of the intermolecular hydrogen bonding in Zn-**3** aggregate may reduce its stability. First, the absorption spectrum of Zn-**3** in an aqueous medium showed a minor Qy band at 656 nm of the remaining monomeric species (the solid line in Fig. 2). Second, deaggregation of the aqueous aggregates of Zn-**2** and Zn-**3** by addition of Triton X-100, a nonionic surfactant, was monitored by their absorption spectra. The Qy band of Zn-**3** aggregate decreased more easily than that of Zn-**2**, concomitant with increase in a Qy band of the monomeric form. Therefore, zinc 3-methoxy-chlorin Zn-**3** molecules were more loosely packed in the aqueous aggregate. The moderate intermolecular association in Zn-**3** aggregate may provide the highly ordered aggregate, which is expected from its sharp Qy absorption band and intense CD signals (Fig. 2). In the growth process of the aggregate, a monomeric species would associate to a nucleus of aggregated species.[13] If a Zn-**3** molecule associated to the aggregate nucleus with a distorted arrangement, the misfitting molecule might easily reorder to make a favorable tidily ordered aggregate. In contrast, in Zn-**2** aggregation each molecule packed more tightly by using additional intermolecular hydrogen bonding (Fig. 3a),[14] and the misfitting molecule reordered very little and gave a relatively disordered aggregate.

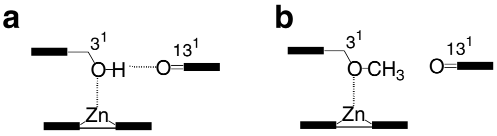


Figure 3. Schematic drawing of local structures of Zn-**2** (a) and Zn-**3** (b) aggregates.

The amphiphilic zinc chlorins provided stable aqueous aggregates, which mimic a supramolecular LH system in a chlorosome. Especially, zinc 3^1-methoxy-chlorin Zn-**3** gave its highly ordered *J*-aggregate with a sharp Qy absorption band and a large CD couplet. Thus, the 3^1-hydroxy group is not a requisite for the formation of the chlorosome-type *J*-aggregate, while Zn-**2** possessing the naturally occurring 3^1-hydroxy group gave its aqueous aggregate with a broad absorption band. The optical property would be advantageous for an antenna system to collect a wide wavelength range of sunlight.

Acknowledgments

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