

Design of the Artificial Antenna System in Photosynthesis

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Zinc chlorin **1** possessing *tertiary* 3¹-hydroxy and 13¹-oxo groups was synthesized as a model for the antenna chlorophylls of photosynthetic green bacteria. Self-aggregation of **1** in nonpolar organic solvents was examined and compared to **2** and **3** possessing a *secondary* and *primary* 3¹-hydroxy group, respectively. Zinc chlorin **1** self-aggregated in 1%(v/v) CH₂Cl₂–hexane to form oligomers and showed a red-shifted Qy maximum at 704 nm compared to the monomer (648 nm in CH₂Cl₂). This red-shift is larger than that of 3¹S-**2** (648 to 697 nm) and comparable to that of 3¹R-**2** (648 to 705 nm), but smaller than that of **1** (648 to 740 nm), indicating that while a single 3¹-methyl group (*primary* to *secondary* OH) suppressed tight and/or extended aggregation, the additional 3¹-methyl group (*secondary* to *tertiary* OH) did not further suppress aggregation. The relative stability of the aggregates was in the order **3** > 3¹R-**2** ~ **1** > 3¹S-**2** as determined by visible spectral analyses. Molecular modeling calculations on oligomers of zinc chlorins **1**, 3¹R-**2** and **3** gave similar well-ordered energy-minimized structures, while **3** stacked more tightly than 3¹R-**2** and **1**. In contrast, 3¹S-**2** gave a relatively disordered (twisted) structure. The calculated oligomeric structures could explain the visible spectral data of **1**–**3** in nonpolar organic solvents. Moreover, self-aggregation of synthetic zinc 13¹-oxo-chlorins **4**–**6** possessing a 2-hydroxyethyl, 3-hydroxypropyl and 3-hydroxy-1-propenyl group at the 3-position in nonpolar organic solvents was discussed.

Key words: chlorosome, light-harvesting antenna, molecular modeling calculation, self-aggregation, supramolecular structure, visible spectra, zinc chlorophyll

INTRODUCTION

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Special chlorophyllous molecules as in bacteriochlorophyll-*d* (BChl-*d*, Fig. 1) are found in the extramembranous light-harvesting antenna systems (chlorosomes) of photosynthetic green bacteria [1–3]. The molecular structures are

characterized with possession of 1-hydroxyethyl group at the 3-position and lack of methoxycarbonyl group at the 13²-position, while usual (bacterio)chlorophylls possess a less polar 3-vinyl/acetyl group and 13²-COOMe. In organic solvents such as acetone, BChl-*d* gives sharp visible absorption bands at around 426 and 650 nm, compared to the broad and red-shifted bands at around 450 and 730 nm in intact chlorosomes [1]. The former sharp bands are ascribable to monomeric BChl-*d*, and the latter broad ones to self-aggregated oligomers of BChl-*d*, despite the lack of any supporting proteins. The red-shift is a good indicator for the self-aggregation. Here we report on self-aggregation of synthetic zinc chlorins 1–6 (Fig. 1) possessing a hydroxy group on the substituent at the 3-position in nonpolar organic solvents.

MATERIALS AND METHODS

Synthesis of all zinc chlorins has been reported [4,5]. Visible spectra were measured in air-saturated solvents at room temperature on Hitachi U-3500 spectrophotometer. Molecular modeling calculations were performed using

PM3 and MM+ in the HYPERCHEM version 5.1 (HYPERCUBE Co.) software package [4].

RESULTS AND DISCUSSION

Visible spectra of zinc 3¹-hydroxy-13¹-oxo-chlorins

The absorption spectrum of tertiary alcoholic zinc chlorin 1 in CH₂Cl₂ (ca. 6 mM) gave that the Soret and Qy absorption maxima were 423 and 648 nm, respectively, characteristic of the monomeric spectrum. These values are almost identical with those of the monomeric secondary alcoholic 2 and primary alcoholic 3. When a concentrated CH₂Cl₂ solution of 1 was diluted with hexane, the Soret and Qy bands due to the monomer decreased and new bands appeared at 445 and 704 nm. In 1%(v/v) CH₂Cl₂-hexane, the new Soret and Qy bands were red-shifted by 1170 cm⁻¹ and 1230 cm⁻¹, respectively, from those of monomer. These visible spectral changes are typical of the oligomerization of metallochlorins, and are remarkably similar to those of 2 and 3, indicating 1 oligomerized in the nonpolar organic solvents.

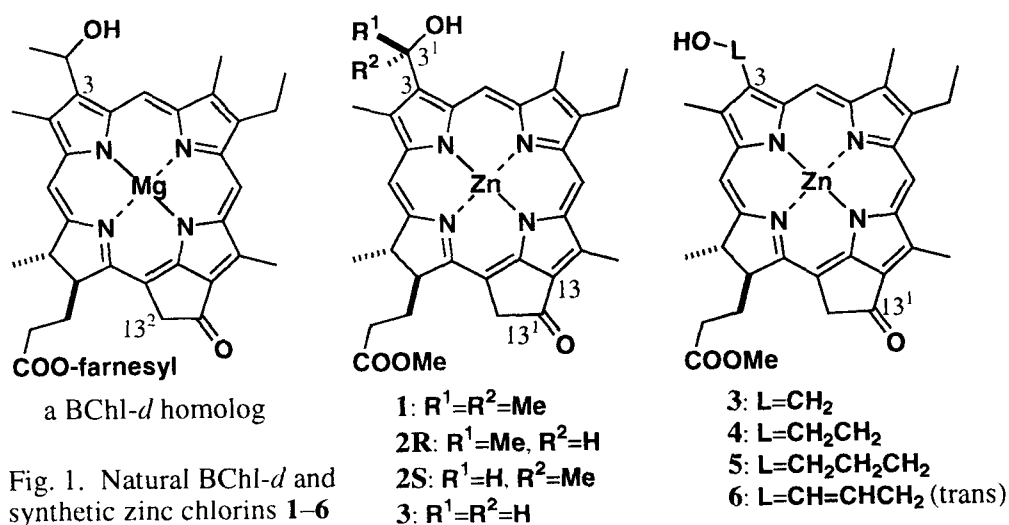


Fig. 1. Natural BChl-*d* and synthetic zinc chlorins 1–6

The large red-shift of Qy band is due to the strong interaction of the Qy transition moments of the compositional chromophores in the highly-ordered aggregate. Such supramolecules could be obtained by *J*-aggregation of the chlorins along the Qy molecular axis. Tertiary alcoholic **1** gave a red-shifted Qy band (1230 cm^{-1}) comparable to that of 3^1R -epimerically secondary alcoholic **2R** (1250 cm^{-1}). These values are smaller than that of primary alcoholic **3** (1940 cm^{-1}), indicating substitution of methyl group(s) at the 3^1 -position of **3** (*pri*-OH \rightarrow *sec*-OH and *tert*-OH) suppressed oligomerization markedly. On the other hand, **1** showed a more red-shifted Qy maxima than 3^1S -epimerically secondary alcoholic **2S** (1085 cm^{-1}), which indicates a closer interaction and/or higher aggregation for **1** than **2S**.

The residual monomeric peak intensity in nonpolar organic solvents and the deaggregation behavior by addition of pyridine to oligomeric species indicate that the stability of aggregates is in the following order: **3** > **2R** \sim **1** > **2S**.

Molecular modeling study of zinc chlorin aggregation

The visible spectroscopic observations showed that substitution of a methyl group at the 3^1 -position in **3** suppressed closer and/or higher oligomerization and decreased the stability of the aggregates (**3** \rightarrow **2R** and **2S**) as expected from steric effect around the interactive 3^1 -hydroxy group.

However, a second additional methyl group not only failed to further disrupt aggregation (**2R** \rightarrow **1**) but in the case of **2S**, actually increased the stability of the aggregates and induced tighter and/or more homogeneous oligomerization (**2S** \rightarrow **1**). To explain these results, we performed a molecular modeling study of small aggregates of the zinc chlorins by MM+ and PM3 calculations.

Three step-type tetramers of **1**–**3** prepared by coordination of 3^1 -O with Zn were docked parallel to each other by hydrogen bond of 3^1 -OH with 13^1 -O on the basis of the aggregate model shown in Fig. 2 [3,6], and energy-minimized by MM+. As each chromophore of dodecameric **1**, **2R** and **3** similarly overlaps its neighbor in the adjacent stack to the same degree along the Qy direction, the shorter Zn-to-Zn distance of **3** (7.5 Å) in comparison with those of **2R** (8.2 Å) and **1** (8.3 Å) is caused entirely by the closer stack-to-stack (π - π plane) distance of dodecameric **3** (*ca.* 3.5 Å), compared to those of **2R** (*ca.* 4.1 Å) and **1** (*ca.* 4.2 Å). Thus, self-aggregated molecules of zinc chlorin **3** exhibit tighter π - π stacking of the chromophores, both stabilizing the aggregates and causing a stronger exciton interaction which induces a more drastic red-shift of the absorption wavelength (\rightarrow 740 nm) than with **2R** (\rightarrow 705 nm) and **1** (\rightarrow 704 nm). The similar Zn-to-Zn and stack-to-stack distances in the dodecamers of **2R** and **1** are reflected

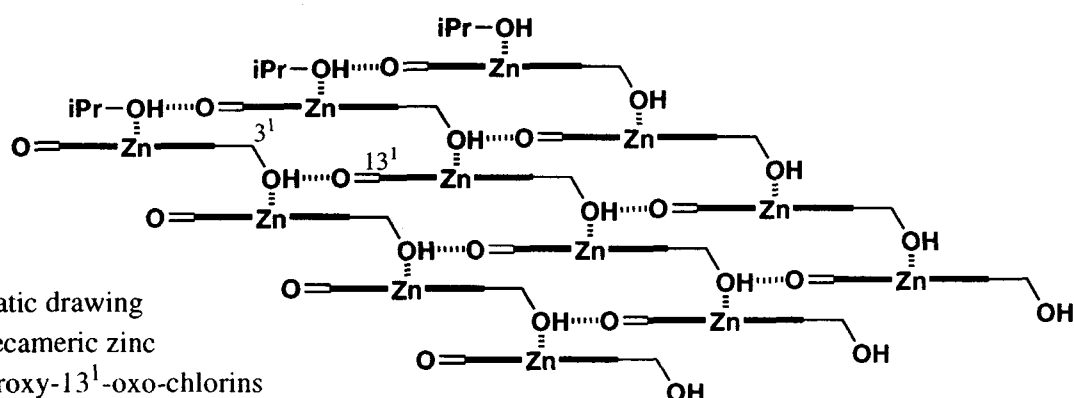


Fig. 2.
Schematic drawing
of dodecameric zinc
 3^1 -hydroxy- 13^1 -oxo-chlorins

in their similar observed stabilities and visible spectrum absorption wavelengths. In contrast, dodecameric **2S** exhibited a twisted structure in which the direction of the Qy transition moments of each chlorin diverged. This is in agreement with the less red-shifted value of **2S** aggregate (\rightarrow 697 nm) in nonpolar organic solvents compared with those of **1**, **2R** and **3**.

Self-aggregation of zinc 3- ω -hydroxyalkyl-13¹-oxo-chlorins

Self-aggregation of synthetic zinc 13¹-oxo-chlorins **4**, **5** and **6** possessing 2-hydroxyethyl, 3-hydroxypropyl and 3-hydroxy-1-propenyl groups, respectively, at the 3-position in nonpolar organic solvents was compared with that of **3** possessing 3-hydroxymethyl group to determine the effect of the distance between the hydroxy group and the chlorin moiety on the self-aggregation. The visible spectral analyses in hexane containing a small amount (0.1–1% (v/v)) of THF revealed that the aggregation abilities decreased in the order of **3** \rightarrow **4** \rightarrow **5**, with an increase of conformational flexibility of the ω -hydroxyalkyl group in a molecule. Aggregated **4** and **5** gave absorption maxima at 701 and 702 nm, respectively, red-shifted from the corresponding monomeric absorption (644 nm). These red-shifts 1260 and 1280 cm⁻¹ are smaller than that of **3** (647 \rightarrow 740 nm; 1940 cm⁻¹), which is attributable to the expanded chlorin π - π plane distance in the self-aggregates of **4** and **5**. Aggregated **6** showed a relatively small red-shift of absorption from monomer to aggregates (654 \rightarrow 680 nm; 580 cm⁻¹) due to the decreased overlap between the chlorin π -planes in the aggregated state.

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