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## Visible and near-infrared spectra of chlorosomal zinc chlorin self-aggregates dependent on their peripheral substituents at the 8-position

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## ABSTRACT

Zinc complexes of 3-hydroxymethyl-13<sup>1</sup>-oxo-chlorins possessing various  $\pi$ -conjugatable substituents at the 8-position were prepared by chemical modification of naturally occurring chlorophyll-*a*. The synthetic zinc chlorophyll-*a* derivatives self-aggregated in an aqueous Triton X-100 solution to give red-shifted and broadened electronic absorption bands compared with their monomeric species in tetrahydrofuran. Their self-assemblies in an aqueous micelle showed similar electronic absorption spectra to those of the main light-harvesting antennas in green photosynthetic bacteria. The self-aggregated species afforded largely bathochromically shifted Qy maxima to absorb near-infrared light.

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## 1. Introduction

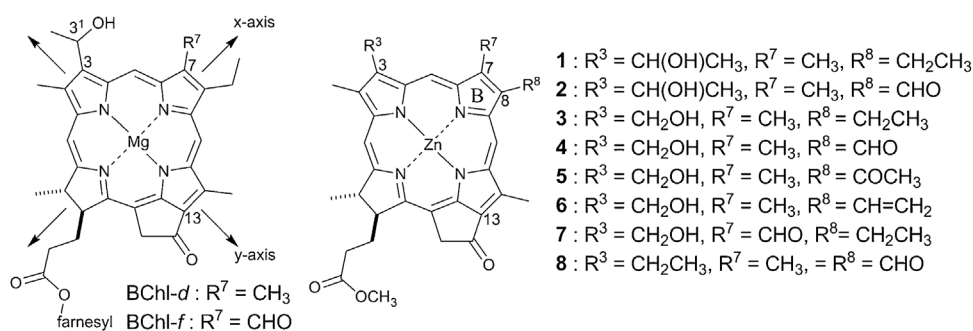
Many chlorophyll molecules are found in nature, which are distinguished by their different peripheral substituents [1–6]. Natural chlorophylls control their electronic absorption properties by modifying their peripheral functional groups [7]. Electron-withdrawing and donating groups directly attached to the main chlorin  $\pi$ -system move their absorption bands to longer and/or shorter wavelengths. Despite being the same carbonyl group, this situation leads to a different outcome [8–12]. A formyl group at the 3-position caused red-shifts in both the Qy (longer wavelength) and Soret (shorter wavelength) absorption bands, while the 7-formyl group made red- and blue-shifts in the Soret and Qy bands, respectively [3,4,11,12]. The substitution effect is controlled by the fact that the 3-position is on the molecular y-axis and the 7-position is on the x-axis (see the left drawing of Fig. 1).

Some chlorophyllous molecules have a hydroxy group at the 3<sup>1</sup>-position, which are only found in the light-harvesting antenna system of green photosynthetic bacteria (chlorosome) [13–16]. Bacteriochlorophyll(BChl)s-*c*, *d*, *e*, and *f* are known as such 3<sup>1</sup>-hydroxy-chlorins (the left drawing of Fig. 1). The chlorosomal chlorophylls use the 3<sup>1</sup>-hydroxy group to construct well-ordered J-aggregates. The driving forces for the molecular assembly are

intermolecular coordination (Mg  $\cdot$  OH) and hydrogen bondings (13-C=O  $\cdot$  H—O) as well as strong  $\pi$ - $\pi$  stackings [13,17]. As models of these BChls, we have reported zinc chlorins possessing a C=O group at the 7- or 8-position (see 2 and 7 in the right drawing of Fig. 1) [18–20], which had potential to be an intermolecular interaction site as did the 13-C=O. However, it has been demonstrated that the additional C=O group on the B-ring in synthetic zinc chlorins as well as the 7-C=O group in natural BChls-*ef* was not involved in the intermolecular interactions producing the self-aggregates [18,21,22]. The specific bondings in the supramolecule were exclusively dependent on the 3<sup>1</sup>-OH, central metal (Mg or Zn) and 13-C=O situated along the y-axis. Earlier we reported self-aggregation of zinc 3-(1-hydroxyethyl)-8-formyl-chlorins (3<sup>1</sup>R)-2 and (3<sup>1</sup>S)-2, and the latter S-isomer showed a large red-shift value ( $\Delta$ ) of 1940 cm<sup>-1</sup> in the Qy band by self-aggregation in an aqueous tetrahydrofuran (THF) solution [20]. The  $\Delta$ -value of (3<sup>1</sup>S)-2 self-aggregates was larger than those of the R-isomer (1140 cm<sup>-1</sup>) as well as (3<sup>1</sup>R)-1 and (3<sup>1</sup>S)-1 possessing the 8-ethyl group instead of the 8-CHO (1200 cm<sup>-1</sup>). The larger value was comparable to that of self-aggregated 3 (1940 cm<sup>-1</sup>) bearing a less sterically hindered 3-hydroxymethyl group as the 3<sup>1</sup>-demethylated analog of 1 in non-polar organic solvents [23]. The additionally introduced 8-CHO group thus affected chlorosomal self-aggregation, where the 3<sup>1</sup>-diastereomeric control was operative. To investigate such a relatively large shift in self-aggregation of the 8-formyl-chlorin, here we synthesized zinc 3-hydroxymethyl-chlorins 4–6 possessing the 8-formyl, acetyl, and vinyl

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**Fig. 1.** Molecular structures of natural chlorosomal chlorophylls (left) and their synthetic models (right).

groups and their analogs **3/7/8** and examined their self-aggregation in an aqueous micellar solution. The present models having no 3<sup>1</sup>-epimers would be suitable for elucidation of the effect of the 8-substituents.

## 2. Experimental

### 2.1. General

Electronic absorption and circular dichroism (CD) spectra in a solution were measured by a Hitachi U3500 spectrophotometer and a Jasco J-720W spectropolarimeter, respectively, with a 10-mm quartz cell. FT-IR spectra were recorded on a Shimadzu IRAffinity-1 spectrophotometer; a 0.1-mm KBr cell was used for measurement of a THF solution sample (transmission mode) and a Shimadzu AIM-8000R microscope was used for measurements of solid films on an aluminum coated glass (reflection mode). <sup>1</sup>H NMR spectra in chloroform-*d* were recorded by a JEOL ECA-600 (600 MHz); tetramethylsilane ( $\delta = 0.00$  ppm) was used as an internal standard. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer: atmospheric pressure chemical ionization (APCI) and positive mode in an acetonitrile solution.

Preparation of zinc chlorins **3–8** was described in Supplementary data, where <sup>1</sup>H NMR spectra of new compounds **4–6** and **8** are also obtained. Before optical measurements, chlorophyll pigments were purified by reverse phase (RP) HPLC: a Shimadzu LC-10ADVP pump, SPD-M10AVP diode-array detector, SCL-10AVP system controller, and a packed ODS column (Cosmosil 5C18AR-II, 10  $\phi$  x 250 mm) with an aqueous methanol eluent.

### 2.2. Spectral data of zinc chlorins

#### 2.2.1. Zinc methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (**3**, zinc methyl 3<sup>1</sup>-demethyl-bacteriopheophorbide-d)

VIS (THF)  $\lambda_{\text{max}} = 647$  (relative intensity, 0.73), 602 (0.11), 566 (0.06), 518 (0.06), 425 (1.00), 405 nm (0.57); see its spectral data in ref. 23.

#### 2.2.2. Zinc methyl 8-deethyl-3-devinyl-8-formyl-3-hydroxymethyl-pyropheophorbide-a (**4**)

VIS (THF)  $\lambda_{\text{max}} = 650$  (relative intensity, 0.32), 600 (0.05), 536 (0.03), 447 (1.00), 421 nm (0.29); <sup>1</sup>H NMR (3% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>)  $\delta = 11.22$  (1H, s, 8-CHO), 10.35 (1H, s, 10-H), 9.48 (1H, s, 5-H), 8.35 (1H, s, 20-H), 5.84 (2H, s, 3-CH<sub>2</sub>), 5.13, 5.01 (each 1H, d,  $J = 19$  Hz, 13-CH<sub>2</sub>), 4.87 (1H, br-s, 3<sup>1</sup>-OH), 4.40 (1H, dq,  $J = 2, 8$  Hz, 18-H), 4.18 (1H, m, 17-H), 3.66 (3H, s, 12-CH<sub>3</sub>), 3.59 (3H, s, 7-CH<sub>3</sub>), 3.55 (3H, s, 17<sup>2</sup>-CO<sub>2</sub>CH<sub>3</sub>), 3.30 (3H, s, 2-CH<sub>3</sub>), 2.58, 2.43, 2.24, 2.04 (each 1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.74 (3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub>); HRMS (APCI) found:  $m/z$  615.1579. Calcd. for C<sub>32</sub>H<sub>31</sub>N<sub>4</sub>O<sub>5</sub>Zn: MH<sup>+</sup>, 615.1580.

#### 2.2.3. Zinc methyl 3-devinyl-3-hydroxymethyl-81-oxo-pyropheophorbide-a (**5**)

VIS (THF)  $\lambda_{\text{max}} = 646$  (relative intensity, 0.42), 598 (0.06), 531 (0.03), 442 (1.00), 419 nm (0.33); <sup>1</sup>H NMR (3% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>)  $\delta = 10.35$  (1H, s, 10-H), 9.51 (1H, s, 5-H), 8.35 (1H, s, 20-H), 5.85 (2H, s, 3-CH<sub>2</sub>), 5.14, 5.02 (each 1H, d,  $J = 19$  Hz, 13-CH<sub>2</sub>), 4.39 (1H, dq,  $J = 2, 8$  Hz, 18-H), 4.19 (1H, m, 17-H), 4.11 (1H, br-s, 3<sup>1</sup>-OH), 3.68 (3H, s, 12-CH<sub>3</sub>), 3.58 (3H, s, 17<sup>2</sup>-CO<sub>2</sub>CH<sub>3</sub>), 3.56 (3H, s, 7-CH<sub>3</sub>), 3.31 (3H, s, 2-CH<sub>3</sub>), 3.16 (3H, s, 81-CH<sub>3</sub>), 2.58, 2.41, 2.25, 2.00 (each 1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.73 (3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub>); HRMS (APCI) found:  $m/z$  629.1736. Calcd. for C<sub>33</sub>H<sub>33</sub>N<sub>4</sub>O<sub>5</sub>Zn: MH<sup>+</sup>, 629.1737.

#### 2.2.4. Zinc methyl 8<sup>1</sup>,8<sup>2</sup>-didehydro-3-devinyl-3-hydroxymethyl-pyropheophorbide-a (**6**)

VIS (THF)  $\lambda_{\text{max}} = 647$  (relative intensity, 0.71), 604 (0.10), 571 (0.04), 526 (0.05), 432 (1.00), 411 nm (sh, 0.54); <sup>1</sup>H NMR (3% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>)  $\delta = 9.71$  (1H, s, 10-H), 9.39 (1H, s, 5-H), 8.32 (1H, s, 20-H), 8.02 (1H, dd,  $J = 12, 18$  Hz, 8-CH), 6.17 (1H, dd,  $J = 1, 18$  Hz, 8<sup>1</sup>-CH *trans* to C8<sup>1</sup>-H), 5.95 (1H, dd,  $J = 1, 12$  Hz, 8<sup>1</sup>-CH *cis* to C8<sup>1</sup>-H), 5.83 (2H, s, 3-CH<sub>2</sub>), 5.15, 5.03 (each 1H, d,  $J = 19$  Hz, 13-CH<sub>2</sub>), 4.38 (1H, dq,  $J = 2, 8$  Hz, 18-H), 4.17 (1H, m, 17-H), 3.86 (1H, br-s, 3<sup>1</sup>-OH), 3.65 (3H, s, 12-CH<sub>3</sub>), 3.55 (3H, s, 17<sup>2</sup>-CO<sub>2</sub>CH<sub>3</sub>), 3.33 (3H, s, 7-CH<sub>3</sub>), 3.30 (3H, s, 2-CH<sub>3</sub>), 2.54, 2.37, 2.24, 1.96 (each 1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.70 (3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub>); HRMS (APCI) found:  $m/z$  613.1786. Calcd. for C<sub>33</sub>H<sub>33</sub>N<sub>4</sub>O<sub>4</sub>Zn: MH<sup>+</sup>, 613.1788.

#### 2.2.5. Zinc methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-b (**7**, zinc methyl 3<sup>1</sup>-demethyl-bacteriopheophorbide-f)

VIS (THF)  $\lambda_{\text{max}} = 629$  (relative intensity, 0.33), 582 (0.08), 555 (0.05), 534 (0.05), 449 (1.00), 426 nm (0.33); see its spectral data in ref. 18.

#### 2.2.6. Zinc methyl 8-deethyl-8-formyl-mesopyropheophorbide-a (**8**)

VIS (THF)  $\lambda_{\text{max}} = 649$  (relative intensity, 0.32), 600 (0.05), 534 (0.03), 445 (1.00), 420 nm (0.30); <sup>1</sup>H NMR (3% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>)  $\delta = 11.28$  (1H, s, 8-CHO), 10.36 (1H, s, 10-H), 9.22 (1H, s, 5-H), 8.29 (1H, s, 20-H), 5.12, 5.00 (each 1H, d,  $J = 19$  Hz, 13-CH<sub>2</sub>), 4.37 (1H, dq,  $J = 2, 8$  Hz, 18-H), 4.16 (1H, m, 17-H), 3.76, 3.72 (each 1H, dq,  $J = 13, 8$  Hz, 3-CH<sub>2</sub>), 3.68 (3H, s, 12-CH<sub>3</sub>), 3.65 (3H, s, 7-CH<sub>3</sub>), 3.58 (3H, s, 17<sup>2</sup>-CO<sub>2</sub>CH<sub>3</sub>), 3.20 (3H, s, 2-CH<sub>3</sub>), 2.56, 2.40, 2.24, 1.98 (each 1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.72 (3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub>), 1.70 (3H, t,  $J = 8$  Hz, 3<sup>1</sup>-CH<sub>3</sub>); HRMS (APCI) found:  $m/z$  613.1788. Calcd. for C<sub>33</sub>H<sub>33</sub>N<sub>4</sub>O<sub>4</sub>Zn: MH<sup>+</sup>, 613.1788.

### 2.3. Preparation of zinc chlorin self-aggregates in an aqueous micellar solution

The synthetic zinc chlorin and Triton X-100 (TX-100) were dissolved in distilled THF, then the mixture was dispersed in warm distilled water (ca. 50 °C) and incubated at 50 °C for 30 min. Final concentrations of THF and TX-100 were 1.0% (v/v) and 0.025% (wt/

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