



Self-aggregation of a synthetic zinc chlorophyll derivative possessing a 13¹-dicyanomethylene group as a light-harvesting antenna model



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ARTICLE INFO

Article history:

Received 14 February 2014

Revised 13 March 2014

Accepted 17 March 2014

Available online 21 March 2014

Keywords:

Bacteriochlorophyll

Chlorosome

J-aggregate

Photosynthesis

ABSTRACT

Zinc methyl 3-hydroxymethyl-13¹-dicyanomethylene-pyropheophorbide-*a*, one of the bacteriochlorophyll-*d* analogs, was prepared by modifying chlorophyll-*a*. The semi-synthetic compound self-aggregated in an aqueous Triton X-100 solution to give large oligomers with red-shifted and broadened electronic absorption bands. The J-aggregates were similar to self-aggregates of bacteriochlorophyll-*d* molecules in natural light-harvesting antennas of green photosynthetic bacteria. The strongly electron-withdrawing dicyanomethylene group was an alternative functional moiety of the hydrogen-bond accepting 13¹-oxo group which had been necessary for such self-aggregation.

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Light-harvesting antenna systems are essential for natural photosynthesis.¹ Most of the systems are constructed by specific interaction of pigments with peptides and some models using chlorophyll pigments and helical peptides have been already reported.² In contrast, self-aggregates of chlorophylls are available in the main antenna complexes of green photosynthetic bacteria, called chlorosomes.³ Self-assemblies of chlorosomal chlorophylls and their model compounds have been reported and are promising for artificial antenna systems.⁴ Bacteriochlorophyll(BChl)-*d* is one of the naturally occurring chlorosomal chlorophylls (see the left drawing of Fig. 1)⁵ and zinc chlorophyll derivatives **4a/4a'** (right drawing of Fig. 1) were effective for their synthetic models.^{6,7} Almost all the self-aggregative models reported to date are coordinatable metal complexes of cyclic tetrapyrroles bearing 3¹-hydroxy and 13¹-oxo groups and the three linearly situated moieties were specifically interacted to form chlorosomal J-aggregates: M...O—H...O=C. Zinc 3¹-hydroxy-chlorins **4a/4a'** possessing the 13¹-oxo moiety aggregated in a non-polar organic solvent, an aqueous micelle solution, and the solid thin film to form large oligomers with red-shifted and broadened electronic absorption bands, but the analog **5a/5a'** lacking the 13¹-oxo moiety could not self-aggregate under the same conditions.^{6,8} In the supramolecular structures of chlorosomal self-aggregates, the 13¹-oxo group of a molecule was hydrogen-bonded with the 3¹-hydroxy group of another molecule (vide supra). The 13¹-hydroxylated analogs including **6a** have been reported to be partially effective

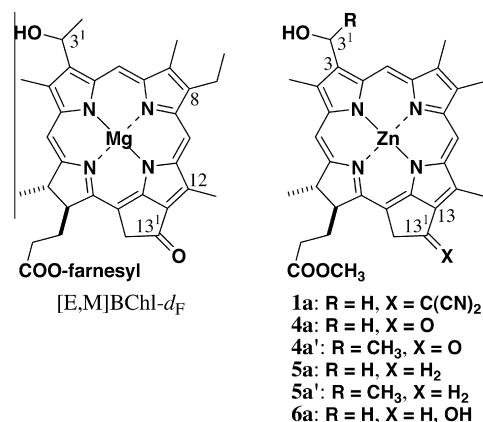


Figure 1. Molecular structures of one of the chlorosomal chlorophyll homologs, farnesylated 8-ethyl-12-methyl-bacteriochlorophyll-*d* (left), and its synthetic analogs, zinc methyl 3¹-hydroxy-pyropheophorbide-*a* derivatives (right).

for the alternative models of chlorosomal chlorophylls due to the hydrogen-bond accepting ability of the 13¹-O moiety.⁹

The central metal of porphyrinoids was coordinated with the oxygen atom of the 3¹-hydroxy group to form the chlorosomal self-aggregates mentioned above. The electron-withdrawing carbonyl group at the 13-position enhanced the coordinated ability of the metals including zinc.¹⁰ Therefore, the 13-C=O provides dual functions for chlorosomal self-aggregation. Here, a dicyanomethylene group was introduced at the 13¹-position of **4a** to give **1a** and

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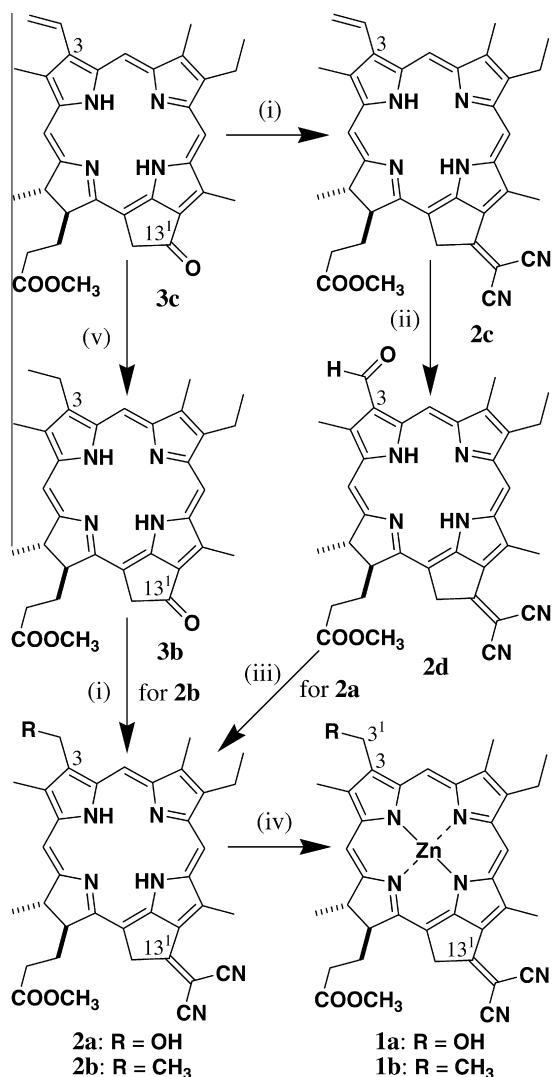
its self-aggregation was examined in an aqueous micelle solution and the solid film by visible, near infrared, and infrared absorption as well as circular dichroism (CD) spectroscopies. The dicyanomethylene moiety is a strongly electron-withdrawing functional group but has less ability as a hydrogen-bonding acceptor. It is discussed whether the dicyanomethylene could be an alternative functional group of the 13¹-oxo moiety in chlorosomal chlorophylls.

According to reported procedures,¹¹ the 13¹-oxo group of methyl pyropheophorbide-*a* (**3c**) prepared by modifying chlorophyll-*a* was transformed into a dicyanomethylene group as in **2c** by Knoevenagel reaction with malononitrile and the 3-vinyl group of **2c** was converted to a formyl group as in **2d** by Lemieux–Johnson oxidation [see steps (i) and (ii) in Scheme 1]. The 3-formyl group of **2d** was selectively reduced by *tert*-butylamine borane complex⁶ to give 3-hydroxymethyl-13¹-dicyanomethylene-chlorin **2a** in an excellent yield [93%, step (iii)].¹² The resulting free base **2a** was treated with zinc acetate to afford the corresponding zinc complex **1a** in an excellent yield [92%, step (iv)].¹² The 3-ethyl analog of **1a** as in **1b** was produced by the following sequential steps:¹² hydrogenation of 3-vinyl to ethyl group [**3c** → **3b**, step

(v)], Knoevenagel reaction of 13¹-oxo to dicyanomethylene group [**3b** → **2b**, step (i)], and zinc-metallation of **2b** to **1b** [step (iv)].

When zinc 3¹-hydroxy-13¹-dicyanomethylene-chlorin **1a** was dissolved in THF, a bright-green colored solution was obtained. The diluted THF solution (10 μM) gave an intense absorption band at 696 nm and four peaks at 455, 436, 386, and 348 nm (see the blue broken line of Fig. 2A): the former and latter are called Qy and Soret bands, respectively. The solution showed small CD bands (see the blue broken line of Fig. 2B), and especially a weak negative peak was observed at the Qy position. Compared to reported data of the related compounds,^{6,11} **1a** was axially coordinated to a THF molecule to be a monomeric species in the solution. A THF solution of **1a** containing Triton X-100 was diluted with 99-fold water at room temperature to give a pale-green colored solution: the final concentrations of **1a**, THF, and Triton X-100 were 10 μM, 1% (v/v), and 0.025% (wt/v), respectively. The aqueous solution showed red-shifted and broadened bands compared with the monomeric THF solution (Fig. 2A). The Qy band was shifted from 696 to 804 nm and the full width at half maximum increased from 530 to 860 cm⁻¹ (see also Table 1). The red-shift value Δ was 1920 cm⁻¹ and the bandwidth was 1.6 times wider. In the Soret bands, similar changes were obtained. In the aqueous solution, large CD bands were observed and particularly an intense S-shaped signal was measured at the red-shifted Qy region.

The spectral changes in **1a** were similar to those by chlorosomal self-aggregation of **4a** reported earlier^{6,13} (see Fig. 3A and Table 1; Δ = 1980 cm⁻¹ and 1.8 times broadening), so **1a** self-aggregated in the aqueous micelle solution to give large oligomers with π–π stacking of chlorin chromophores. Zinc 3-ethyl-13¹-dicyanomethylene-chlorin **1b** afforded less red-shifted bands in the aqueous solution (Fig. 3B), while both **1a** and **1b** showed almost the same absorption bands in THF. The Δ-value of **1b** was estimated to be 190 cm⁻¹ and 10 times smaller than that of **1a**. The small but apparent shift could be due to the environmental effect. Therefore no chlorosomal aggregation of **1b** was observed under the present conditions. Metal-free form **2a** of **1a** also showed slight red-shifts (Fig. 3C) and could not give chlorosomal self-aggregates. Lack of the 3¹-hydroxy group or the central zinc metal completely



Scheme 1. Synthesis of zinc methyl 13¹-dicyanomethylene-pyropheophorbides **1a/b** from methyl pyropheophorbide-*a* (**3c**): (i) CH₂(CN)₂, Et₃N/THF, reflux; (ii) OsO₄, NaIO₄/aq AcOH–THF; (iii) (CH₃)₃CNH₂·BH₃/CH₂Cl₂; (iv) Zn(OAc)₂·2H₂O/CHCl₃–pyridine, reflux for **1a** and /CH₂Cl₂–MeOH, rt for **1b**; (v) H₂, Pd–C/acetone.

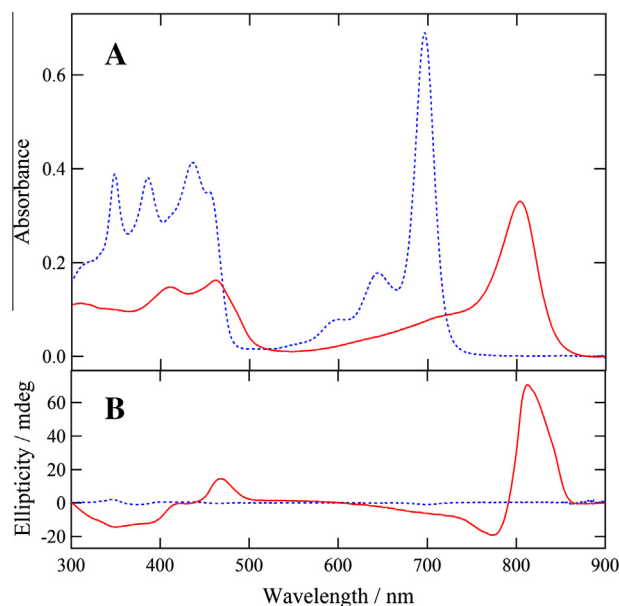


Figure 2. Electronic absorption (A) and CD spectra (B) of zinc 3-hydroxymethyl-13¹-dicyanomethylene-pyropheophorbide-*a* (**1a**) in THF (blue broken line) and an aqueous 1% (v/v) THF solution containing 0.025% (wt/v) Triton X-100 (red solid line): [**1a**] = 10 μM.

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