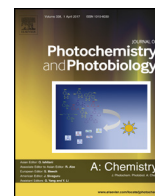




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A:
Chemistryjournal homepage: www.elsevier.com/locate/jphotochem20-Substitution effect on self-aggregation of synthetic zinc bacteriochlorophyll-*d* analogs

Hitoshi Tamiaki*, Ayaka Wada, Shogo Matsubara

Graduate School of Life Sciences, Ritsumeikan University, Kusatsu, Shiga, 525-8577, Japan

ARTICLE INFO

Article history:

Received 9 June 2017

Received in revised form 26 July 2017

Accepted 27 July 2017

Available online xxx

Keywords:

Chlorophyll

Chlorosome

Electronic absorption spectrum

Photosynthetic light-harvesting antenna

Steric factor

Supramolecular chemistry

ABSTRACT

Zinc methyl 20-substituted 3¹-demethyl-bacteriopheophorbides-*d* were prepared through palladium-catalyzed cross-coupling of chlorophyll-*a* derivatives. The synthetic zinc 3¹-hydroxy-13¹-oxo-chlorins possessing a(n) (un)substituted ethynyl or butadiynyl group at the 20-position were good models for bacteriochlorophylls-*c/d* found solely in chlorosomes, the main light-harvesting antennas of green photosynthetic bacteria. Similarly as in natural chlorosomes, the synthetic models self-aggregated in an aqueous Triton X-100 solution to form large oligomers with red-shifted and broadened electronic absorption bands. While a phenyl group directly connected with the chlorin π -system at the 20-position disturbed the chlorosomal self-aggregation, the insertion of an ethynylene group between the two functional groups reduced the steric hindrance around the 20-position and was useful for the facile formation of the self-aggregates. A similar substitution effect was observed in the 20-ethynyl to butadiynyl moieties bearing a sterically bulky trimethylsilyl group at the terminal position.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Light-harvesting antenna systems are important apparatuses in photosynthesis, where sunlight is efficiently absorbed and the excited energy is rapidly migrated toward a reaction center [1,2]. In oxygenic phototrophs, chlorophyll(Chl)-*a* is usually used for the photosynthetic antenna pigment but does not absorb green light effectively [3–5]. To enhance the efficiency of solar energy absorption, some improvements are performed in natural organisms: (1) use of the other type pigments including bilins and carotenoids [6,7], (2) interaction of Chl-*a* with environmental peptides and pigments [8–10], and (3) functionalization of the Chl-*a* molecule [3,11]. When the 7-methyl group of Chl-*a* is oxidized to a formyl group [12], the resulting Chl-*b* absorbs green light better than Chl-*a*. Dehydrogenation at the C17H–C18H bond of Chl-*a* leads to Chls-*c* [13], which are able to utilize green light more efficiently as well.

In anoxygenic green photosynthetic bacteria, the main light-harvesting antennas are chlorosomes constructed by the self-aggregation of composite chlorophyll pigments [14–17]. This is in sharp contrast with the conventional antennas constructed from the specific interaction of pigments with peptides. Chlorosomes

use a variety of bacteriochlorophyll (BChl) molecules as shown in the left drawing of Fig. 1 [18], because their cores lack specifically interacting peptides. These structurally different molecules self-aggregate to efficiently harvest incident sunlight in the naturally growing environments. As in the Chl-*a* to *b* change, the 7-methyl groups of BChls-*c/d* are oxidized to the 7-formyl group of BChls-*e/f*: R⁷ = CH₃ → CHO [19,20]. Additionally, methylation often occurs at the 8²-, 12¹-, and 20-positions [21,22]: R⁸ = CH₂CH₃ → CH₂CH₂CH₃ → CH₂CH(CH₃)₂ → CH₂C(CH₃)₃, R¹² = CH₃ → CH₂CH₃, and R²⁰ = H → CH₃. The esterifying group (R') in the 17-propionate residue is altered: farnesol (an isoprenoid alcohol) is usually used for green sulfur bacteria and stearyl alcohol (a linear alcohol) are observed in filamentous anoxygenic phototrophs [23]. These chlorosomal BChls are also structurally changed by culturing conditions in laboratory: light power [24–28], temperature [29–31], and supplements [32–41].

In a chlorosome, BChl-*c/d/e/f* molecules self-aggregate to form large oligomers through coordination of the 3¹-hydroxy group to the central magnesium atom, hydrogen bonding of the coordinating hydroxy group with the 13-carbonyl group, and π - π stacking of chlorin moieties [14,42–44]. The resulting J-aggregates covered by a lipid monolayer give red-shifted and broadened electronic absorption bands, compared with the monomeric species. The absorption spectral changes are characteristic of chlorosomal self-aggregation. As a model of such chlorosomal BChls, zinc complex of 3-hydroxymethyl-13¹-oxo-chlorin Zn-**1a** (see the right drawing of

* Corresponding author.

E-mail address: tamiaki@fc.ritsumei.ac.jp (H. Tamiaki).

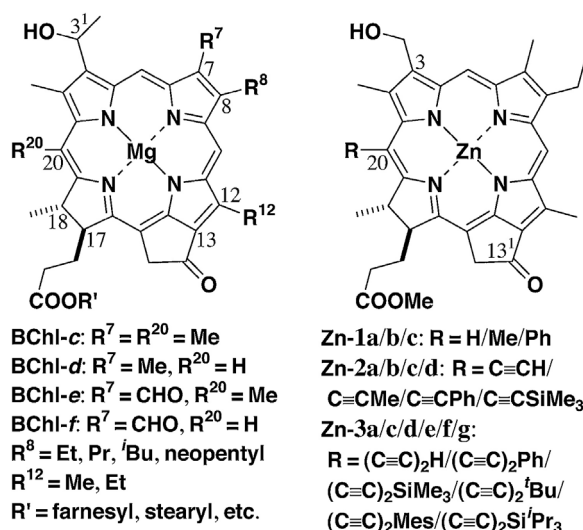


Fig. 1. Molecular structures of natural BChls in chlorosomes (left) and their synthetic models (right).

Fig. 1) was prepared and self-aggregated in hydrophobic environments [43]. In an aqueous Triton X-100 micelle solution, Zn-1a showed red-shifted and broadened Soret and Qy bands, which were comparable to those of the natural chlorosomes [45].

Halogenation at the 20-position of Zn-1a affected the Soret and Qy bands in their self-aggregates [46,47], although they self-aggregated similarly as in 20-unsubstituted Zn-1a. Chlorosomal self-aggregation of 20-alkylated analogs including Zn-1b ($R = \text{Me}$) was recently reported and the 20-alkylation effect has already been elucidated [48]. Here, we report on the synthesis of zinc methyl 3-hydroxymethyl-pyropheophorbides-a Zn-1-3 possessing a variety of groups at the 20-position (R in Fig. 1), the substitution effects of sterically bulky groups on their self-aggregation in an aqueous Triton X-100 micelle [$\text{H} < \text{Ph} < \text{Ph}$ (2,4,6-Me₃), $\text{H} < \text{CH}_3 < \text{CMe}_3$, and $\text{H} < \text{Si}(\text{CH}_3)_3 < \text{Si}(\text{CHMe}_2)_3$], and suppression of the substitution effect by insertion of ethynylene group(s). A part of this work is available in the previous communication [49].

2. Experimental

2.1. General

Electronic absorption spectra in a solution were measured by a Hitachi U3500 spectrophotometer. ¹H NMR spectra were recorded by a JEOL AL-400 (400 MHz) or ECA-600 (600 MHz) spectrometer; tetramethylsilane ($\delta = 0.00$ ppm) was used as an internal standard. Mass spectra (MS) were obtained using laser desorption/ionization (LDI) in positive mode by a Shimadzu AXIMA-CFR plus spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer: atmospheric pressure chemical ionization (APCI) and positive mode in acetonitrile (for free bases) or methanol (for zinc complexes).

Methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (H₂-1a) and its zinc complex Zn-1a [43], methyl 3-devinyl-3-hydroxymethyl-20-methyl-pyropheophorbide-a (H₂-1b) and its zinc complex Zn-1b [48], methyl 20-bromo-3-devinyl-3-hydroxymethyl-pyropheophorbide-a (H₂-1h) [46,49], methyl 3-devinyl-20-ethynyl-3-hydroxymethyl-pyropheophorbide-a (H₂-2a) and its zinc complex Zn-2a [49], methyl 3-devinyl-3-hydroxymethyl-20-phenylethynyl-pyropheophorbide-a (H₂-2c) and its zinc complex Zn-2c [49], and methyl 3-devinyl-3-hydroxymethyl-20-

trimethylsilylethynyl-pyropheophorbide-a (H₂-2d) and its zinc complex Zn-2d [49] were prepared according to reported procedures. Dry tetrahydrofuran (THF) was obtained from distillation over calcium hydride. Commercially available solvents (Nacalai Tesque) were used for the synthetic procedures. Gravity column chromatography (GCC) was performed with silica gel (Merck Kieselgel 60, 40–63 μm , 230–400 mesh). Before the optical measurements, zinc complexes were purified by reverse phase (RP) HPLC: a Shimadzu LC-10AD_{VP} pump, SPD-M10A_{VP} diode-array detector, SCL-10A_{VP} system controller, and a packed ODS column (Nacalai Tesque Cosmosil 5C₁₈AR-II, 10 ϕ x 250 mm) with an aqueous methanol eluent. In the case of Zn-3, a small amount of THF was added to the eluent. All HPLC solvents were obtained as HPLC grade from Nacalai Tesque and distilled water was prepared by a Yamato AutoStill WG250 system. The mixed solvents were degassed before use.

Triton X-100 was purchased from Nacalai Tesque and used as received. For optical spectroscopy, THF and distilled water were purchased from Nacalai Tesque as reagents prepared specially for HPLC.

2.2. Synthesis of methyl 20-substituted 3-devinyl-3-hydroxymethyl-pyropheophorbides-a H₂-1-3

2.2.1. Synthesis of methyl 3-devinyl-3-hydroxymethyl-20-phenyl-pyropheophorbide-a (H₂-1c)

To a dry THF solution (10 ml) of 20-bromo-chlorin H₂-1h (24.2 mg, 38.2 μmol) were added phenylboronic acid (50.0 mg, 410 μmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride with dichloromethane (Pd(dppf)Cl₂·CH₂Cl₂, 2.3 mg, 2.8 μmol), and cesium carbonate (127.7 mg, 392 μmol) and the mixture was refluxed in the dark under nitrogen for 2 h. The reaction mixture was washed with an aqueous 4% sodium hydrogen carbonate solution and water, dried over sodium sulfate, and evaporated. The residue was purified by GCC (AcOEt : hexane = 2 : 3) and recrystallization (CH₂Cl₂-hexane) to give 20-phenyl-chlorin H₂-1c (11.5 mg, 18.3 μmol) in a yield of 48%: black solid; mp 135–139 °C; VIS (CH₂Cl₂) λ_{max} 672 (relative intensity, 0.47), 615 (0.07), 547 (0.13), 515 (0.09), 416 (1.00), 324 nm (0.20); ¹H NMR (CDCl₃, 400 MHz) δ 9.61 (1H, s, 5-H), 9.56 (1H, s, 10-H), 8.09 (1H, dd, $J = 8, 2$ Hz, 6-H of 20-Ph), 7.77 (1H, t, $J = 8$ Hz, 5-H of 20-Ph), 7.69 (1H, ddt, $J = 3, 2, 8$ Hz, 4-H of 20-Ph), 7.62 (2H, m, 2,3-H of 20-Ph), 5.90, 5.86 (each 1H, d, $J = 9$ Hz, 3-CH₂), 5.24, 5.20 (each 1H, d, $J = 20$ Hz, 13¹-CH₂), 4.31 (1H, q, $J = 7$ Hz, 18-H), 4.13 (1H, dd, $J = 8, 4$ Hz, 17-H), 3.75 (2H, q, $J = 8$ Hz, 8-CH₂), 3.70 (3H, s, 17²-COOCH₃), 3.55 (3H, s, 12-CH₃), 3.31 (3H, s, 7-CH₃), 2.44 (3H, s, 2-CH₃), 2.48, 2.23 (each 2H, m, 17-CH₂CH₂), 1.74 (3H, t, $J = 8$ Hz, 8¹-CH₃), 1.57 (3H, d, $J = 7$ Hz, 18-CH₃), -1.54 (1H, s, NH) [The 3¹-OH and one of the two NH signals could not be observed.]; MS (LDI) found m/z 628, calcd. for C₃₉H₄₀N₄O₄: M⁺, 628; HRMS (APCI) found m/z 629.3125, calcd. for C₃₉H₄₁N₄O₄: MH⁺, 629.3122.

2.2.2. Synthesis of methyl 3-devinyl-3-hydroxymethyl-20-(1-propynyl)-pyropheophorbide-a (H₂-2b)

To a dry THF solution (30 ml) of 20-bromo-chlorin H₂-1h (34.0 mg, 53.8 μmol) were added tributyl(1-propynyl)tin (81.0 μl , 266 μmol) and tetrakis(triphenylphosphine)palladium(0) (46.4 mg, 40.2 μmol) and the mixture was refluxed in the dark under argon for 2 h. After evaporation, the residue was purified by GCC (AcOEt : hexane = 2 : 3) and recrystallization (CH₂Cl₂-hexane) to give 20-(1-propynyl)-chlorin H₂-2b (10.8 mg, 18.3 μmol) in a yield of 34%: black solid; mp 189–190 °C; VIS (CH₂Cl₂) λ_{max} 679 (relative intensity, 0.43), 620 (0.08), 562 (0.19), 528 (0.08), 419 (1.00), 331 nm (0.19); ¹H NMR (CDCl₃, 400 MHz) δ 9.46 (1H, s, 5-H), 9.41 (1H, s, 10-H), 5.91 (2H, s, 3-CH₂), 5.17, 5.11 (each 1H, d, $J = 20$ Hz, 13¹-CH₂), 4.73 (1H, q, $J = 7$ Hz, 18-H), 4.13 (1H, dd, $J = 9, 3$ Hz, 17-H),

Download English Version:

<https://daneshyari.com/en/article/6492893>

Download Persian Version:

<https://daneshyari.com/article/6492893>

[Daneshyari.com](https://daneshyari.com)