

Self-Aggregation of Synthetic Magnesium Bacteriochlorins as a Photosynthetic Antenna Model

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We prepared 3-(1-hydroxyethyl)-bacteriopyrochlorophyll-*a* (**3**) possessing magnesium atom and phytol ester from modification of natural bacteriochlorophyll(BChl)-*a*. A dichloromethane solution of (3¹R) and (3¹S)-**3** was diluted with 100~1000 fold volume of cyclohexane to give new species absorbing near-infrared lights. The resulting Q_y maximum of (3¹R)-**3** was 860 nm and red-shifted by 2150 cm⁻¹ from the monomeric. In the nonpolar organic solvent, epimeric (3¹S)-**3** showed a less red-shifted peak at 798 nm as well as a residual monomeric band. Such visible spectra indicated that **3** diastereoselectively aggregated in cyclohexane to afford oligomers possessing a similar supramolecular structure with chlorosomal aggregates of natural BChl-*d*, 7,8-dehydro-form of **3**.

Key words: bacteriochlorophyll-*a*, chlorosome, photosynthetic antenna, self-assembly, stereoisomers

INTRODUCTION

Inner-membranous light-harvesting (LH) complexes 1 and 2 of photosynthetic bacteria have oligomeric bacteriochlorophyll(BChl)s-*a* as major antenna pigments. In the LHs, BChls-*a* are fixed on proteins with well-ordered orientations, and some Q_y absorption peaks as in B875 of LH1 and B850 of LH2 show large red-shifts compared to that of monomeric BChl-*a*. Besides such intermolecular interactions between bacteriochlorin pigments, self-aggregates

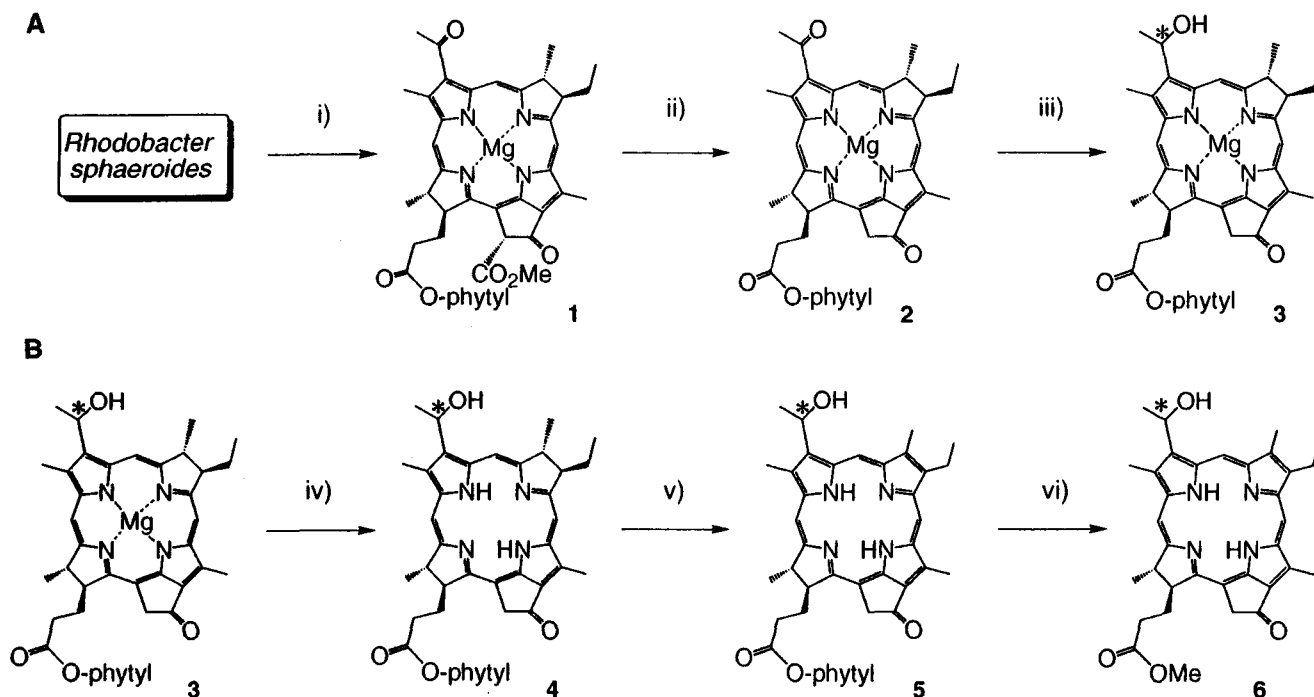
of BChls-*c*, *d* and *e* possessing a chlorin π -conjugate without any assistance of proteins are available in an extra-membranous antenna system of green bacteria (=chlorosome). Here we report preparation of novel chlorosome-type pigments possessing a bacteriochlorin moiety and their self-aggregation in non-polar organic solvents.

MATERIALS AND METHODS

We prepared novel 3-(1-hydroxyethyl)-bacteriopyrochlorophyll-*a* (**3**) possessing magnesium atom and phytol

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Scheme 1. (A) Synthesis of 3-(1-hydroxyethyl)-bacteriopyrochlorophyll-a (**3**). (B) Modification of **3** toward 3¹-R/S determination. i) extraction, ii) collidine, reflux, iii) *t*-BuNH₂BH₃, iv) aq. HCl, v) DDQ, vi) MeOH, H₂SO₄.

ester as described below (see Scheme 1A). BChl-*a* (**1**) was extracted from a purple bacterium, *Rhodospira rubra*. Removal of methoxycarbonyl group at the 13²-position of **1** and reduction of the resulting bacteriochlorin **2** gave desired product **3** as a diastereomeric mixture. A 3¹-epimeric mixture of **3** was completely separated as **3-f1** (first fraction) and **3-f2** (second fraction) by several runs of normal phase HPLC (Cosmosil 5SL-II, 6φ×250 mm, Nacalai Tesque, acetone / hexane = 23 / 77, 1.0 mL / min).

The stereochemistry of **3-f1/2** was determined by the following procedures. Bacteriochlorin **4** prepared by demetallation of **3** (**3-f1:3-f2** = *ca.* 3:1), was oxidized by 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) and successively transesterification of the resulting product **5** afforded methyl bacteriopyropheophorbide-*d* (**6**) (see

Scheme 1B). According to the previous report [1], 3¹R/S-**6** was assigned by HPLC analysis; the first eluted 3¹S-**6**: the second 3¹R-**6** = *ca.* 3 : 1. Therefore, we could determine the absolute configuration of the 3¹-position in HPLC-separated **3**; **3-f1** is (3¹S)-**3** and **3-f2** is (3¹R)-**3**.

RESULTS AND DISCUSSION

The visible spectra of (3¹R)-**3** and (3¹S)-**3** in polar or non-polar organic solvent are shown in Figure 1. In acetone, both the epimers (3¹R/S)-**3** gave the same sharp absorption spectra (the thin line of Fig. 1), indicated that they were monomeric in the solution. In 0.1(v/v)% dichloromethane-cyclohexane, all the peaks of the epimers (3¹R/S)-**3** were red-shifted (the solid and broken lines of Fig. 1 for (3¹R)-**3**

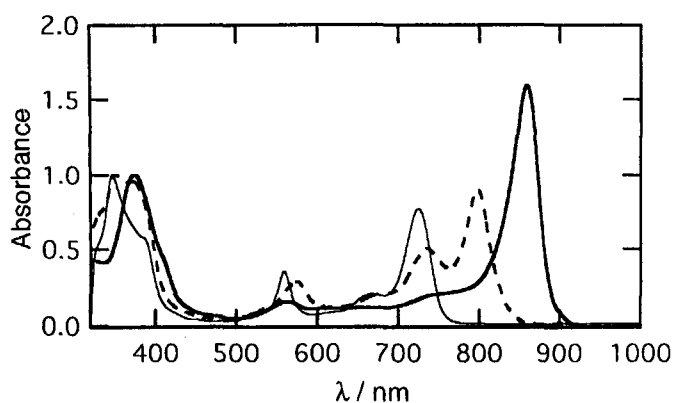


Figure 1. UV-VIS-NIR spectra of (3¹R) and (3¹S)-3. Thin curve, (3¹R) and (3¹S)-3 in acetone; solid curve, (3¹R)-3 in 0.1%(v/v) dichloromethane-cyclohexane; broken curve, (3¹S)-3 in 0.1%(v/v) dichloromethane-cyclohexane.

and (3¹S)-3, respectively) indicated that these compounds aggregate to give oligomers in the less polar organic solvents. In the self-aggregation, a diastereomeric control was observed. Self-aggregation of (3¹R)-3 proceeded predominantly, the oligomer showed large red-shifted Q_y peak at 860 nm and the Q_y band absorbed up to 920 nm wavelengths of the near-infrared region, whereas (3¹S)-3 was partly monomeric even in the non-polar solvents and the Q_y maximum of the self-aggregates was less red-shifted than that of (3¹R)-3.

We also compared the aggregation of synthetic (3¹R)-3 with that of natural chlorosomal BChl (Fig. 2). As the natural pigment, we employed R[E,M]BChl-*d*_F, which essentially differed from (3¹R)-3 in 7,8-dehydrogenation. The 7,8-reduction to bacteriochlorin from chlorin made absorption maxima of Q_y peaks in both monomeric and oligomeric states shifted to longer wavelength; 651→720 and 725→858 nm [1, 2]. Self-aggregation of BChl-*d* red-shifted the Q_y-peak by 1470 cm⁻¹ and (3¹R)-3 gave a longer shift of 2150 cm⁻¹.

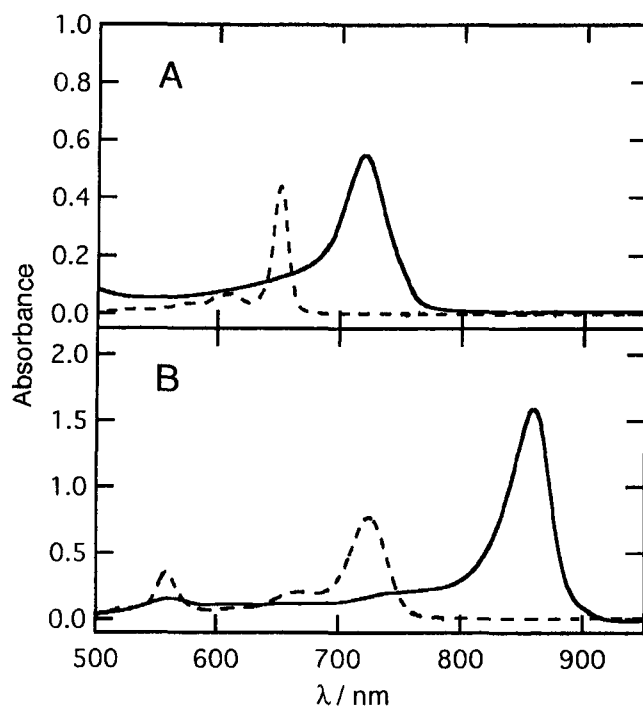


Figure 2. VIS-NIR spectra of self-aggregates of (A) chlorosomal R[E,M]BChl-*d*_F and (B) synthetic (3¹R)-3. Broken curve, monomer; solid curve, oligomer.

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