



Synthesis and self-assembly of amphiphilic zinc chlorophyll derivatives possessing a crown ether at the 17-propionate residue



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ARTICLE INFO

Article history:

Received 26 January 2013

Received in revised form 28 February 2013

Accepted 5 March 2013

Available online 13 March 2013

Keywords:

Bacteriochlorophyll

Chlorosome

Crown ether

Green photosynthetic bacterium

Photosynthesis

ABSTRACT

Zinc 3¹-hydroxy-13¹-oxo-chlorins **1–3** possessing a 12-crown-4, 15-crown-5, and 18-crown-6 ether at the 17-propionate residue were synthesized and self-assembled in aqueous and non-polar organic media. Zn chlorins **1–3** exhibited red-shifted Q_y absorption bands and large CD signals around 730 nm in an aqueous solution after standing for 2 h or 2 days, indicating the formation of their oligomeric self-aggregates as in chlorosomes of green photosynthetic bacteria. Incubation for 2 weeks decreased the absorption bands around 730 nm, accompanying an appearance of the absorption band around 675 nm. These show that Zn chlorins **1–3** finally formed thermodynamically stable anti-parallel dimers in the aqueous solution. 17⁶-Epimerically pure **1–3** exhibited essentially the same spectral properties as the corresponding epimeric mixtures, but larger CD signals were observed around 730 nm in the spectra of epimerically pure **1** and **2** after standing for 2 h or 2 days than those of their epimeric mixtures. In a non-polar organic solvent, Zn chlorins **1–3** formed less time-dependent chlorosomal self-aggregates that exhibited Q_y absorption bands around 735 nm.

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1. Introduction

Photosynthetic light-harvesting complexes have chlorophyll (Chl) and bacteriochlorophyll (BChl) molecules, which are highly organized to capture light energy and to transfer it to reaction center complexes in a high efficiency. In most light-harvesting complexes, (B)Chl molecules are immobilized in protein scaffolds.¹ The exception is extramembranous light-harvesting complexes called chlorosomes of green photosynthetic bacteria. In chlorosomes, BChls *c*, *d*, and *e* self-aggregate without help of proteins and the large oligomers were surrounded by a lipid monolayer.^{2–5} Fig. 1A shows the molecular structure of BChl *d* in green photosynthetic bacteria. Essential moieties required for self-aggregates of chlorosomal BChls are a central magnesium, 3¹-hydroxy, and 13-keto carbonyl groups: the central Mg in one BChl is coordinated axially with the 3¹-OH in another BChl and the coordinating OH forms a hydrogen-bond with the 13-C=O group in a third BChl.^{2–5} Chlorosomal BChls are esterified with a long hydrocarbon alcohol at the 17-propionate such as farnesol in green sulfur bacteria.^{6,7} Hydrophobic interaction among esterifying alcohols would have considerable effects on the formation and stabilization of chlorosomal self-aggregates. From this viewpoint,

in vivo esterification of unnatural alcohols with bacteriochlorophyllide (*BChlide*) *c* in green photosynthetic bacteria^{8–11} and organic synthesis of Zn Chl derivatives esterified with various alcohols, which serve as model compounds of natural BChls *c*, *d*, and

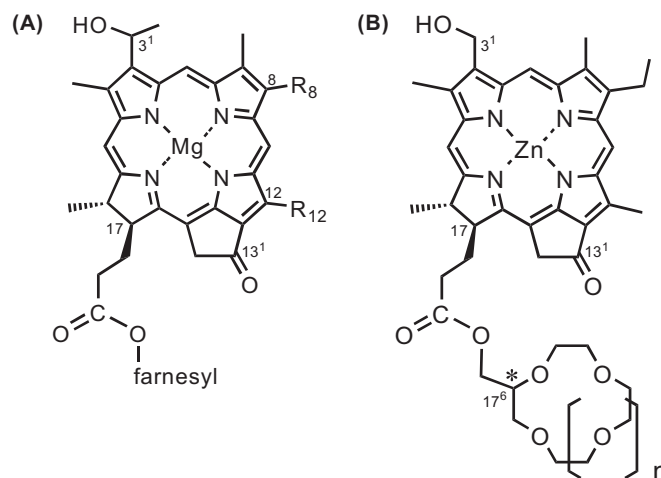


Fig. 1. (A) Molecular structures of BChl *d*. R₈=C₂H₅, *n*-C₃H₇, *iso*-C₄H₉, R₁₂=CH₃, C₂H₅. (B) Molecular structures of synthetic Zn chlorins **1**, **2**, and **3** possessing a crown ether; **1**: *n*=1, **2**: *n*=2, **3**: *n*=3.

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e,^{12–25} have been performed to examine the effects of esterifying chains of chlorophyllous pigments on chlorosomal self-aggregates.

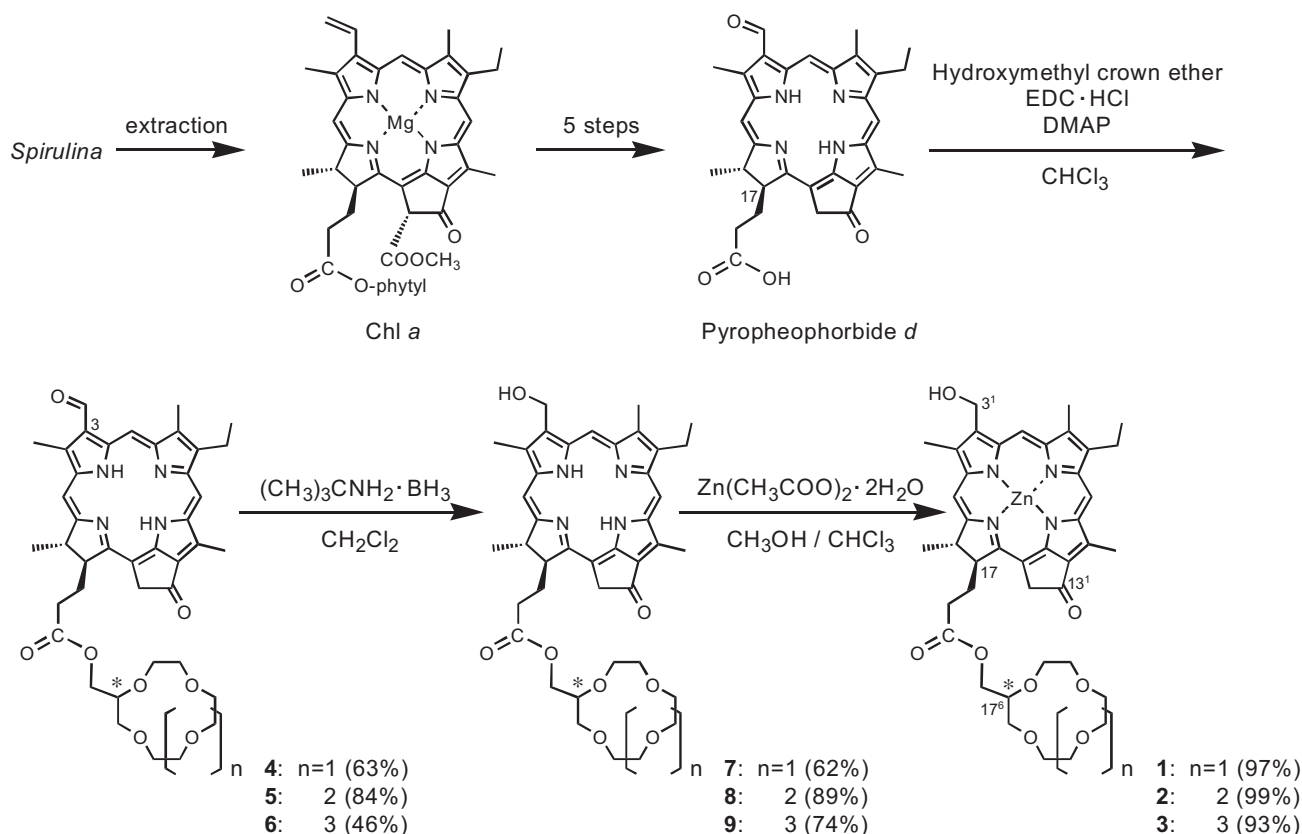
Self-assemblies of amphiphilic π -conjugated molecules exhibit unique supramolecular structures and functions, and thus have attracted considerable attention.^{26–28} In the research area of chlorosomal self-assemblies, Miyatake et al. synthesized amphiphilic Zn chlorins esterified with a linear polyethylene glycol (PEG) at the 17-propionate residue.¹⁷ The Zn chlorins possessing shorter and longer hydrophilic PEG chains tended to form the anti-parallel dimeric structure with the 675-nm Q_y band and the monomeric form with the 657-nm Q_y band in an aqueous solution. We recently reported drastic changes of assembling states of these amphiphilic Zn chlorins in aqueous solutions by treatment with dichloromethane and chloroform, which induced conversion from the dimeric and monomeric forms to chlorosomal self-aggregates.¹⁹ Tamiaki et al. synthesized Zn chlorins possessing a hydrophilic sugar moiety at the 17-propionate residue and characterized their self-aggregates.²⁰ However, little information is available, to our best knowledge, on other amphiphilic metallochlorins mimicking chlorosomal BChls of green photosynthetic bacteria. The variety of molecular structures of amphiphilic metallochlorins that are capable of self-assembly will provide useful information to investigate the effects of hydrophilic chains on their supramolecular structures and to construct photoactive supramolecular nanodevices based on photosynthetic apparatus. Here we report synthesis and self-assembly of amphiphilic Zn 3^{17} -hydroxy-13¹-oxo-chlorins **1–3** possessing a crown ether at the 17-propionate residue (Fig. 1B). Crown ethers are cyclic polyoxyethylenes and provide hydrophilicity to the esterifying groups of Zn chlorins. Comparison of self-assemblies of the Zn chlorins **1–3** with those of Zn chlorins esterified with linear PEG¹⁷ allows us to discuss the structural effects of hydrophilic moieties on assembling states of metallochlorins.

2. Results and discussion

2.1. Synthesis and separation of epimers

Zn chlorins **1–3** possessing three kinds of crown ether with a methylene spacer were synthesized by condensation of pyropheophorbide *d* with hydroxymethyl crown ethers in the presence of 1-[3-(dimethylamino)propyl]-3-ethyl-carbodiimide hydrochloride (EDC·HCl) and 4-*N,N*-dimethylaminopyridine (DMAP), followed by reduction of the 3-formyl to 3-hydroxymethyl group and Zn insertion, as shown in Scheme 1. The yields at the esterification of pyropheophorbide *d* with hydroxymethyl crown ethers to obtain **4–6** were 46–84%. One possible reason for the lower yield in the synthesis of **6** compared with those of **4** and **5** is a loss during HPLC purification, since more hydrophilic **6** had some difficulty in purification by flash silica gel column chromatography (FCC). Reduction of the formyl group at the 3-position in **4–6** with *tert*-butylamine borane complex afforded **7–9** in 62–89% yield. Zn chlorins **1–3** were obtained by Zn insertion into the chlorin macrocycles of **7–9** in 93–99% yield.

The separation of 17⁶-epimers of **1–3**, which were derived from chiral centers in commercially available racemic crown ether alcohols (denoted by asterisk in Fig. 1B), was performed by reverse-phase HPLC as shown in Fig. 2. All fractions exhibited the same visible absorption spectra (λ_{\max} =425 and 652 nm in the HPLC eluent). Hereafter, the former (fast eluting) fractions of the epimeric pairs of **1, 2**, and **3** were denoted as **1-F, 2-F**, and **3-F**, respectively, and the latter (slow eluting) fractions were denoted as **1-L, 2-L**, and **3-L**, since the absolute stereochemistry in the epimers of **1–3** could not be determined here. The isolated epimers were self-assembled in aqueous media under the same conditions as those of epimeric mixtures.



Scheme 1. Synthetic scheme of Zn chlorins **1, 2, and 3** from naturally occurring Chl *a*.

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