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Self-aggregation of synthetic zinc-chlorophylls possessing an interactive ω-hydroxyalkyl group

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Introduction

Bacteriochlorophyll(BChl)s-*c* and *d* (Figure 1) are the light-harvesting antenna pigments found only in the green photosynthetic bacteria [Tamiaki 1996]. Organization of these pigments in photosynthetic antennas is very unique in that they form highly-ordered self-aggregates without structural supports by any proteins [Olson 1998]. BChls-*c* and *d* possess 1-hydroxyethyl group at the 3-position instead of vinyl group that protein-binding Chls-*a* and *b* have. It has been established

BChl-*c*: R^{20}=Me
BChl-*d*: R^{20}=H

1 (R = CH$_2$OH)
2 (R = CH$_2$CH$_2$OH)
3 (R = CH$_2$CH$_2$CH$_2$OH)

Figure 1. Natural pigments (left) and synthetic zinc chlorins (right)

that the hydroxy group of BChls-*c* and *d* simultaneously form coordinate bond with the central magnesium of second molecule and hydrogen bond with the 13-keto group of third molecule as in C=O···H–O···Mg [Hildebrandt et al. 1994]. Therefore, position and steric environment of such interactive hydroxy group drastically affect the structure of self-aggregates [Yagai et al. 1999 and 2001]. It is reasonable to assume that coordination of the hydroxy group to the central zinc of adjacent molecule could keep the chlorin molecules very close to each other, and thereby these pigments can form closely packed and highly ordered aggregates, accompanied by overlap of the chlorin macrocyclic π-conjugates. Such a supramolecular structure leads to a large red-shift of Q$_y$ absorption maxima (~750 nm), which is vital for the green bacterial survive.
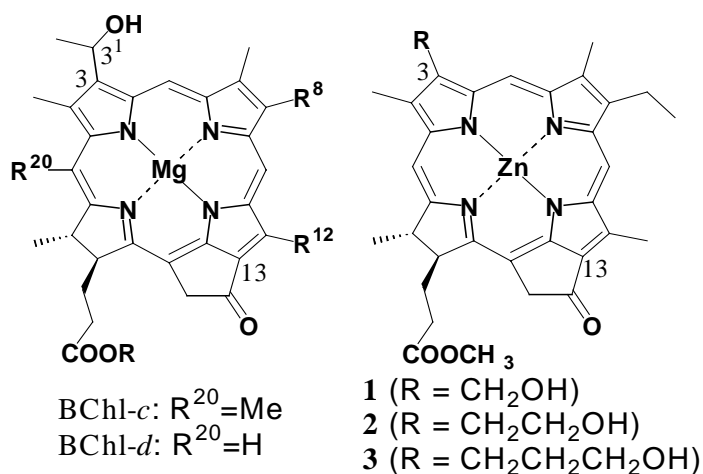
   In our previous studies, zinc chlorin **1** (Figure 1) was shown to be a good model of BChls-*c* and *d* [Tamiaki et al. 1996 and Miyatake et al. 1999]. In 1% THF-hexane, **1** formed self-aggregates to give Q_y maximum at 740 nm and strong CD signals in the Q_y region (solid curves in Figures 2A and 3A). These spectroscopic properties are similar to those of the in-vitro aggregates of BChls-*c* and *d*, indicating structural similarity between both the self-assemblies of the synthetic and the natural pigments. Moreover, IR spectra of the solid aggregates of **1** revealed that **1** formed the intermolecular C=O···H–O···Zn linkage in the aggregates. Here, we addressed the extension of covalent linkage between the interactive hydroxy group and the chlorin moiety in chlorosomal Chls. We efficiently prepared zinc chlorins **2** and **3** (Figure 1). Self-aggregation behaviour of zinc chlorins **2** and **3** in nonpolar organic solvents was examined and compared with that of **1** to elucidate the importance of the distance between the hydroxy group and the chlorin moiety.

Materials

Zinc chlorin **2** was prepared from methyl pyropheophorbide-*a* by following synthetic procedures; ketal-protection of the 13-C=O group of the 3-vinylchlorin → hydroboration of the 3-CH=CH$_2$ group by BH_3 and oxidation by $NaOH$-H_2O_2 → ketal-deprotection → zinc-complexation.
   Zinc chlorin **3** was prepared from methyl pyropheophorbide-*d*; indium-mediated Barbier type reaction of the 3-CHO group with allyl bromide → oxidative cleavage of the resulting 3-CH(OH)CH$_2$CH=CH$_2$ group by OsO_4-$NaIO_4$ → dehydration of the resulting 3-CH(OH)CH$_2$CHO group by *p*-TsOH → reduction of the resulting 3-CH=CHCHO group by *t*-BuNH$_2$BH$_3$ → hydrogenation of the resulting 3-CH=CHCH$_2$OH with H$_2$ over PtO$_2$ → zinc-complexation.

Results and discussion

Visible and CD spectra of monomeric **2** in neat THF are almost identical to those of **1** (dotted curves in Figures 2A, 2B, 3A and 3B). In 0.1% THF-hexane, **2** (15 µM) formed aggregates having Q_y maximum at 701 nm (solid curve in Figure 2B). Red-shifted value of the Q_y maximum from the monomer to the aggregates of **2** is 1260 cm^{-1}, which is considerably smaller than that of **1** (1940 cm^{-1}). This result indicates that the aggregates of **2** are less closely packed than those of **1**. The CD spectrum of the aggregates of **2** in 0.1% THF-hexane exhibited specific CD signals in the Q_y region (solid curve in Figure 3B). The CD signals are composed of a relatively broad and small S-shaped signal in shorter wavelength region and a sharp and intense reverse S-shaped signal in longer wavelength region. Such a signal shape resembles to that of **1** (solid curve in Figure 3A), indicating that orientation of the pigments in the aggregates of **2** is not largely different from that of **1**; the aggregates of **2** are ordered and Q_y transition moments in the aggregates are parallel to each other. IR spectrum of the solid aggregates of **2** was identical to that of **1**. This indicates that **2** in the aggregates formed the intermolecular C=O···H–O···Zn linkage. It can be concluded that insertion of a methylene group into the C3–C3^1 bond of **1** (**1** → **2**) prevents the formation of close π-π packing but hardly affects the formation of ordered aggregates and the C=O···H–O···Zn linkage.
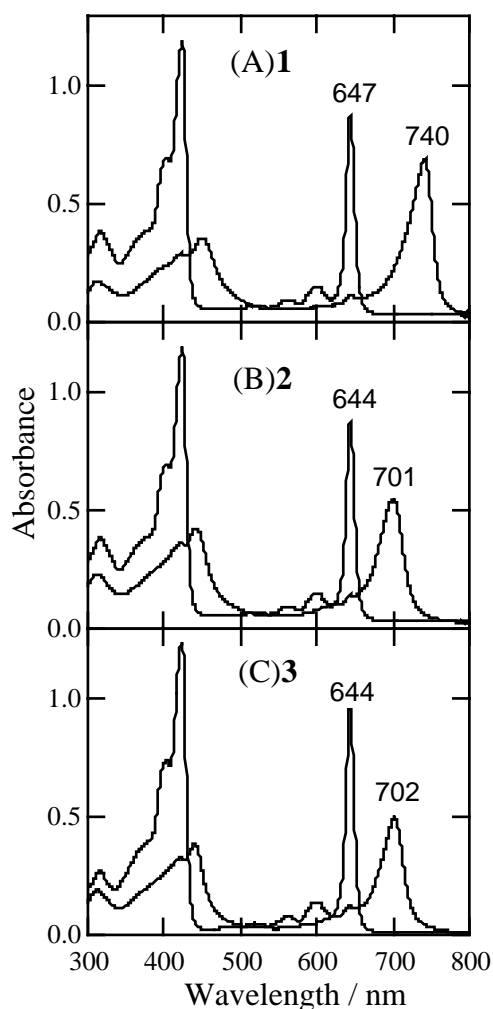
Figure 2. Visible spectra of **1** (A), **2** (B) and **3** (C). Solid curve, in 1% THF (**1**) and 0.1% THF-hexane (**2** and **3**); dotted curve, in neat THF. Concentrations of all the solutions are ca. 15 μM.
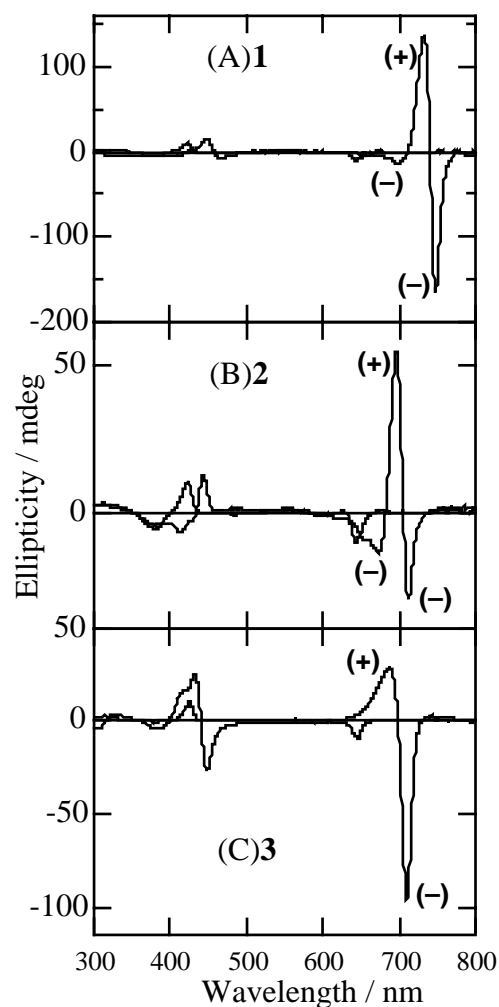
Figure 3. CD spectra of **1** (A), **2** (B) and **3** (C). Solid curve, in 1% THF (**1**) and 0.1% THF-hexane (**2** and **3**); dotted curve, in neat THF. Concentrations of all the solutions are ca. 15 μM.

   Visible and CD spectra of monomeric **3** in neat THF are almost identical to those of **1** (dotted curves in Figures 2A, 2C, 3A and 3C). In 0.1% THF-hexane, **3** (15 μM) formed aggregates having Q_y maximum at 702 nm (solid curve in Figures 2C). Red-shifted value of the Q_y maximum from the monomer to the aggregates of **3** is 1280 cm^{-1}, which is considerably smaller than that of **1** (1940 cm^{-1}). Therefore, the aggregates of **3** are less closely packed than those of **1**. The CD spectrum of the aggregates of **3** in 0.1% THF-hexane exhibited only a highly asymmetric reverse S-shaped CD signals in the Q_y region, where the negative signal is approximately three-fold larger than the positive signal (Figure 3C). Such a CD signal in the Q_y region is clearly distinguished from that of **1**. Furthermore, **3** gave clear CD signals in the Soret region in comparison with **1**. These results indicate that the orientation of the pigments in the aggregates of **3** is fairly different from that of **1**; the aggregates of **3** are not as ordered as those of **1**. Furthermore, IR spectrum of the solid aggregates of **3** revealed that the C=O···H–O···Zn linkage in the aggregates of **3** was very weak in comparison with **1**.

It can be concluded that insertion of two methylene groups into C3–C3^1 bond of **1** (**1** → **3**) prevents not only the formation of closely packed aggregates but also the ordered association of pigments and formation of the intermolecular C=O⋯H–O⋯Zn linkage.

Self-aggregates of **2** and **3** were less closely packed and/or disordered than those of **1**. Furthermore, self-aggregates of **3** had weak intermolecular C=O⋯H–O⋯Zn linkage. Since the self-aggregates of **2** and **3** may not be efficiently stabilized by the π-π interaction between chlorin chromophores and the intermolecular C=O⋯H–O⋯Zn linkage in comparison with the aggregates of **1**, aggregated **2** and **3** may have structural defects like a lattice defect of crystals. Such defects are disadvantageous for the efficient energy migration in the aggregates. Furthermore, smaller red-shifted values in the Q_y bands of the aggregates of **2** and **3** than that in **1** are energetically disadvantageous for collecting the dim lights and efficient energy-transfer to bacteriochlorophyll-*a* in a baseplate. It is concluded that the position of the interactive hydroxy group in the naturally occurring chlorosomal Chls, separated from the chlorin moiety by only one methylene linkage, is necessary for the formation of the antenna aggregates appropriate for the efficient light-harvesting and energy transfer.

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