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Review

Self-aggregates of natural chlorophylls and their synthetic analogues in aqueous media for making light-harvesting systems

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ABSTRACT

Chlorophyll molecules are well organized for efficient energy or electron transfer in a light-harvesting antenna or a reaction center of photosynthetic organisms. In order to make effective photosynthetic mimics, self-aggregates of natural chlorophylls and their synthetic analogues have been prepared with the specific intermolecular interactions. Many studies have been carried out to prepare aqueous chlorophyll aggregates by use of surfactants or chemical modifications of the natural pigments, because chlorophylls basically are poorly soluble in water. This review article focuses on the preparation and function of aqueous chlorophyll aggregates used in making artificial photosynthetic systems.

1. Introduction

Photosynthesis is nature's effective energy conversion system that produces foods, fuels and useful materials. Mimicking natural photosynthesis has been a great challenge in both science and technology, as it offers the potential to solve many problems of the energy crisis and the destruction of some environment [1–4]. However, photosynthesis is composed of a huge number of sequential reactions, and the mechanisms of the natural energy conversion reactions have not yet been clarified. Many attempts at making artificial photosynthetic systems have been made, and some of them successively produced practical energy conversion systems. For example, irradiation of ultraviolet light on a titanium oxide crystal splits water molecules into hydrogen and oxygen gases [1]; however, it is difficult for an artificial energy conversion system to use visible and near-infrared light effectively. Some energy conversion systems utilize synthetic pigments to absorb longer wavelength light [2,3]. Natural photosynthetic systems use numerous chlorophyll(Chl) molecules to absorb the sunlight more effectively. Chls have large absorption coefficients around the visible and near-infrared regions and are found in both the light-harvesting (LH) antennae and reaction centers, which play important roles in the early events of photosynthesis [5]. Light energy absorbed at Chl

Abbreviations: BChl, bacteriochlorophyll; CD, circular dichroism; Chl, chlorophyll; CPC, cetyl pyridinium chloride; LH, light-harvesting; MGDG, monogalactosyl diglyceride; ODTES, octadecyltriethoxysilane; RR, resonance Raman; SDBS, sodium 4-dodecylbenzenesulfonate.

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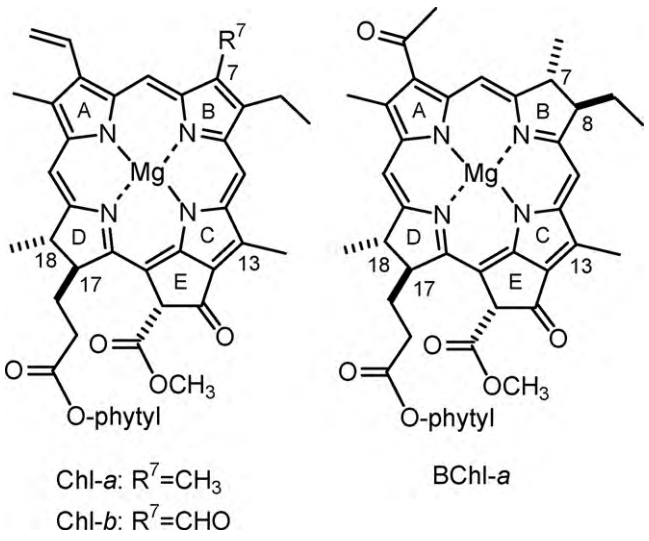


Fig. 1. Structures of chlorophyll(Chl)s-*a*, *b* and bacteriochlorophyll(BChl)-*a*.

molecules in LH antennae is rapidly and effectively transferred to a reaction center, in which efficient electron transfer occurs among Chls and other redox active molecules such as quinone to form a charge separated state. The electrochemical potential is used to produce higher energy products, such as ATP and NAD(P)H. In these natural photosynthetic devices, Chl molecules are organized for the effective intermolecular energy and electron transfers.

Chl molecules are magnesium complexes of cyclic tetrapyrroles with an additional 5-membered ring, the ring E in Fig. 1, and have some substituents at the peripheral positions of the macrocycles [6]. A keto carbonyl group located at the 13-position is a particularly important functional group responsible for the large absorption coefficients in visible and near-infrared regions. Photosynthesis uses several different Chls to absorb sunlight effectively and to carry out the sequential photochemical reactions, and the pigment contents are dependent on organisms. For example, Chl-*a*, the most abundant Chl contained in plants, cyanobacteria, etc., has a chlorin macrocycle (17,18-dihydroporphyrin) π-system (Fig. 1 left). In contrast, bacteriochlorophyll(BChl)-*a*, found in anoxygenic photosynthetic bacteria, has a bacteriochlorin (7,8,17,18-tetrahydroporphyrin) π-system (Fig. 1 right). The subtle structural difference in tetrapyrrole macrocycles makes a big difference in absorption spectra; BChl-*a* has the redmost (Qy) band at 770 nm which is about 100 nm longer than that of Chl-*a*. Photosynthetic organisms select (B)Chls to adapt to the environments where they are living. A purple bacterium that lives in the deep-sea or -lake, uses BChl-*a* as an antenna pigment, because the near-infrared light is only available in this habitat area. In addition, a substituent at the peripheral position of the tetrapyrrole ring also affects the absorption spectrum. A formyl group at the 7-position of Chl-*b* (Fig. 1 left) induced a red-shifted Soret band (the main visible band) and a blue-shifted Qy band compared to Chl-*a* possessing the 7-methyl group: ca. 430 → 450/660 → 640 nm in diethyl ether. LH complexes in plants contain both Chl-*a* and Chl-*b*, which allows the LH antenna to absorb a wide range of sunlight [7].

Intermolecular interactions among the Chl molecules are important for the photochemical reactions occurring in photosynthesis, and therefore Chl molecules as well as carotenoids and quinones are adequately arranged in photosynthetic apparatuses. Generally, Chls form a complex with proteins to make LH antennae and reaction centers, and their structures were examined by an X-ray crystallographic technique [8–12]. The results showed Chl molecules are embedded in the protein mainly by binding to the amino acid residues. For instance, coordination bonding between an imidazolyl nitrogen atom of His and a central Mg of Chl was found in the crystal structures [13,14]. Because the efficiencies of intermolecular energy or electron transfers are very sensitive to the molecular arrangements of donor and acceptor, the distance and orientation of the Chl molecules are adequately controlled in the natural pigment-protein complexes.

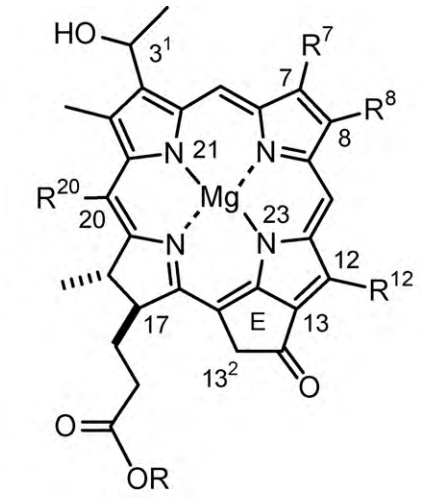
The structures of these complexes of LH antennae and reaction centers are so complicated that it is very difficult to fabricate such photosynthetic apparatus by conventional chemical techniques; therefore, simplified models of natural photosynthetic apparatuses are required. LH antenna or reaction center models have been prepared with covalently linked (B)Chls, carotenoids, quinones or fullerenes [15–17]. Organizing (B)Chls using covalent bonding is, of course, a possible strategy to fabricate the artificial photosynthetic units. However, binding many (B)Chls or the synthetic analogues to form a macromolecule requires many sequential and troublesome reaction steps. In contrast, self-aggregation is a useful technique to use in organizing a large number of molecules. Actually, some of the photosynthetic organisms use self-aggregation to form LH antenna structures. In addition, artificial self-aggregates of (B)Chls have been prepared in order to mimic the photosynthetic systems. In this review, self-aggregates of (B)Chls for LH antenna systems in natural and artificial systems will be discussed. Especially, we would like to focus on the artificial self-aggregates prepared in aqueous media, which reproduce not only the structures but also the function of natural LH antenna systems.

2. Self-aggregates of bacteriochlorophylls for a light-harvesting antenna

2.1. Self-aggregates of natural bacteriochlorophylls

As described in Section 1, most LH antenna systems consist of (B)Chls–protein complexes in natural photosynthetic organisms. However, green photosynthetic bacteria have a unique LH antenna system called a chlorosome [18–23]. The chlorosome is an extramembranous antenna and has an ellipsoidal body about 70–180 nm long, 30–60 nm wide and 25 nm high. Within a chlorosome, a large number (ca. 10^5) of BChl molecules self-aggregate to form oligomers surrounded with a monolayer of glyco/phospholipids [24–26]. Light energy absorbed at the supramolecular LH systems is efficiently transferred into a reaction center via other pigment-protein complexes [27–35]. The precise structure of the chlorosomal aggregate has not yet been clarified, although some structural models have been proposed for the antenna structure [36–46].

Chl pigments found in chlorosomes are BChls-*c*, *d* and *e*, which possess a chlorin π-system (Fig. 2). Both BChls-*c* and *d* have a methyl substituent at the 7-position, and BChl-*c* has an additional methyl group at the 20-position which distinguishes it from BChl-*d*. The characteristic structural feature of BChl-*e* is the presence of the 7-formyl group. The CHO group affects the absorption spectrum as in Chl-*b* and BChl-*e* has red-shifted Soret and blue-shifted Qy bands compared to BChl-*c* [47]: ca. 430 → 460/660 → 650 nm in acetone. Chlorosomal BChls commonly have variable alkyl substituents at the 8- and 12-positions [47–51]. The long tail at the 17-propionate side chain is also somewhat variable dependent on the pigments [44,52]. In addition, a chiral center at the 3^1-position produces the pigment heterogeneity, both 3^1R- and 3^1S-epimers are found in natural chlorosomes [45,52–55]. Normally, BChls in a chlorosome is not a single compound, and that extracted from chlorosomes is a mixture of 8,12-homologues, 17-propionates and 3^1-epimers. The contents of the chlorosomal BChls are varied in organisms. The unique feature of the chlorosomal BChls is the lack of a methoxycarbonyl group at the 13^2-position of ring E, which is



BChl-*c*: R^7=CH_3, R^{20}=CH_3
BChl-*d*: R^7=CH_3, R^{20}=H
BChl-*e*: R^7=CHO, R^{20}=CH_3
R^8, R^{12}=CH_3, CH_2CH_3, $CH_2CH_2CH_3$,
$CH_2CH(CH_3)_2$, etc.
R=farnesyl, stearyl, etc.

Fig. 2. Structures of bacteriochlorophyll(BChl)s-*c*, *d* and *e* in a chlorosome.

found in all the other natural (B)Chls. The bulky substituent gives the chlorin macrocycle a steric hindrance that partially disturbs the self-aggregation via π–π stacking [56]. In addition, chlorosomal BChls characteristically possess of a hydroxy group at the 3^1-position which is believed to play an important role in associating with neighboring molecules (Fig. 3). An intermolecular coordination bond between the 3^1-OH group and the central magnesium of another molecule is found in the chlorosomal aggregate. Moreover, there is believed to be a hydrogen bond between the OH group and a carbonyl group at the 13-position of the third molecule in the aggregate. The specific intermolecular interactions, C=O···H–O···Mg, among chlorosomal BChls were supported by resonance Raman (RR) and IR studies of the *in vitro* aggregates [57]. Self-aggregation of chlorosomal BChls induces red-shifted absorption bands. Especially, the Qy absorption band observed at 667 nm in a monomeric form of BChl-*c* was dramatically red-shifted to 740 nm in a chlorosome (Fig. 4). In addition, the red-shifted Qy band accompanies strong exciton-coupled circular dichromism (CD) signals. These spectroscopic results indicate that in chlorosomal aggregates BChl molecules form a kind of *J*-aggregate, in which the transition dipole moments along the *y*-axis (the N21–N23 axis) are oriented in a well-ordered manner [43,58–61].

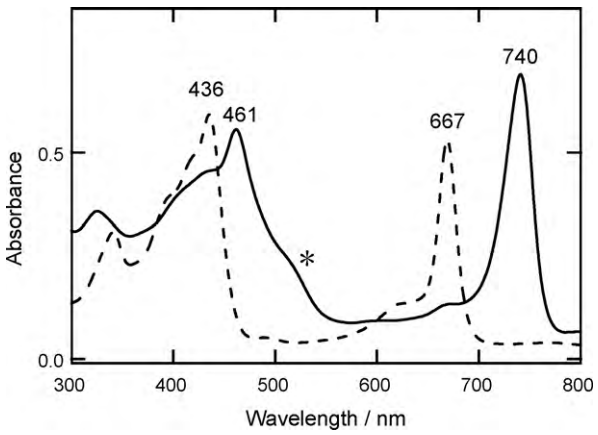


Fig. 4. Visible and near-infrared absorption spectra of natural chlorosome (aggregated form: the solid line) and isolated BChl-*c* in methanol solution (monomeric form: the dashed line). The band at * is an absorption band of carotenoids.

The chlorosomal supramolecular system shows us the possibility of making artificial photosynthetic units using self-assemblies of Chls. The desirable photosynthetic apparatuses would be provided by a simple mixing and stirring method. Self-aggregates of isolated Chl-*a* were prepared to make models for reaction center and LH antenna systems [62–64]. In non-polar organic solvents and an aqueous medium, Chl-*a* molecules self-aggregated to form dimers or oligomers depending on the preparation conditions. For example, in an aqueous alcoholic solution, Chl-*a* complexed with water molecules to give colloidal oligomers composed of lamellar sheets of stacked Chls [64]. The basic supramolecular structures of the Chl-*a* aggregates were different from that of the chlorosomal aggregate, because a Chl-*a* molecule has no hydroxy group that contributes the intermolecular coordination and hydrogen bonds found in chlorosomal aggregate. In contrast, the chlorosomal Chls, BChls-*c*, *d* and *e* as well as their model compounds self-aggregated along the Qy transition moment to give a highly ordered suprastructure. Actually, chlorosome-type self-aggregates of BChls and their mimics provided a useful LH antenna system. BChl-*c* isolated from a natural chlorosome self-aggregated in a non-polar organic solvent with a red-shifted Qy band and exciton-coupled CD signals [65–67]. Therefore, a chlorosomal

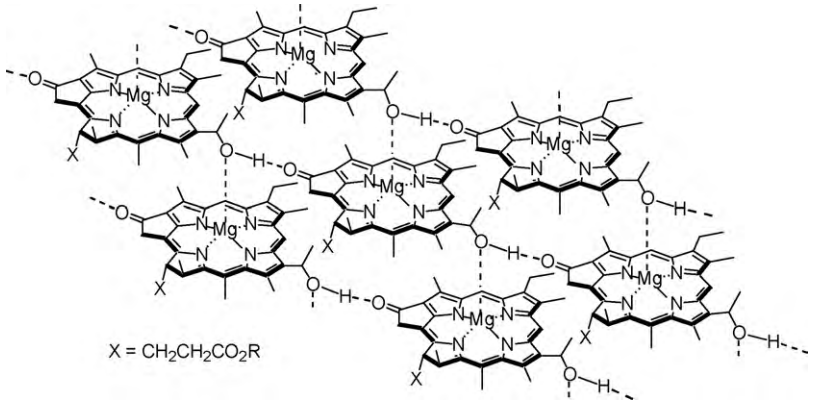


Fig. 3. Proposed supramolecular structure of BChl-*c* aggregate in a chlorosome.

supramolecular LH system is reproducible by a self-aggregation technique.

As described above, (B)Chl molecules possess a hydrophobic long hydrocarbon group at the 17-propionate side chain. Chlorosomal BChls have farnesyl, stearyl, etc., and contents of the hydrocarbon chain are dependent on the organisms. In addition, the central magnesium in (B)Chls readily makes axial coordination bonds with hetero atom(s) of organic solvent(s) to produce 5- and 6-coordinated states in a solution [68–70]. As a result, (B)Chl molecules are very soluble in polar organic solvents with a coordinating N or O atom such as pyridine, THF, or DMSO, but hardly soluble in water or non-polar organic solvents. Therefore, self-aggregates of (B)Chls can be prepared in an aqueous medium or in non-polar organic solvents through their π–π interaction. Actually, many *in vitro* self-aggregates of BChls-*c*, *d* and *e* were prepared in non-polar organic solvents [65–67] as well as Langmuir–Blodgett monolayers [71], spin-coated solid films [72,73] and solid powders [74,75]. In case of the natural chlorosome, BChl aggregates are in a microheterogeneous hydrophobic environment built by a lipid monolayer.

2.2. Aqueous self-aggregates of natural bacteriochlorophylls

To dissolve functional organic molecules in an aqueous medium is of great interest, because biomolecules basically act in an aqueous environment and such water-soluble compounds can be used for medical applications. Some attempts were carried out to solubilize natural Chl-*a* in an aqueous medium by using organic solvents [64], surfactants [76] and cyclodextrins [77,78]. The aqueous Chls or pheophytins (metal-free Chls) can be used for photodynamic therapy. Chlorophyllous pigments have large absorbances in a therapeutic window (650–800 nm) and the photo-excited pigments generate a long-lived triplet state that produces reactive oxygen species. In an aqueous surfactant or cyclodextrin solution, Chl molecules were in a hydrophobic environment of surfactant assemblies or a cyclodextrin pocket. In these cases, Chl-*a* molecules were in monomeric or oligomeric forms dependent on the conditions.

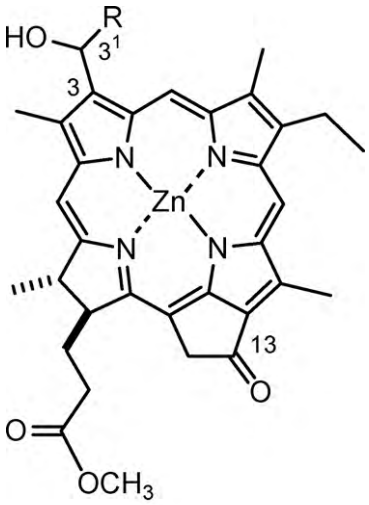
Chlorosome-type *J*-aggregates can be prepared not only in the non-polar solvent but also in an aqueous medium. BChls-*c*, *d* and *e* were hardly soluble in water, and it is difficult to disperse the natural pigment into an aqueous medium. Therefore, a small portion of polar organic solvents was used for preparation of the aqueous aggregates [55]. When a concentrated DMSO or acetone solution of BChl-*c* was diluted with a large volume of water, chlorosomal aggregates were reproduced in the aqueous medium with a red-shifted Qy absorption band. In addition, stable aqueous aggregates of chlorosomal BChls were prepared in the presence of surfactants. An aqueous aggregate of isolated BChl-*c* was prepared in the presence of monogalactosyl diglyceride (MGDG), one of the lipids consisting of a chlorosomal envelope [79]. The pigment-lipid assembly provided a stable chlorosome model. Self-aggregates of BChl-*c* were surrounded with the MGDG assembly and stabilized in a hydrophobic environment in the aqueous solution, similar to natural chlorosomes. In addition, chloroform or chloroform/methanol extracts from isolated chlorosomes, which contain BChl-*c*, carotenoids, lipids and a trace amount of BChl-*a*, were dispersed into water [80–82]. The absorption and CD spectra of the aqueous solution were very similar to those of intact chlorosomes. Moreover, electron microscopic measurements showed the morphology of the natural chlorosome was also reproduced by the simple dilution method of the BChl-lipid mixture. These *in vitro* aqueous BChl aggregates prepared with a surfactant provided good structural models for chlorosomes, in which BChl molecules organized in a similar manner as the natural system. These *in vitro* aqueous BChl aggregates prepared with a surfactant pointed out that the self-assembly technique is a good tool with which to prepare the structural model of chlorosomes. The artificial aggregate mimicked not only the molecular arrangement in the *J*-aggregate but also the microstructure of the molecular assembly.

3. Self-aggregates of synthetic analogues of bacteriochlorophylls

3.1. Synthesis and self-aggregates of zinc chlorins

Natural BChl-*c*/*d*/*e* molecules self-aggregate to form an effective structural model of chlorosomes. However, the natural pigments are relatively unstable, and the isolated BChls from green bacteria are not a single compound but a mixture of different stereoisomers and/or homologues. Therefore, simplified model pigments would be more useful for making the chlorosomal model. Most Chl models are zinc complexes of tetrapyrroles instead of the magnesium complexes [3,83–88], because the zinc analogues are readily prepared by treatment of free base tetrapyrroles with zinc(II) acetate, and the resulting zinc complexes are more stable than the naturally occurring magnesium complexes. In addition, zinc complexes have similar optical properties as the corresponding magnesium complexes [87]. Both zinc and magnesium tetrapyrroles have relatively long fluorescence lifetimes, which are favorable for efficient energy and electron transfers [89]. Moreover, zinc substituted BChl-*a* was found in *Acidiphilium rubrum* which is an aerobic bacterium growing under acidic conditions [90–92]. The fact that the naturally occurring zinc complex actually works in the early event of photosynthesis encourages us to use zinc tetrapyrroles for photosynthesis mimics.

A synthetic zinc chlorin **1** (Fig. 5) was prepared from Chl-*a* which is the most abundant Chls in nature [87]. The synthetic analogue overcomes some problems that occur in handling the natural BChl-*c*/*d*/*e*. Zinc chlorin **1** possesses a hydroxymethyl group at the 3-position instead of a chiral 1-hydroxyethyl group in BChl-*c*/*d*/*e*. The chemical modification avoided the problem of epimerization at the 3^1-position and dehydration to the 3-vinyl group. The synthetic model was well soluble in THF and showed a Qy band at 650 nm. When the monomeric solution of **1** was diluted with 99-fold volume of hexane, the Qy band was red-shifted to 740 nm due to the self-aggregation (Fig. 6). The artificial aggregate gave intense inverse-S shaped CD signals at the red-shifted Qy absorp-



1: R=H
2: R=CH_3

Fig. 5. Structures of synthetic zinc chlorins **1** and **2**.

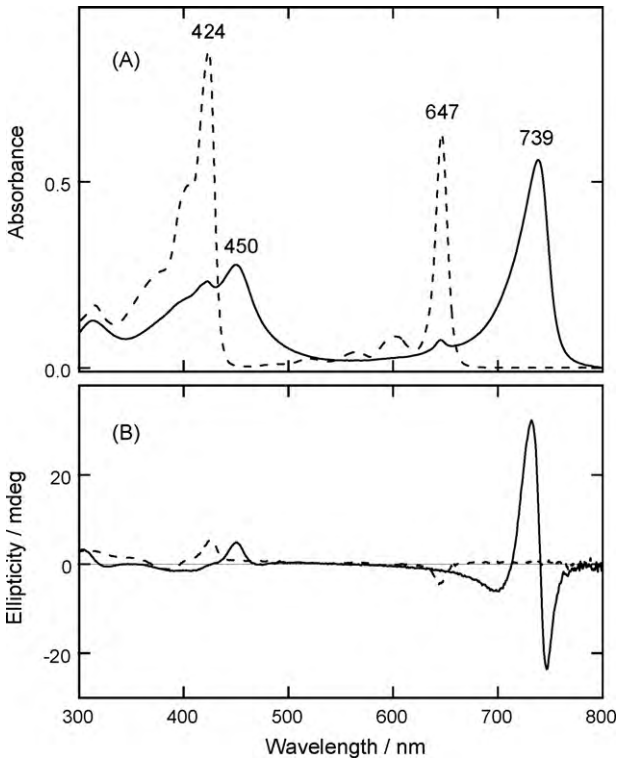


Fig. 6. Visible absorption (A) and CD (B) spectra of zinc chlorin **1** in neat THF (monomeric form: the dashed line) and in 1% THF-hexane (aggregated form: the solid line).

tion region. In addition, IR spectra supported the formation of the same intermolecular interactions as in BChl-*c*/*d*/*e* aggregates: C=O···H–O···Zn bonds among the 13-keto, 3^1-hydroxy groups and central zinc. These spectroscopic results indicated that the self-aggregate of the model compound **1** had the same supramolecular architecture as that of natural chlorosomes, i.e., the semi-synthetic model provides a good structural model for the natural supramolecular LH antenna system [87,93,94]. Chl derivatives lacking 13-keto or 3^1-hydroxy groups or central zinc were prepared, and these pigments did not show any red-shifted absorption bands in the same solvent. The results of the systematic chemical modifications obviously agree with the chlorosomal model structure in which the 13-keto and 3^1-hydroxy group and central zinc are essential for making the aggregate.

3.2. Aqueous self-aggregates of synthetic zinc chlorins

Similar to natural Chls, synthetic zinc chlorins self-aggregated not only in a non-polar solvent but also in an aqueous medium. Synthetic zinc chlorin **2** possessing a chiral 3-(1-hydroxyethyl) group (Fig. 5) was prepared as a mixture of the 3^1R- and 3^1S-stereoisomers, and each diastereomer was isolated by a single reversed-phase HPLC run [86]. The monomeric form of diastereomerically pure 3^1R- and 3^1S-isomers gave identical absorption spectra in THF. In THF-water, aggregates of 3^1R- and 3^1S-isomers gave different absorption spectra, indicating that the absolute configuration at the 3^1-position of **2** affected the structure of the *J*-aggregate. In addition, kinetics in self-aggregation was examined by a stopped-flow technique [95]. A monomeric solution of **2** in THF was rapidly mixed with water, and the absorbance of the mixed solution was monitored immediately after mixing. Interestingly, the aggregation kinetics of the stereoisomers were different, the 3^1R-isomer self-aggregated more rapidly than the 3^1S-isomer. In addition, a short-lived intermediate, a small aggregate of the 3^1R-isomer was found in the experiments. These model studies suggest that the 3^1R-isomer might self-aggregate to form a critical nucleus, which controls the pigment arrangement in the following aggregation process. Therefore, the stopped-flow studies on the aqueous aggregate would be useful to examine the aggregation process of the supramolecular antenna system.

In order to prepare a stable aqueous aggregate of synthetic zinc chlorins, some surfactants were added into the aqueous aggregate. A methanol solution of zinc chlorin **1** and α-lecithin, egg yolk phosphatidyl-choline, was diluted with a 99-fold volume of aqueous buffer solution, 10 mM Tris–HCl (pH = 7.5) [96]. A clear solution was obtained, giving a red-shifted Qy band at 730 nm. In the lipid–pigment mixture, the aggregates of **1** were surrounded with the assembly of the lipid to stabilize the aqueous aggregate. The dynamic light scattering measurement supported the formation of micelle-like aggregates with about a 200 nm hydrodynamic diameter. Moreover, the absorbance of the red-shifted Qy band of aggregated **1** was enhanced with an increase of the concentration of α-lecithin in the mixture. This result suggests that the addition of α-lecithin provided a micro-hydrophobic environment in the aqueous medium, in which zinc chlorin **1** formed the chlorosomal *J*-aggregates. Other (semi)natural surfactants, such as MGDG, β-octyl glucoside and cholic acid, as well as synthetic surfactants such as Triton X-100 were available for making the stable aqueous aggregates of **1**.

Natural chlorosomal aggregates consist of a mixture of the homologues and/or stereoisomers of BChls (Fig. 2). *In vitro* studies of BChl aggregates showed that the structural differences in both the absolute configuration at the 3^1-position and alkyl substituents at the 8- and 12-positions affected the supramolecular structure of chlorosome-type aggregates [49,97]. Actually, the Qy absorption peak of living cells was red-shifted as the 8^2-position of BChl-*d* was methylated [51]. The pigment heterogeneity might be important in making chlorosomal aggregates, but effect of the homologues and/or stereoisomers of BChls and the distribution of the pigments in a natural chlorosome are under discussion [98–100]. Aqueous chlorosome-like aggregates were prepared with a mixture of structurally different zinc analogues of BChls. Such a mixture of zinc chlorins gradually self-aggregated in an aqueous medium with α-lecithin when a methanol solution of two zinc chlorins and α-lecithin in a cellulose tube was dialyzed with water [101]. The dialysis technique offers a good preparation method for chlorosome-type aggregates, because a number of BChl molecules may slowly self-aggregate in an intact chlorosome [102]. The absorption spectra of the artificial aggregates prepared with a homologous or stereoisomeric mixture were not reproduced by the linear combinations of the two basic spectra of the pure aggregates. These results indicated that the zinc chlorin aggregates prepared with such mixtures were not composed of separated pure aggregates, but of scrambled aggregates of the two pigment components. These results suggest that natural chlorosomes consist of scrambled aggregates of homologues and stereoisomers of BChls.

The aqueous aggregates of the modified Chls provide a good model of chlorosomal LH antenna, in which the self-organized pigments were enveloped with a surfactant monolayer. The chlorosome mimics give us hope that the artificial LH antenna models practically collect sunlight as natural chlorosomal LH systems do. In order to make a functional model for chlorosomes, the aggregates of zinc chlorin **1** were prepared in the presence of an energy acceptor molecule. In a natural chlorosomal LH system of green non-sulfur bacteria, the light energy absorbed at the BChl aggregates efficiently transferred to a baseplate, which is a BChl-*a*-protein complex located on the lipid monolayer of the chlorosomal envelope facing the cytoplasmic membrane. The excitation energy transferred to the baseplate (λ_{abs} = 795 nm) focused on a special pair of reaction center (λ_{abs} = 865 nm) via other BChl-*a*-protein

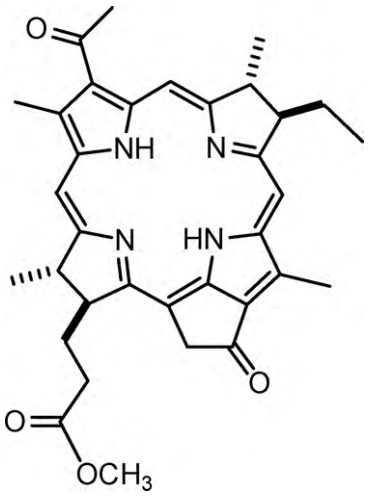


Fig. 7. Structure of free base bacteriochlorin acceptor molecule used in the artificial chlorosome.

complexes (λ_{abs} = 808, 866 nm). The time-resolved fluorescence measurements indicated that extremely fast and efficient energy transfer from chlorosomal BChl aggregate to the baseplate BChl-*a* occurs in a few picoseconds [103].

In order to reproduce the efficient energy transfer in chlorosome, the self-aggregate of zinc chlorin **1** and free base bacteriochlorin (Fig. 7) were used as an energy donor and an energy acceptor, respectively [93,94,96,104]. The energy acceptor molecule has a bacteriochlorin macrocycle as in BChl-*a* of baseplate, and the free base tetrapyrrole was readily prepared from BChl-*a* [105]. Zinc chlorin **1** and a small amount of bacteriochlorin acceptor were mixed (**1**:bacteriochlorin = 25:1) in a methanol solution of α-lecithin, and the mixture was dispersed into a buffer solution to give an energy transfer model. The absorption spectrum of aggregates containing the energy acceptor showed a Qy absorption band at 740 nm concomitant with a small absorption band at around 800 nm of free base bacteriochlorin; therefore, added bacteriochlorin acceptor did not disturb the self-aggregation of zinc chlorin **1**. Fluorescence spectra showed a fluorescence emission from aggregates of **1** at 745 nm, which decreased to about one-fifth by 4% addition of the energy acceptor. And a new emission band of bacteriochlorin acceptor appeared at around 820 nm by predominant excitation of zinc chlorin aggregate. In addition, fluorescence excitation spectra supported that the new emission band at 820 nm had come from excitation of the aggregated zinc chlorin. These spectroscopic results showed that the energy transfer from an oligomer of zinc chlorin **1** to a single free base bacteriochlorin molecule occurred, and the artificial aggregate acted as an LH antenna system (Fig. 8).

The time-resolved fluorescence measurements showed that the energy transfer in the artificial LH system was a very fast process. The timescale was about 8 ps [104], which is similar to that of energy transfer in a natural chlorosome. Therefore, the function of chlorosome is reproducible if chlorophyllous pigments are organized in the same manner as BChl aggregate in a chlorosome. The arrangement of energy acceptor molecule is thus important for the functional model of an LH antenna. When zinc chlorin **1** and bacteriochlorin acceptor were assembled in a non-polar organic solvent, no efficient energy transfer was observed. In the aqueous system described above, both zinc chlorin aggregate and bacteriochlorin are self-organized for efficient energy transfer in the microheterogeneous environment produced by the surfactant assembly.

Normally, a self-assembled supramolecule is in equilibrium with the monomeric form, and the aggregate easily disaggregates with the addition of other molecules. For example, aggregates of zinc chlorin **1** disaggregated to the monomeric form when excess amount of surfactant was added [96]. In addition, BChl-*c* self-aggregate in an intact chlorosome was disaggregated by the addition of 1-hexanol [106,107]. Stabilizing the supramolecular aggregate is necessary to fabricate a supramolecular device. In order to make a chemically and mechanically stable supramolecular antenna system, the sol-gel method was employed to form an organic-inorganic hybrid LH device [108,109]. An aqueous aggregate of zinc chlorin **1** was prepared in the presence of octadecyltriethoxysilane (ODTES) and tetraethoxysilane. ODTES worked

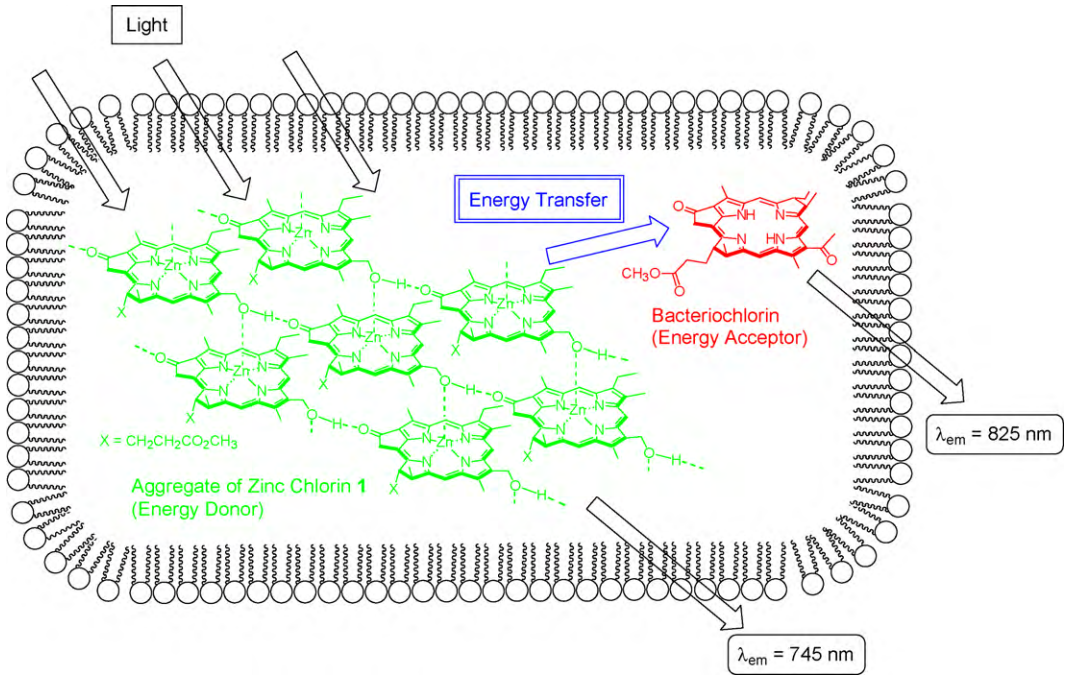


Fig. 8. Energy transfer from the photo-excited self-aggregate of zinc chlorin **1** to a bacteriochlorin acceptor.

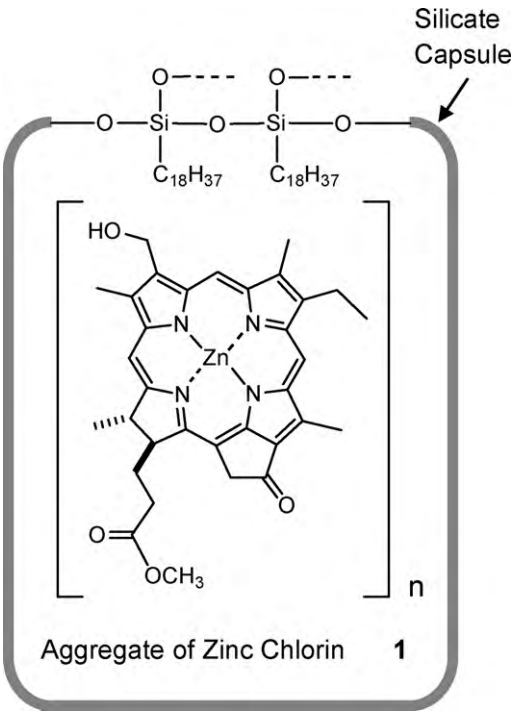


Fig. 9. Self-aggregate of zinc chlorin **1** surrounded with a silicate capsule.

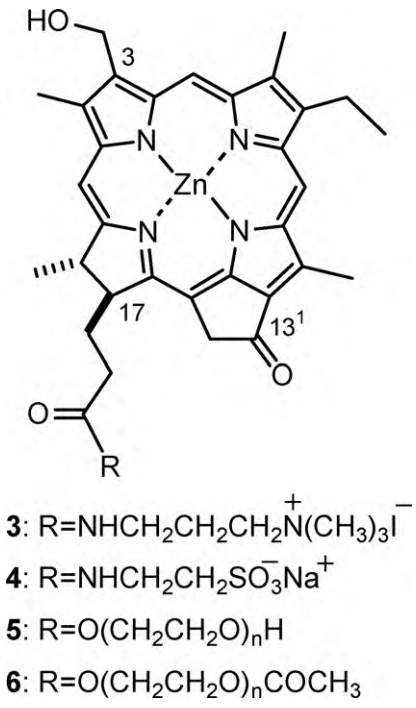


Fig. 10. Structures of amphiphilic zinc chlorins **3**–**6**.

as a surfactant to surround self-aggregates of the zinc chlorin. After acidic treatment, siloxane networks were formed on the surface of the aqueous aggregate to form a silicate capsule (Fig. 9). The silicate coated aqueous aggregates were obviously stabilized in comparison with the corresponding silicate-free aggregate. Therefore, such aqueous aggregates of Chl analogues provided a stable aqueous aggregate that acted as an LH antenna device.

3.3. Synthesis and self-aggregates of amphiphilic zinc chlorins

Amphiphilic molecules readily form stable aggregates in aqueous media, and the supramolecular structures of these aqueous aggregates are dependent on their molecular structure. By introducing a hydrophilic group into a hydrophobic cyclic tetrapyrrole, amphiphilic photo-active molecules were prepared. Synthetic amphiphilic porphyrins possessing anionic [110] or cationic groups [111] self-aggregated in an aqueous environment, which could be used for an LH antenna in an artificial energy conversion system. In addition, amphiphilic (B)Chls-*a* derivatives possessing an ammonium or carboxylate group were prepared [112–114]. The introduced hydrophilic group increased their solubility in an aqueous medium, and the amphiphilic (B)Chls and their free base derivatives were applied for photodynamic therapy.

Chlorosomal Chl pigments were also modified to amphiphilic molecules which provided unique aggregation properties in an aqueous medium. A hydrophilic group such as a cationic ammonium, anionic sulfonate or nonionic oligo(oxyethylene) group, was introduced into the 17-propionate side chain of zinc 3-hydroxymethyl-13^1-oxochlorin (Fig. 10) [115]. The propionic acid residue readily reacted with alcohols or amines in the action of a condensation agent to give the corresponding esters or amides, and the modification of the side group at the 17-position may not disturb the specific intermolecular interactions, C=O···H–O···Mg(Zn) [116], found in chlorosome-type self-aggregates of BChls and the model compounds. These ionic zinc chlorins were soluble in 1% methanol–water without adding any surfactants, and showed a slightly red-shifted Qy band at 675 nm. Their absorption spectra suggest that the ionic zinc chlorins **3** and **4** form small aggregates such as dimers in the aqueous medium. The introduced hydrophilic group might be strongly hydrated, and thus disturbed the further aggregation of the zinc chlorins.

Fig. 11 shows the proposed scheme of self-aggregation of zinc chlorin. First, monomeric species form an open (I) or closed (II) dimer with intermolecular coordination bond(s). The open dimer (I) will grow into a large aggregate with an intermolecular hydrogen bond, but the closed dimer (II) does not form the large aggregate. RR spectra of the dimeric zinc chlorin indicated that the central zinc was 5-coordinate, and the cationic derivatives lacking central zinc or 3^1-hydroxy group did not show the 675 nm Qy band.

The nonionic zinc chlorin **5** possessing an oligo(oxyethylene) chain showed a 675 nm Qy band concomitant with an additional 730 nm band of large aggregate immediately after aggregation. However, this 730 nm band gradually decreased with increase of the 675 nm band of the dimeric form in a few days. Therefore, the large aggregate of nonionic amphiphilic zinc chlorin was unstable, and was changed to a thermodynamically stable dimeric form. In addition, the nonionic **5** with a longer oxyethylene chain (n = 34.0 and 44.1) showed a 652 nm band of monomeric zinc chlorin. The long oxyethylene chain completely disturbed the self-aggregation and produced monomeric species in an aqueous medium.

The dimeric or monomeric forms of amphiphilic zinc chlorin changed to the chlorosome-type large aggregate when a small amount of surfactant was added to the aqueous solutions. An aqueous aggregate of nonionic zinc chlorin **5** (n = 2) prepared in the presence of Triton X-100 showed a Qy band at 740 nm of large aggregate [117]. The red-shifted band increased with increasing concentration of Triton X-100, and the addition of Triton X-100 obviously induced the further aggregation of the nonionic zinc chlorin **5**. The amphiphilic zinc chlorin co-aggregated with Triton X-100, and the surfactant provided a hydrophobic environment which stabilized the aggregates of zinc chlorin moiety. Other Triton-type surfactants with a different number of oligo(oxyethylene) units, Triton X-45 (n = 4 and 5) was available to make the large aggregate (Fig. 12); but the formation ratio of large aggregates over dimer was changed by the number of oligo(oxyethylene) units in both

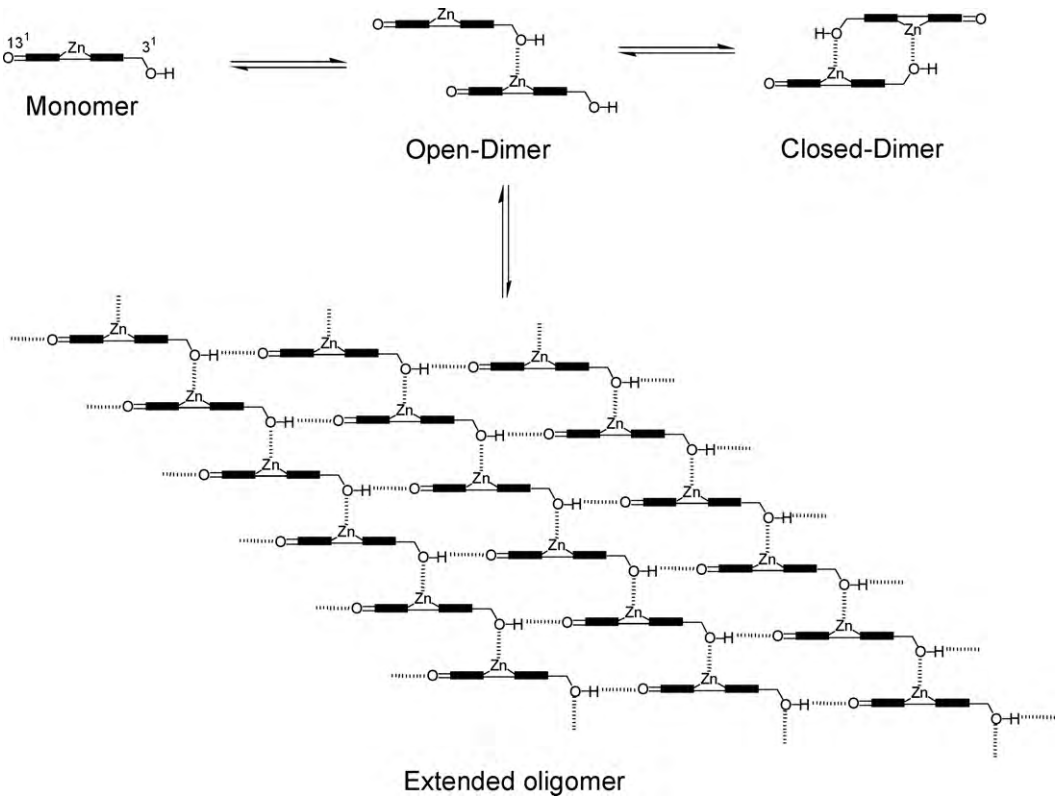


Fig. 11. Schematic drawings of proposed self-aggregation of zinc chlorin.

zinc chlorins and Triton surfactants. Co-aggregate of zinc chlorin **5** (n = 2) with Triton X-100 (n = 9 and 10) gave a large amount of chlorosome-type aggregate, but zinc chlorin **5** with longer oxyethylene chain (n = 6) favored Triton X-45 (n = 4 and 5) more than Triton X-100 (n = 9 and 10) to form large aggregates. Therefore, in the co-aggregate of zinc chlorin **5** and a Triton surfactant, the total amount of oxyethylene units in both the molecules determined the stability of chlorosomal aggregate. That is, the balance of the whole hydrophobic and hydrophilic parts in a supramolecule is important to make a stable aggregate.

In the case of ionic zinc chlorins, the addition of a specific surfactant accelerated the aggregation. The cationic zinc chlorin **3** formed a large aggregate with a 724 nm band when sodium 4-dodecylbenzenesulfonate (SDBS), an anionic surfactant, was added. However, the cationic zinc chlorin **3** did not accept cetyl pyridinium chloride (CPC), a cationic surfactant, for fabricating the chlorosomal aggregate. Therefore, the positive and negative charges in the ionic pigment and surfactant, respectively, are important for co-aggregation. Similarly, anionic zinc chlorin **4** provided a large aggregate with cationic CPC but not with anionic SDBS.

In addition, the presence of an organic solvent also induced the self-aggregation of the amphiphilic zinc chlorins [118]. To an aqueous solution of nonionic zinc chlorin **5** (n = 13.3), having a 675 nm band, a portion of dichloromethane was added and stirred. The aqueous phase obtained, showed a Qy absorption band at 720 nm, indicating the formation of chlorosome-type aggregate. Before treatment of dichloromethane, the zinc chlorin **5** was a dimeric species in an aqueous medium. Treatment of dichloromethane converted the dimeric form of zinc chlorin to the large aggregate. A micro-hydrophobic environment provided by the organic solvent caused the amphiphilic pigment molecules to form the chlorosome-type aggregate, in which the hydrophobic zinc chlo-

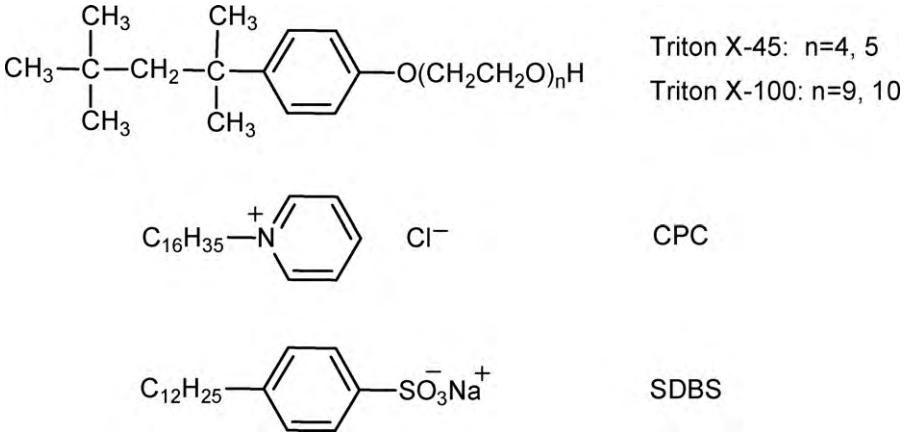


Fig. 12. Structures of surfactants used for the preparation of aqueous self-aggregates of amphiphilic zinc chlorins.

rin moiety and the hydrophilic oxyethylene chain were arranged inside and outside of the aqueous assembly, respectively.

Self-assembly of amphiphilic molecules strongly depended on the molecular structure, especially the balance of hydrophilic and hydrophobic parts in the molecule. Modified amphiphilic zinc chlorins possessing an end-capped oxyethylene chain were prepared [118–120]. The OH group at the terminal position of the oxyethylene chain was acetylated by acetic anhydride to give zinc chlorins **6**. Interestingly, the modified amphiphilic zinc chlorins **6** (n = 2–6.4) showed a 730 nm absorption band in 1% methanol–water without addition of surfactant or dichloromethane. The aqueous aggregate was stable and no precipitates were found when the solution was allowed to stand for several months. The end-capped oxyethylene chain surrounded the aggregated zinc chlorin moiety and stabilized the aqueous aggregate. The hydrophilic–lipophilic balance can be controlled by changing the number of oxyethylene units in an amphiphilic molecule. Zinc chlorin **6** possessing a longer oxyethylene unit (n = 13.3) showed a Qy band at 675 nm, which is characteristic of the formation of its dimer. Moreover, **6** with much longer oxyethylene chain (n = 44.1) was the monomeric form in the aqueous medium: λ_{max} = 652 nm. Therefore, the aggregation properties of zinc chlorins in aqueous media were controlled by changing the size of the hydrophilic group in the molecule. Monomer, dimer and large aggregate were selectively obtained by the simple dilution of a methanol solution of the model compounds with a large volume of water.

The amphiphilic zinc chlorins possessing an oxyethylene chain had an additional unique property. If the aqueous aggregate was prepared at a high concentration (>1 mM) and heated at 50 °C, the aqueous solution of **6** (n = 6–34.0) solution was gelated. An absorption spectrum of the gelated sample showed a red-shifted band at 730 nm, indicating that the zinc chlorin formed chlorosome-type *J*-aggregate in the gel form. Amphiphilic (zinc)chlorins lacking central zinc or 3^1-hydroxy group did not show such a gelation. Therefore, the amphiphilic zinc chlorin **6** (n = 6) formed a supramolecular gel, and aggregation of zinc chlorin macrocycle with the specific intermolecular interactions assisted the gelation. The amphiphilic (B)Chl analogue provides soft materials which act as LH antenna systems.

4. Conclusion

Self-assembled oligomers of isolated (B)Chls and their synthetic analogs have been studied in making structural and functional models of natural LH antennae including main extramembranous antennae of green photosynthetic bacteria, chlorosomes. All the (B)Chl molecules have a π–π interactive cyclic tetrapyrrole, a Lewis acidic Mg (or Zn) and Lewis basic carbonyl groups, and readily form supramolecular aggregates in various environments. In a chlorosomal LH system in particular, the characteristic BChl molecules are arranged without any help of peptides to give highly ordered self-aggregates by using specific intermolecular hydrogen and coordination bonds. Such a well-ordered and less-defected chlorosomal *J*-aggregate successfully functions as an efficient LH antenna. It is noteworthy that the other (B)Chl molecules also self-aggregate *in vitro* to form amorphous large oligomers with many structural defects and to be less or non-fluorescent due to newly produced decay pathways, giving no LH systems *in vivo*.

Self-aggregation of specific chlorophyllous pigments in an aqueous medium gave useful supramolecular LH antennae, while aqueous aggregates of (B)Chls-*a* did not. The former cyclic tetrapyrrole π-system assembled to form nanostructures in an aqueous medium, and addition of surfactants stabilized the aqueous supramolecular systems. The surfactant assemblies provided a microheterogeneous environment, in which such (B)Chl molecules were well organized for efficient excited energy migration. Consequently, aqueous aggregates of these (B)Chls reproduced the supramolecular structure and morphology of chlorosomal aggregates as well as their light-harvesting, energy-migrating and energy-transferring abilities. Introduction of a hydrophilic group into a chlorosomal Chl molecule is an alternative strategy to fabricate aqueous LH systems. The synthetic amphiphilic pigments formed stable aqueous aggregates, in which the tetrapyrrole chromophores were arranged in the same manner as chlorosomal Chls. Moreover, the self-aggregates of chemically modified amphiphilic Chls gave not only water-soluble nanoparticles but also hydrogels, which can be used as soft materials. It is promising that the chemically modified Chls or their synthetic mimics will provide useful energy conversion devices.

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