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Self-aggregation of synthetic multi-hydroxylated zinc chlorophylls

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ABSTRACT

A series of zinc 3-hydroxymethyl-13^1-oxo-(bacterio)chlorins possessing additional hydroxy group(s) on the B-ring were synthesized as models of bacteriochlorophylls-*c*/*d*/*e*, self-aggregative light-harvesting pigments of green photosynthetic bacteria. Tertiary and secondary alcoholic moieties on the 7- and/or 8-position(s) did not significantly interact with any other functional groups in their well-ordered self-aggregates. In contrast, the less sterically hindered primary alcoholic hydroxy group at the 7- and 8-substituents slightly caused random orientations of their molecular transition dipole moments in the supramolecule by unfavorable hydrogen bonding, which was competitive with the original 3^1-OH.

1. Introduction

Self-aggregates of dye molecules with a well-ordered supramolecular fashion is attractive matter with which to construct artificial light-harvesting systems and photo-active molecular nano-devices.[1] Bacteriochlorophyll(BChl)s-*c*, *d*, and *e* (see upper left of Fig. 1 as molecular structure of BChl-*d*), major chlorophyllous pigments found in green photosynthetic bacteria,[2–4] are such representatives in nature, that self-aggregate to form their light-harvesting antenna systems (called chlorosomes) by specific intermolecular interactions.[4–6] Natural chlorosomal BChls have a common structural motif programmed for self-aggregation: 3^1-OH, central Mg, and 13-C=O moieties inevitably present on the y-axis (see upper left of Fig. 1). Detailed supramolecular structures for self-aggregates of BChls in chlorosomes have not yet been obtained, but some recent investigations including solution-[7–11] and solid-state NMR data[12–17] and imaging techniques[18–20] as well as molecular modeling calculation,[21–25] provided partial progress in elucidating the structures. The protein-free light-harvesting self-assemblies are made by coordination bonding (3^1-O···Mg), hydrogen bonding (3^1-OH···O=C-13), and π–π stackings among the BChl molecules, and show red-shifted electronic absorption peaks due to the formation of excitonically coupled *J*-aggregates.[17,26,27] Such natural *J*-aggregates of chlorosomal BChls have also been reproduced by in vitro self-aggregates of their extracted BChls; similar chlorosomal self-aggregates were readily observed in non-polar organic solvents[28–34] as well as hydrophobic inner spaces of aqueous micelles formed by ionic and nonionic lipids as lecithin[32] and monogalactosyldiacylglycerol,[32,35–37] and nonionic surfactant as Triton X-100 (TX-100).[38] The latter microheterogeneous hydrophobic environments are somewhat closer to the natural chlorosomes where BChl self-aggregates are enveloped by a (glyco)lipid monolayer.

In addition to natural BChl self-aggregates, self-aggregation of their synthetic model compounds have been reported. Zinc chlorin **1** (see upper middle of Fig. 1) is one of the chlorosomal BChl models,[39] and has a molecular structure quite similar to natural BChl-*d*, except for the 3^1-demethylation, transmetallation of Mg to Zn, and transesterification of farnesyl to methyl group. These chemical modifications increase its chemical stability to be handled easily, but do not decrease the performance of making *J*-aggregates. Based on the molecular structure of zinc chlorin **1**, we have modified the peripheral substituent groups in chlorosomal models to elucidate how they affected the chlorosomal *J*-aggregation.

Removal of the interactive moieties in the chlorosomal models, at least one of the 3^1-OH, coordinative central metal and 13-C=O, resulted in no formation of chlorosomal *J*-aggregates,[28,39,40] while changing their chlorin π-system (to porphyrin and bacteriochlorin) as well as chemical modifications of the less interactive peripheral substituents, except for 3^1-OH and 13-C=O, did not affect the supramolecules significantly. Conversion of the chlorin to bacteriochlorin (as in **2**, Fig. 1)[41,42] and porphyrin π-system[43] dramatically shifted their redmost Q bands (≈ singlet excited energy levels) to longer and shorter wavelength regions, respectively. Modifying some peripheral substituents induced a slight influence on their optical properties, but did not decrease self-aggregativity of chlorosomal chlorins.[44–48] In contrast, introduction of additional functional groups, such as carbonyl and hydroxy groups, might have the potential to show undesired interconnectivity among the molecules.

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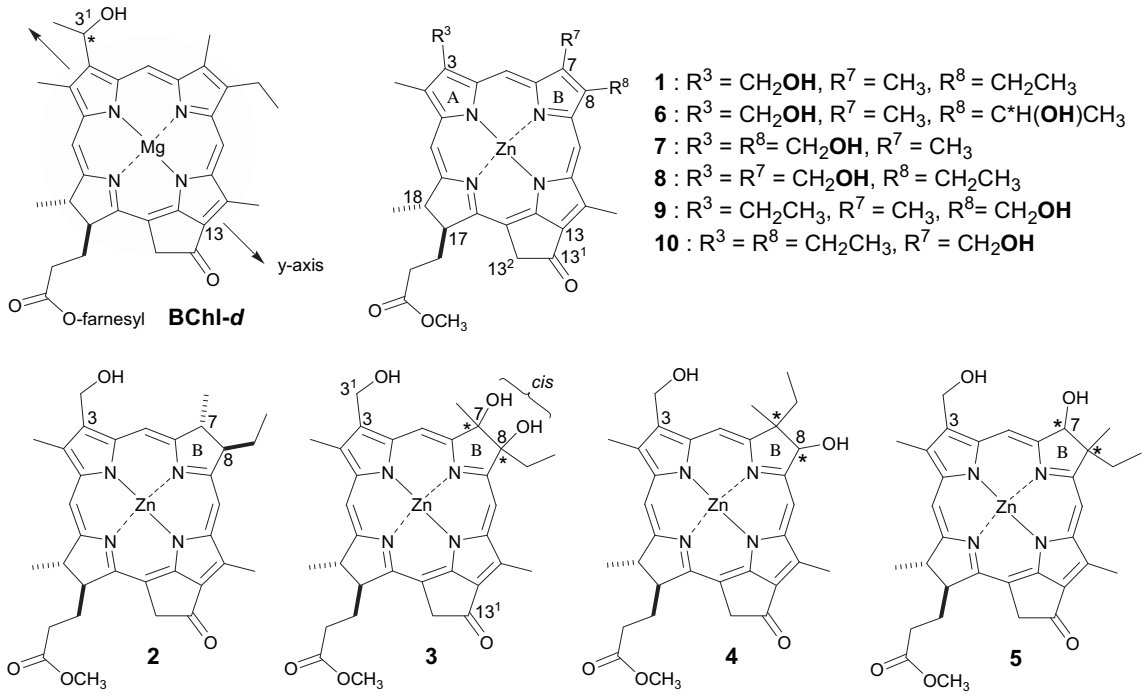
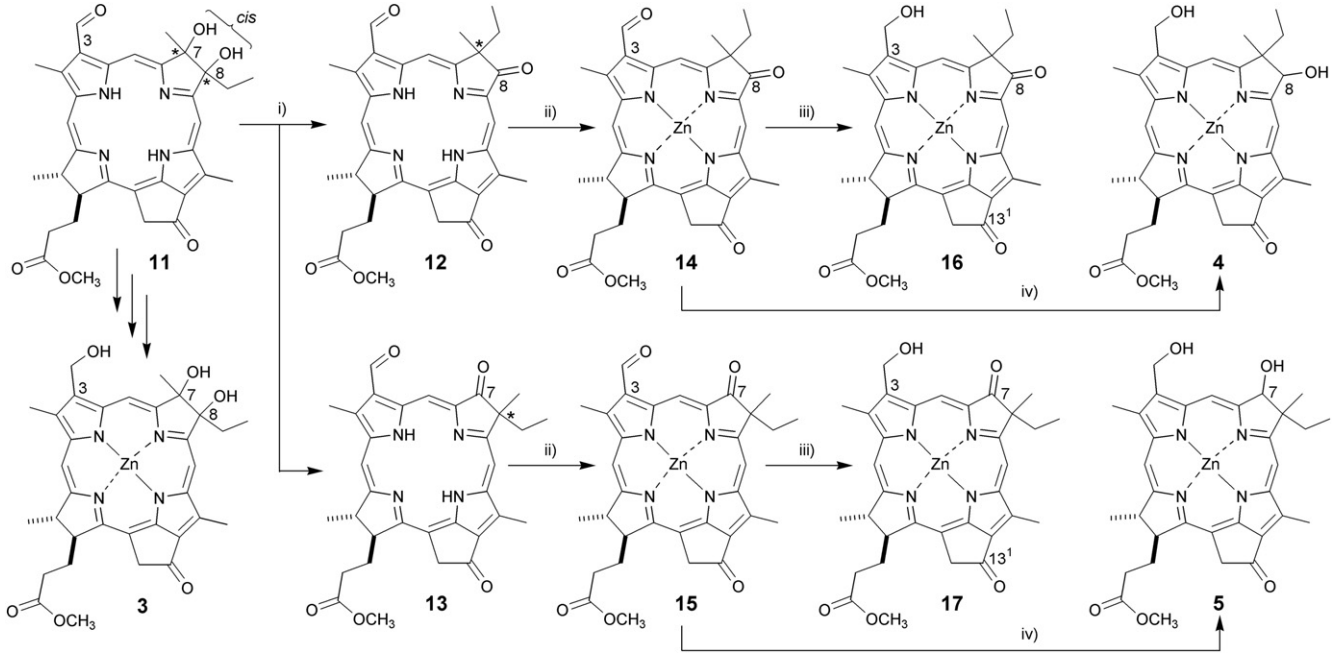


Figure 1. Molecular structures of natural BChl-*d* and synthetic zinc (bacterio)chlorins **1**–**10** possessing hydroxy group(s) on the A- and/or B-ring(s).

Zinc 3-hydroxymetyl-13^1-oxo-bacteriochlorins **16** and **17** possessing the 8- and 7-oxo groups, respectively, synthesized from 3-formyl-7,8-*cis*-dihydroxy-bacteriochlorin (**11**, see Scheme 1), self-aggregated in a non-polar organic solvent without any intermolecular interactions by the additional C8=O or C7=O group on the B-ring.[49] Synthetic zinc chlorins possessing 7- or 8-CHO group also gave chlorosomal *J*-aggregates without any disturbance by the additional C=O group on the B-ring.[50,51] Introduction of the additional C=O group on the 13^2-position, as an anhydride and an imide ring instead of an *exo*-five-membered E-ring, also provided chlorosomal *J*-aggregates.[52,53] These results are quite reasonable, because natural chlorosomal BChl-*e* also has an interactive 7-CHO, but many reports supported no involvement of the 7-C=O group in the chlorosomal supramolecular interaction.[32,33] The additional C=O groups in chlorosomal models had potential to form hydrogen bonding in the supramolecular structure but could not substitute for the role by the original 13-C=O. Changing positions of the interactive moieties in chlorosomal models greatly influenced their self-aggregation behavior.[54,55] Especially, exchanging the 3-hydroxymethyl group with 8-ethyl group in **1** to 3-CH_2CH_3-8-CH_2OH-**9** (Fig. 1) afforded disordered aggregates.[56]

In this report we prepared zinc 3-hydroxymethyl-13^1-oxo-(bacterio)chlorins **1**–**10** (Fig. 1) as chlorosomal model pigments



Scheme 1. Synthesis of self-aggregative zinc bacteriochlorins **3**–**5** possessing additional hydroxy group(s) at the 7- and/or 8-position(s). Reagents and conditions: (i) conc. H_2SO_4, FCC separation; (ii) $Zn(OAc)_2\cdot 2H_2O$, $CHCl_3$–pyridine, reflux; (iii) $^t BuNH_2\cdot BH_3$, CH_2Cl_2; (iv) $NaBH_4$, CH_2Cl_2–MeOH.

and examined the effect of the additional OH group(s) in the chlorosomal model compounds on their self-aggregation in aqueous micelles. Many reports have examined the substituent effect of the B-ring including alkyl, alkenyl, and carbonyl groups (vide supra),[57] but compounds possessing more interactive OH group(s) on the B-ring have been limited. The role of the 3^1-OH group in the natural BChls and synthetic models is thought to be more important than that of the 13-C=O group, because the 3^1-OH acts as the linkage between the central metal and C=O in a chlorosomal supramolecule by coordination and hydrogen bondings. Zinc 3-hydroxymethyl-7,8-*cis*-dihydroxy-13^1-oxo-bacteriochlorin **3** self-assembled in an aqueous micelle to form chlorosomal aggregates without any intermolecular disturbance by the additional 7,8-*cis*-dihydroxy moiety, which had been ascribed to the steric hindrance around the tertiary 7,8-OH groups.[42] Intramolecular hydrogen bonding between the two neighboring 7,8-OH groups in **3** should suppress their intermolecular interaction. Zinc bacteriochlorins **4** and **5** have the chlorosomal structural motif as do **1**–**3**, and an additional hydroxy group at the 8- and 7-positions, respectively, as a secondary alcoholic moiety. Zinc chlorins **6**–**8** are much closer to the original molecule **1** with the same chlorin framework, and their additional OH groups at the 7^1- or 8^1-position are more accessible to other chlorins because of their less sterically hindered primary and secondary hydroxy moieties. Self-aggregation behaviors of these synthetic pigments in aq TX-100 solution were examined by electronic and CD absorption spectroscopies.

2. Results and discussion

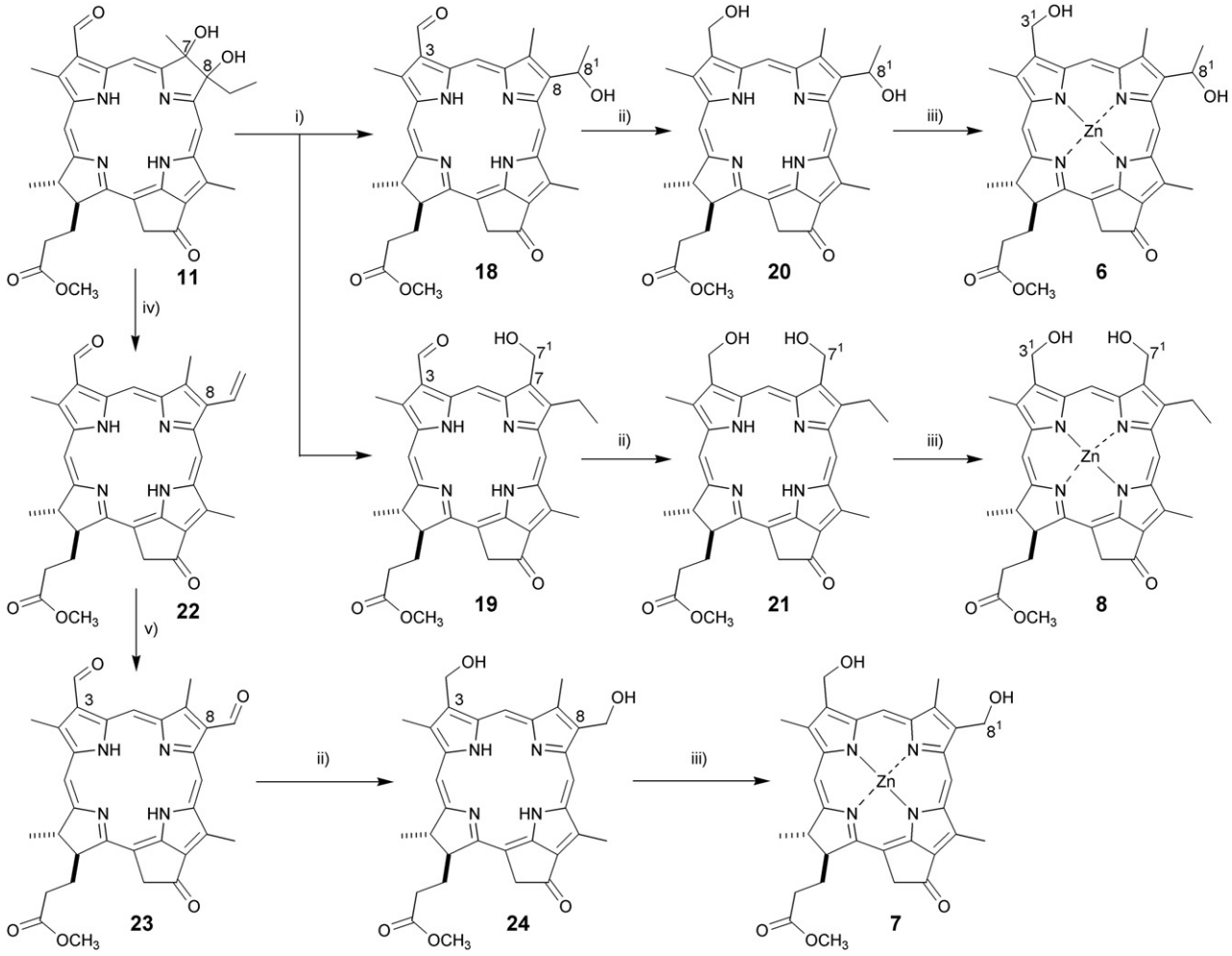
2.1. Synthesis of multi-hydroxylated zinc bacteriochlorins

Zinc 3-formylated 8-oxo- and 7-oxo-bacteriochlorins **14** and **15** were prepared from 3-formyl-7,8-*cis*-diol **11**[58] according to the reported procedures.[49] Reduction of the 3-formyl group in **14** or **15** was selectively achieved by a mild reductant such as ^{t}BuNH$_2\cdot$BH$_3$ (step iii in Scheme 1) to give 3-hydroxymethylated product **16** or **17**,[49] while the use of NaBH$_4$ (step iv) afforded doubly reduced product **4** (71% yield) or **5** (65%) possessing an additional secondary OH group at the 8- or 7-position on the B-ring. The reduction proceeded stepwise: the reduction of 3-CHO (aldehyde) followed by that of C8/7=O (ketone). The products **4** and **5** consist of four diastereoisomers due to the two newly and non-stereoselectively produced chiral centers at the 7- and 8-positions, and their stereochemical mixtures were used for the following optical measurements.

Zinc 3-hydroxymethyl-bacteriochlorin **2** lacking OH group around the 7,8-positions was synthesized (lower left of Fig. 1).[41] Zinc 3-hydroxymethyl-7,8-*cis*-dihydroxy-bacteriochlorin **3** was prepared[42] and its 5:6 diastereomeric mixture of 7,8-*cis*-dihydroxy moiety (7*R*,8*S* and 7*S*,8*R*) was used.

2.2. Synthesis of multi-hydroxylated zinc chlorins

Mono-dehydration of 7,8-*cis*-diol **11** afforded a regioisomeric mixture of 8-(1-hydroxyethyl)-**18** and 7-hydroxymethyl-**19** (step i in Scheme 2). The molar ratio of **18** and **19** was determined as 5:1 by



Scheme 2. Synthesis of self-aggregative zinc chlorins **6**–**8** possessing an additional hydroxy group at the 7^1- or 8^1-position. Reagents and conditions: (i) conc. HCl, 1,4-dioxane–H_2O, 50 °C; (ii) ^{t}BuNH$_2\cdot$BH$_3$, CH_2Cl_2; (iii) Zn(OAc)$_2\cdot$2H$_2$O, CH_2Cl_2–MeOH; (iv) *p*-TsOH, CH_2Cl_2–benzene, rt→reflux, then ethereal CH_2N_2; (v) cat. OsO_4, $NaIO_4$, THF–AcOH–H_2O.

the integral ratio in its ^{1}H NMR spectrum in $CDCl_3$. The major dehydration of **11**–**18** possessing secondary 8^1-OH (8^1R:S=1:1) was explained by different stabilities of the intermediate cations on the 7^1- and 8^1-carbon; a similar situation was previously reported.[50] The two products were largely overlapped on a silica gel column, so that the mixture was used for the following reduction without further separation (54%). The 3-formyl groups in **18** and **19** were reduced by ^{t}BuNH$_2$·BH$_3$ and gave a mixture of **20** and **21** (step ii). The separation of **20** with **21** by silica gel chromatography was easier than that of **18** with **19**, giving regioisomeric pure 8^1-OH-**20** (60%) and 7^1-OH-**21** (12%). Finally, zinc metalation of **20** and **21** afforded zinc 3^1,8^1-dihydroxylated **6** and 3^1,7^1-dihydroxylated **8**, respectively, in quantitative yields (step iii). 3,8-Bis(hydroxymethyl)-chlorin **24** was also synthesized from *cis*-diol **11** according to the procedures recently reported[59]: **11**→**22**→**23**→**24**. Finally, zinc metalation of **24** gave the corresponding zinc complex **7** quantitatively.

Zinc 3-hydroxymethyl-8-ethyl-chlorin **1**[39] and zinc 3-ethyl-8-hydroxymethyl-chlorin **9**[56] were prepared, and zinc 3-ethyl-7-hydroxymethyl-chlorin **10** was synthesized by zinc metalation of the corresponding free-base chlorin.[59]

2.3. Self-aggregation of zinc 3-hydroxymethyl-bacteriochlorins 2–5 in aq TX-100

In neat THF, zinc bacteriochlorins **2**–**5** showed sharp and intense electronic absorption bands (see Fig. S1). Three major bands observed at ultraviolet, visible, and near infrared regions were characteristic of the electronic absorption spectrum of a bacteriochlorin π-system and assigned to Soret (Bx+By), Qx, and Qy bands, respectively. Their CD signals were observed in the wavelength regions corresponding to the above three absorption peaks, whose intensities were small and all nearly the same (Fig. S1). These are typical of the exclusive presence of monomeric bacteriochlorin species in THF, which were axially ligated by a THF molecule and free from any intermolecular interactions. Their Soret and Qy absorption maxima were slightly different from each other (Table 1), which was ascribable to their different 7,8-substituents: 7,8-*trans*-dialkyl, 7,8-*cis*-dialkyl, and $(OH)_2$, 7,7-dialkyl/8-OH and 8,8-dialkyl/7-OH for **2**, **3**, **4**, and **5**, respectively. The 7,8-substitution patterns distorted the bond lengths and angles of the pyrrole moiety at the B-ring, which slightly influenced the electron-absorbing bacteriochlorin π-systems.

Table 1
Soret and Qy absorption maxima (λ_{max})[a] of monomeric and oligomeric zinc 3-hydroxymethyl-bacteriochlorins **2**–**5**, and their red-shift values (Δ)[b] in Qy band by self-aggregation

Compound	λ_{max}/nm				Δ/cm^{-1}
	Soret		Qy		
	Monomer	Aggregate	Monomer	Aggregate	
2	346/386	369	727	860	2130
3 (7,8-OH)	349/384	390	721	878	2480
4 (8-OH)	348/384	381	720	868	2380
5 (7-OH)	348/387	379	725	902	2710

[a] Monomers were observed in THF, and aggregates were observed in an aq 0.025% v/v TX-100 solution.
[b] $\Delta=(1/\lambda_{max}[\text{monomer}]-1/\lambda_{max}[\text{aggregate}])\times10^7$.

Even in the presence of additional interactive hydroxy group(s) at the 7- and/or 8-position, chlorosome-like self-aggregation of zinc bacteriochlorins **3**–**5** occurred in aq 0.025% v/v TX-100 solution, as was easily confirmed by their color changes as well as electronic absorption spectra showing red-shifted and broadened Qy absorption peaks above 800 nm, similarly to **2** (Fig. 2). To reach the monomer-aggregate equilibrium smoothly, the aqueous solutions were incubated at 50 °C for 30 min. The resulting solutions did not show any more time-dependent spectral changes even after standing for a couple of days. Induced CD signals at the regions of the newly appeared absorption peaks were observed (Fig. S2), indicating the presence of excitonic coupling among the pigments; chlorosomal *J*-aggregates were formed. Compared to the monomeric Qy band situated at around 720 nm (Table 1), Qy absorption maxima of these bacteriochlorin self-aggregates in the micellar solution moved to near infrared regions (Table 1 and Fig. 2), similarly to the previous reports.[41,42,49]

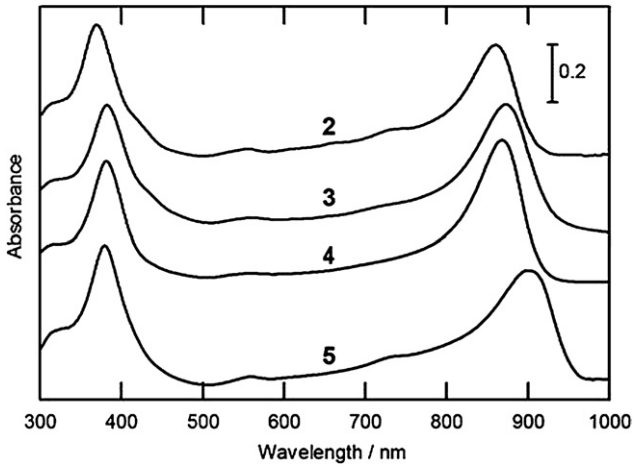


Figure 2. Electronic absorption spectra of zinc 3-hydroxymethyl-bacteriochlorins **2**–**5** in an aq 0.025% v/v TX-100 solution containing 1% v/v THF. Concentrations of all the samples were ca. 10 μM.

Steric bulkiness around the 7,8-positions (B-ring) of **3**–**5** increased more than **2** and their red-shift values (Δ) in the Qy band by self-aggregation also increased (see right column in Table 1). Each sp^3 carbon atom at the 7- and 8-positions in a bacteriochlorin π-system could accommodate two substituents directed toward the spaces above and below the π-plane, which seems unfavorable for tight stacking of the molecules. However, various reports showed that the sterically large substituents on the B-ring rather stabilized *J*-aggregates of chlorosomal chlorophylls in spite of the increase of steric bulkiness.[57] Actually, natural BChls are a complex mixture of homologs with various degrees of the 8^2-methylation as shown in ethyl, propyl, isobutyl, and neopentyl groups, and all of them self-aggregated in vivo as well as in vitro. The Qy bands of the self-aggregates of natural BChls were shifted to a longer wavelength with increase in the 8^2-methylation.[30,31,33,34,38,57] Large red-shifts in the present zinc 7,8-substituted bacteriochlorins **3**–**5** might be attributable to any preferable interaction of the 7,8-substituents in a supramolecule. It is noteworthy that the 3^1-OH group coordinated exclusively to the central zinc atom of another molecule in a self-aggregated supramolecule and that coordination of the 7- and/or 8-OH groups could not be observed in the present system. If the unfavorable coordination of the 7- and/or 8-OH group occurs, molecular stackings in a supramolecule would be disordered, to give a less red-shifted Qy absorption band by the self-aggregation.

The Δ-value of 7-OH-**5** (2710 cm^{-1}) was larger than that of regioisomeric 8-OH-**4** (2380 cm^{-1}) and the similar situation had been already observed in chlorosomal self-aggregation of 7-oxo-**17** (2450 cm^{-1}) and 8-oxo-**16** (1970 cm^{-1}) in a non-polar organic solvent.[49] The latter difference in Δ-values of **16** and **17** had been clearly explained by the steric effect of the neighboring 8/7-dialkyl group. Therefore, the former difference in Δ-values of **4** and **5** were supported to be ascribable to a similar steric effect of the neighboring dialkyl group. The additional secondary OH groups in **4** and **5** were

useless for their self-aggregation, similarly with the C=O group in **16** and **17**. The tertiary and secondary OH group(s) in **3**, **4**, and **5** were not used for the coordination and hydrogen bondings with an adjacent molecule, probably due to their steric inaccessibility.

2.4. Self-aggregation of zinc 3-hydroxymethyl-chlorins 1, 6–10 in aq TX-100

THF solutions of zinc chlorins **1**, **6**–**10** showed similar electronic absorption spectra (Fig. S3), where two sharp absorption bands were observed and assigned as Soret (~420 nm) and Qy bands (~640 nm). These data indicated that no intermolecular interactions among the pigments were observed in THF, which was confirmed by less intense CD signals (Fig. S3). Compared to zinc bacteriochlorins, Qx bands of zinc chlorins were weakened by the less asymmetric π-system (C7=C8, C17–C18). The Qy absorption maxima of the 7^1- or 8^1-hydroxylated zinc chlorins **6**–**10** were shifted to a slightly lower wavelength than that of **1** lacking a hydroxy group at these positions, while all the Soret maxima were situated at almost the same wavelength (Table 2). Especially, Qy bands of Zn-7^1-OH-chlorins **8** and **10** were blue-shifted from those of the corresponding Zn-8^1-OH-chlorins **6**/**7** and **9**. These differences were ascribed to the substitution effect at the 7,8-positions. Synthetic zinc 3-(1-hydroxyethyl)-chlorin possessing a strong electron-withdrawing CHO group at the 7-position showed its Qy absorption maximum at the shorter wavelength region (628 nm, in THF), compared to its regioisomeric 8-CHO-chlorin (645 nm).[51] The present difference between 7- and 8-hydroxymethylation indicated that a hydroxymethyl group at the 7,8-positions influenced the chlorin π-system as a weak electron-withdrawing group.

Table 2
Soret and Qy absorption maxima (λ_{max})[a] of monomeric and oligomeric zinc 3-hydroxymethyl-chlorins **1**, **6**–**8**, and 3-ethyl-chlorins **9**, **10**, and their red-shift values (Δ)[b] in Qy band by self-aggregation

Compound	λ_{max}/nm				Δ/cm^{-1}
	Soret		Qy		
	Monomer	Aggregate[c]	Monomer	Aggregate[c]	
1	425	451	647	743	2000
6 (8^1-OH/CH$_3$)	426	454	645	742	2030
7 (8^1-OH)	426	(431), 454	646	(654), 752	2180
8 (7^1-OH)	426	(431), 461	642	(649), 716, 739	1610, 2040
9 (8^1-OH)	425	(430)	643	(652)	—
10 (7^1-OH)	425	(429)	639	(646)	—

[a] Monomers were observed in THF, and aggregates were observed in an aq 0.025% v/v TX-100 solution.
[b] $\Delta=(1/\lambda_{max}[\text{monomer}]-1/\lambda_{max}[\text{aggregate}])\times 10^7$.
[c] Absorption maxima of oligomeric **7** and **8** were estimated by their second derivatives. The values in parentheses indicate residual monomeric peaks.

Aqueous micellar solutions of these zinc chlorins were prepared by the same procedures described above in zinc bacteriochlorins. 3-Hydroxymethylated chlorins **1**, **6**–**8** self-aggregated in the aqueous media, which were represented by their red-shifted and broadened Soret and Qy bands (Fig. 3) as well as induced CD signals (Fig. S4), compared to their monomeric spectra. The typical absorption spectral change was observed in **1** from monomer in THF (425/647 nm for Soret/Qy maxima) to chlorosomal *J*-aggregates in aq 0.025% v/v TX-100 (451/743 nm), and zinc 3-hydroxymethyl-8-(1-hydroxyethyl)-chlorin **6** showed exactly the same behavior: 426/645 nm to 454/742 nm for monomer to oligomer. The secondary 8^1-OH group in **6** was not involved in the chlorosomal molecular interactions, rather it was exclusively the primary 3^1-OH. Self-aggregation behaviors of zinc chlorins **7**/**8** possessing two primary OH groups at the 3^1- and 8^1/7^1-positions were slightly altered. Zn-3^1,7^1-OH-chlorin **8** in the aq TX-100 solution showed its Qy absorption maxima at 651 and 719 nm in the region above 600 nm. The 651-nm peak was assigned to its residual monomeric species, and the small amount of monomeric **8** was supported by the 431-nm peak of monomeric Soret band (see * in Fig. 3). The relatively broadened band at 719 nm was ascribable to its oligomeric species, which had a shoulder at the longer wavelength region (see Fig. 3). Two components at 716 and 739 nm were estimated from the second derivative (Table 1), indicating that at least two oligomeric species should be present as the self-aggregates of **8**. Electronic absorption spectrum of Zn-3^1,8^1-OH-chlorin **7** in the aq micellar solution showed its broadened Qy band at around 740 nm, which consists of several self-aggregated species. Residual monomer of **7** was observed from peaks at 431 and 654 nm, as shown in * of Figure 3. Double functional roles are given to the OH group in chlorosomal pigments, coordination, and hydrogen bondings as described in the Introduction. The broad spectra in self-aggregated **7** and **8** indicated that the additional OH group at the 8^1- and 7^1-positions of **7** and **8** could intermolecularly interact with the other molecules by coordination with central zinc or hydrogen bonding to 13-C=O to disturb formation of sole stable and large *J*-aggregates.

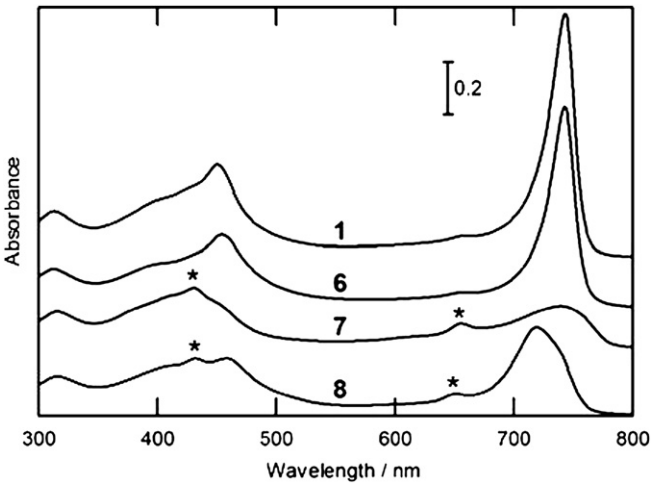


Figure 3. Electronic absorption spectra of zinc 3-hydroxymethyl-chlorins **1**, **6**–**8** in an aq 0.025% v/v TX-100 solution containing 1% v/v THF. Concentrations of all the samples were ca. 10 μM. Asterisk indicates the absorption peaks of residual monomeric species.

We also examined self-aggregation ability of 8^1-OH-**9** and 7^1-OH-**10** lacking the 3^1-OH. Aq TX-100 solutions of zinc 3-ethyl-chlorins **9** and **10** showed sharp absorption spectra, similar to those of their monomeric solutions in THF (see the two at lower left in Figs. S3 and S5). Their CD spectra in the aq TX-100 solution gave small signals similar to those in THF (two lower right in Figs. S3 and S5). These results indicated that zinc chlorins **9** and **10** lacking 3-hydroxymethyl group were unfavorable to make chlorosomal *J*-aggregates in such a micelle. Even the co-presence of chlorosomal pigment **1** and Zn-8^1- or 7^1-OH-chlorin **9** or **10** was not associated with the formation of mixed *J*-aggregates (two upper in Fig. S5). Zn-3^1-OH-chlorin **1** individually self-assembled and Zn-8^1/7^1-OH-chlorins **9**/**10** were left alone to be monomeric. In the initial stage of chlorosomal self-aggregation, coordination of OH with Zn is formed to give linear oligomer, which is stabilized by their π–π stackings, then hydrogen bonding network grows up the oligomer to the three-dimensional supramolecules. No observation of scrambled oligomers of 8^1/7^1-OH-**9**/**10** with 3^1-OH-**1** indicated that a hydroxy group at the 8^1/7^1-positions in **9**/**10** could not act as a chlorosomal substituent effectively, especially, the coordination bonding was not given by the use of the OH group on the B-ring. These results indicated that the intermolecular interaction of 8^1- and 7^1-OHs in **7**

and **8** should be limited to form hydrogen bonding. The two oligomeric species observed in self-aggregated **8** could be explained by two possible hydrogen bonding networks; 3^1-OH···O=C-13 and 7^1-OH···O=C-13. More complicated oligomers in self-aggregates of **7** might be ascribable to a steric factor around the 8^1-OH: less sterically hindered 8^1-OH in **7** possessing a methyl group at the adjacent 7-position had potential to interact more flexibly than 7^1-OH in **8** possessing the larger 8-ethyl group. Thus, the presence of interactive primary OH group on the B-ring as in **7** and **8** partially affected their intermolecular interactions among the chlorosomal self-aggregates. The role of the 8^1/7^1-OHs in **7**/**8** was largely limited to a hydrogen bonding donor to the 13-C=O, but they were not alternatives to the original 3^1-OH having dual functions of hydrogen bond and coordination.

3. Conclusion

Zinc 3-hydroxymethyl-(bacterio)chlorins possessing additional hydroxy group(s) on the B-ring were prepared efficiently from Chl-*a*. Electronic and CD absorption spectral analyses of their synthetic compounds in an aq TX-100 solution showed that the presence of the 3^1-OH was dominantly requisite for the chlorosomal *J*-aggregation. Tertiary and secondary OHs on the B-ring in zinc bacteriochlorins **3**–**5** did not disturb their chlorosomal aggregation due to the steric hindrance around the OH group(s). Secondary 8^1-OH in zinc chlorin **6** was also silent in the formation of such *J*-aggregates. In contrast, primary 8^1- and 7^1-OH groups in **7** and **8** affected their self-aggregation: several oligomeric species having different alignments of the Qy transition dipole moments were confirmed by the electronic absorption spectra. Such additional primary OH groups in chlorosomal chlorins might cause formation of the two hydrogen bonding, 3^1-OH···O=C-13 as well as 7^1/8^1-OH···O=C-13, but most intermolecular interactions would be promoted by the combination of original 3^1-OH, central Zn, and 13-C=O moieties.

4. Experimental

4.1. General

Electronic absorption and CD spectra in a solution were measured by a Hitachi U3500 spectrophotometer and Jasco J-720 W spectropolarimeter, respectively, with a 10-mm quartz cell. ^{1}H NMR spectra in chloroform-*d* were recorded by a JEOL ECA-600 (600 MHz); tetramethylsilane (δ_H=0.00 ppm) was used as an internal standard. For NMR measurements of zinc complexes, 3% v/v pyridine-d_5 was added for their monomerization. ^{1}H–^{1}H COSY and NOESY (τ_m=400 ms) techniques were used to confirm the molecular structures. FCC was performed with silica gel (Merck Kieselgel 60, 9358). HPLC was carried out with a Shimadzu LC-10AD$_{VP}$ pump, SPD-M10A$_{VP}$ diode-array detector, SCL-10A$_{VP}$ system controller and a packed ODS column (Cosmosil 5C18AR-II, 10φ×250 mm). High resolution FAB mass spectra were obtained by a JEOL GC-mate II; samples were dissolved in CH_2Cl_2 ($CHCl_3$–MeOH for zinc complexes) and *m*-nitrobenzyl alcohol and polyethylene glycol were added as a matrix and an internal standard, respectively. All solvents were commercially available and used without further purification. Syntheses were performed under nitrogen atmosphere in the dark, and all spectral measurements were performed at rt.

4.2. Materials

Zinc 3-hydroxymethyl-chlorin **1**,[39] zinc 3-hydroxymethyl-bacteriochlorin **2**,[41] zinc 3-hydroxymethyl-7,8-*cis*-dihydroxy-bacteriochlorin **3**,[42] zinc 3-ethyl-8-hydroxymethyl-chlorin **9**,[56] 3-formyl-7,8-*cis*-dihydroxy-bacteriochlorin **11**,[58] zinc 3-formyl-8-oxo-bacteriochlorin **14**,[49] zinc 3-formyl-7-oxo-bacteriochlorin **15**,[49] 3,8-hydroxymethyl-chlorin **24**,[59] and methyl 7^1-hydroxy-mesopyropheophorbide-*a* (3-ethyl-7-hydroxymethyl-chlorin)[59] were synthesized according to reported procedures.

4.3. Synthetic compounds

*4.3.1. Zinc 3-hydroxymethyl-8-hydroxy-bacteriochlorin **4**.* To a stirred CH_2Cl_2 solution (20 ml) of zinc 3-formyl-8-oxo-**14** (5.2 mg, 8.3 μmol), a MeOH solution saturated with $NaBH_4$ was added dropwise. The reaction was monitored by visible spectroscopy; reduction of 3-CHO caused a blue-shift in the Qy band (738→688 nm for **14**→**16**), followed by that of C8=O giving a red-shift (688→719 nm for **16**→**4**). After complete conversion, the reaction mixture was poured into water and extracted with CH_2Cl_2 until the aqueous layer was colorless. The combined extracts were dried over Na_2SO_4 and evaporated to dryness. The residue was purified with HPLC (pyridine/H_2O/MeOH=1/9/90, 2 ml/min, retention time=7.9 and 8.3 min) and recrystallization from $CHCl_3$ and hexane, affording **4** (3.7 mg, 71%) as a 7,8-diastereomeric mixture of its four stereoisomers: VIS (THF) λ_{max}=720 (rel intensity, 0.67), 549 (0.32), 384 (0.66), 348 nm (1.0); ^{1}H NMR (3% pyridine-d_5–$CDCl_3$) δ=8.48$_8$/8.48$_7$ (1H, s, 10-H), 8.06/8.05 (1H, s, 5-H), 7.94 (1H, s, 20-H), 5.88/5.87 (1H, s, 8-H), 5.58 (2H, s, 3-CH_2), 4.88, 4.76$_5$/4.76$_1$ (each 1H, d, *J*=19 Hz, 13^1-CH_2), 4.09 (1H, m, 18-H), 3.93 (1H, m, 17-H), 3.55 (3H, s, 17^2-CO_2CH_3), 3.37 (3H, s, 12-CH_3), 3.15$_2$/3.14$_9$ (3H, s, 2-CH_3), 2.40, 2.30, 2.18, 1.92 (each 1H, m, 17-CH_2CH_2), 2.29, 2.18 (each 1H, m, 7-CH_2), 1.71/1.67 (3H, s, 7-CH_3), 1.60/1.59 (3H, d, *J*=7 Hz, 18-CH_3), 0.81/0.68 (3H, t, *J*=7 Hz, 7^1-CH_3), two OHs were lost due to chemical exchanges; MS (FAB) *m*/*z* 632.1976 (M^+), calcd for $C_{33}H_{36}N_4O_5Zn$: 632.1977.

*4.3.2. Zinc 3-hydroxymethyl-7-hydroxy-bacteriochlorin **5**.* Similarly to **14**→**4**, zinc 3-formyl-7-oxo-**15** (8.8 mg, 14 μmol) was treated with $NaBH_4$, which was monitored by visible spectra; the Qy band of the reaction mixture was changed by the reduction of 3-formyl group (748→730 nm for **15**→**17**) followed by that of 7-oxo group (730→732 nm for **17**→**5**). HPLC purification (pyridine/H_2O/MeOH=1/9/90, 2 ml/min, retention time=8.5 and 8.9 min) and recrystallization ($CHCl_3$–hexane) gave **5** (5.8 mg, 65%) as a 7,8-diasteremeric mixture: VIS (THF) λ_{max}=725 (rel intensity, 0.97), 550 (0.35), 387 (0.71) 348 nm (1.0); ^{1}H NMR (3% pyridine-d_5–$CDCl_3$) δ=8.44/8.43 (1H, s, 5-H), 8.16/8.15 (1H, s, 10-H), 8.00/7.99 (1H, s, 20-H), 5.91$_1$/5.90$_5$ (1H, s, 7-H), 5.61$_3$/5.61$_0$, 5.58$_0$/5.57$_5$ (each 1H, d, *J*=12 Hz, 3-CH_2), 4.93/4.92, 4.80/4.79 (each 1H, d, *J*=19 Hz, 13^1-CH_2), 4.11 (1H, m, 18-H), 3.96 (1H, m, 17-H), 3.55 (3H, s, 17^2-CO_2CH_3), 3.40$_9$/3.40$_5$ (3H, s, 12-CH_3), 3.18/3.17 (3H, s, 2-CH_3), 2.43, 2.29, 2.15, 1.92 (each 1H, m, 17-CH_2CH_2), 2.21, 2.09 (each 1H, m, 8-CH_2), 1.81/1.80 (3H, s, 8-CH_3), 1.61/1.60 (3H, d, *J*=7 Hz, 18-CH_3), 0.67/0.63 (3H, t, *J*=7 Hz, 8^1-CH_3), two OHs were lost due to chemical exchanges; MS (FAB) *m*/*z* 632.1981 (M^+), calcd for $C_{33}H_{36}N_4O_5Zn$: 632.1977.

*4.3.3. 3-Formyl-8-(1-hydroxyethyl)-chlorin **18** and 3-formyl-7-hydroxymethyl-chlorin **19**.* According to the previous report,[50] monodehydration of **11** (84.7 mg, 145 μmol) gave a 5:1 mixture of 8-(1-hydroxyethyl)-**18** and 7-hydroxymethyl-**19** (44.3 mg, 54%) after purification with FCC (10–15% Et_2O–CH_2Cl_2) and recrystallization (CH_2Cl_2–hexane): ^{1}H NMR ($CDCl_3$, **18**:**19**=5:1, 8^1*R*/*S* of **18**=1:1) δ=11.56 (1H, s, 3-CHO of **18**), 11.52 (1H, s, 3-CHO of **19**), 10.45, 9.67, 8.84 (each 1H, 5-, 10-, 20-H of **19**), 10.33/10.32, 10.15/10.14, 8.83 (each 1H, 5-, 10-, 20-H of **18**), 6.23 (1H, m, 8-CH of **18**), 5.84 (2H, s, 7-CH_2 of **19**), 5.33, 5.18 (each 1H, m, 13^1-CH_2 of **18** and **19**), 4.57 (1H, m, 18-H of **18** and **19**), 4.38 (1H, m, 17-H of **18** and **19**), 3.85 (2H, q, *J*=7 Hz, 8-CH_2 of **19**), 3.77, 3.71/3.70, 3.63/3.62, 3.39$_1$/3.38$_5$ (each 3H, s, 2-, 7-, 12-CH_3, 17^2-CO_2CH_3 of **18**), 3.76, 3.70, 3.62 (each 3H, s, 2-, 12-CH_3, 17^2-CO_2CH_3 of **19**), 2.72, 2.61, 2.29 (1H+1H+2H, m, 17-CH_2CH_2 of **18** and **19**), 2.64 (1H, br s, 8^1- and 7^1-OH

of **18** and **19**), 2.15/2.14 (3H, d, J=7 Hz, 8^1-CH_3 of **18**), 1.85 (3H, m, 18-CH_3 of **18** and **19**), 1.79 (3H, t, J=7 Hz, 8^1-CH_3 of **19**), −0.19, −2.08 (each 1H, br s, NH×2 of **19**), −0.29, −2.17 (each 1H, br s, NH×2 of **18**).

*4.3.4. 3-Hydroxymethyl-8-(1-hydroxyethyl)-chlorin **20** and 3,7-bis(hydroxymethyl)-chlorin **21**.* According to the previous report,[39] reduction of a mixture of **18** and **19** (21.0 mg, 37 μmol, 5:1) by ^{t}BuNH$_2$·BH$_3$ (87 mg, 1.0 mmol) in CH_2Cl_2 (20 ml) afforded **20** and **21**. FCC separation gave fast eluted **20** (1.0–1.5% MeOH–CH_2Cl_2) and slowly eluted **21** (1.5–2.5% MeOH–CH_2Cl_2). Each fraction was evaporated to dryness and recrystallized from CH_2Cl_2 and hexane, giving pure **20** (12.6 mg, 60%, $8^1R/S$ of **18**=1:1) and **21** (2.5 mg, 12%) as a black solid. Compound **20**: VIS (CH_2Cl_2) λ_{max}=661 (rel intensity, 0.43), 605 (0.08), 539 (0.09), 508 (0.12), 415 nm (1.0); ^{1}H NMR ($CDCl_3$, $8^1R/S$ of **18**=1:1) δ=9.82/9.77 (1H, s, 10-H), 9.39 (1H, s, 5-H), 8.50/8.48 (1H, s, 20-H), 6.12 (1H, m, 8-CH), 5.84 (2H, m, 3-CH_2), 4.89 (2H, m, 13^1-CH_2), 4.36 (1H, m, 18-H), 4.03 (1H, m, 17-H), 3.65/3.63 (3H, s, 17^2-CO_2CH_3), 3.53/3.48 (3H, s, 12-CH_3), 3.39 (3H, s, 2-CH_3), 3.28 (3H, s, 7-CH_3), 2.50, 2.19 (each 2H, m, 17-CH_2CH_2), 2.03 (3H, m, 8^1-CH_3), 1.73/1.69 (3H, d, J=7 Hz, 18-CH_3), −0.23, −2.11/15 (each 1H, s, NH×2), two OHs were lost due to chemical exchanges; HRMS (FAB) m/z 568.2678 (M^+), calcd for $C_{33}H_{36}N_4O_5$: 568.2686. Compound **21**: VIS (CH_2Cl_2) λ_{max}=659 (rel intensity, 0.37), 603 (0.08), 539 (0.08), 509 (0.11), 416 nm (1.0); ^{1}H NMR ($CDCl_3$) δ=9.59 (1H, s, 5-H), 9.28 (1H, s, 10-H), 8.49 (1H, s, 20-H), 5.86 (2H, s, 3-CH_2), 5.71 (2H, s, 7-CH_2), 5.06, 4.97 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.40 (1H, m, 18-H), 4.16 (1H, m, 17-H), 3.68 (2H, m, 8-CH_2), 3.62 (3H, s, 17^2-CO_2CH_3), 3.45 (3H, s, 12-CH_3), 3.37 (3H, s, 2-CH_3), 2.53, 2.23, 2.09 (2H+1H+1H, m, 17-CH_2CH_2), 1.75 (3H, d, J=7 Hz, 18-CH_3), 1.66 (3H, t, J=7 Hz, 8^1-CH_3), 0.08, −1.93 (each 1H, s, NH×2), two OHs were lost due to chemical exchanges; HRMS (FAB) m/z 568.2689 (M^+), calcd for $C_{33}H_{36}N_4O_5$: 568.2686.

*4.3.5. Zinc 3-hydroxymethyl-8-(1-hydroxyethyl)-chlorin **6**.* As reported previously,[39] a CH_2Cl_2 solution of **20** was treated by a MeOH solution saturated with zinc acetate dihydrate. After standard work-up, HPLC purification (pyridine/H_2O/MeOH=1/9/90, 2 ml/min, retention time=11.0 min) and recrystallization (CH_2Cl_2–hexane) gave the corresponding zinc complex **6** (93%): VIS (THF) λ_{max}=645 (rel intensity, 0.63), 602 (0.08), 567 (0.04), 521 (0.03) 426 nm (1.0); ^{1}H NMR (3% pyridine-d_5–$CDCl_3$, 1:1 mixture of 8^1R and 8^1S) δ=10.06/10.05 (1H, s, 10-H), 9.38_1/9.37_8 (1H, s, 5-H), 8.35/8.34 (1H, s, 20-H), 6.36–6.30 (1H, s, 8-CH), 5.85 (2H, s, 3-CH_2), 5.17, 5.05_4/5.04_9 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.46, 4.37 (each 1H, br s, 3^1-, 8^1-OH), 4.39 (1H, m, 18-H), 4.19 (1H, m, 17-H), 3.67 (3H, s, 12-CH_3), 3.57_0/3.56_7 (3H, s, 17^2-CO_2CH_3), 3.32 (3H, s, 2-CH_3), 3.31/3.30 (3H, s, 7-CH_3), 2.56, 2.38, 2.26, 1.95 (each 1H, m, 17-CH_2CH_2), 2.15/2.14 (3H, d, J=7 Hz, 8^1-CH_3), 1.72/1.71 (3H, d, J=7 Hz, 18-CH_3); HRMS (FAB) m/z 630.1828 (M^+), calcd for $C_{33}H_{34}N_4O_5Zn$: 630.1821.

*4.3.6. Zinc 3,8-bis(hydroxymethyl)-chlorin **7**.* Similarly to the synthesis of **6**, zinc metalation of **24** gave pure **7** (94%) after HPLC purification (pyridine/H_2O/MeOH=1/9/90, 2 ml/min, retention time=8.6 min) and recrystallization (CH_2Cl_2–hexane): VIS (THF) λ_{max}=646 (rel intensity, 0.62), 602 (0.08), 567 (0.04), 521 (0.03) 426 nm (1.0); ^{1}H NMR (3% pyridine-d_5–$CDCl_3$) δ=9.79 (1H, s, 10-H), 9.41 (1H, s, 5-H), 8.37 (1H, s, 20-H), 5.86 (2H, s, 3-CH_2), 5.84 (2H, s, 8-CH_2), 5.18, 5.06 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.41 (1H, dq, J=2, 7 Hz, 18-H), 4.20 (1H, m, 17-H), 3.64 (3H, s, 12-CH_3), 3.57 (3H, s, 17^2-CO_2CH_3), 3.33 (3H, s, 2-CH_3), 3.30 (3H, s, 7-CH_3), 2.57, 2.40, 2.26, 1.97 (each 1H, m, 17-CH_2CH_2), 1.73 (3H, d, J=7 Hz, 18-CH_3); HRMS (FAB) m/z 616.1667 (M^+), calcd for $C_{32}H_{32}N_4O_5Zn$: 616.1664.

*4.3.7. Zinc 3,7-bis(hydroxymethyl)-chlorin **8**.* Similarly to the synthesis of **6**, zinc metalation of **21** gave **8** (91%) after HPLC purification (pyridine/H_2O/MeOH=1/9/90, 2 ml/min, retention time=8.4 min) and recrystallization (CH_2Cl_2–hexane): VIS (THF) λ_{max}=642 (rel intensity, 0.60), 599 (0.10), 566 (0.05), 516 (0.06) 426 nm (1.0); ^{1}H NMR (3% pyridine-d_5–$CDCl_3$) δ=9.61 (1H, s, 10-H), 9.55 (1H, s, 5-H), 8.32 (1H, s, 20-H), 5.81 (2H, s, 3-CH_2), 5.76 (2H, s, 7-CH_2), 5.17, 5.05 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.38 (1H, dq, J=2, 7 Hz, 18-H), 4.19 (1H, m, 17-H), 3.83 (2H, q, J=7 Hz, 8-CH_2), 3.69 (3H, s, 12-CH_3), 3.57 (3H, s, 17^2-CO_2CH_3), 3.30 (3H, s, 2-CH_3), 2.56, 2.38, 2.26, 1.96 (each 1H, m, 17-CH_2CH_2), 1.74 (3H, t, J=7 Hz, 8^1-CH_3), 1.71 (3H, d, J=7 Hz, 18-CH_3); HRMS (FAB) m/z 630.1821 (M^+), calcd for $C_{33}H_{34}N_4O_5Zn$: 630.1821.

*4.3.8. Zinc 3-ethyl-7-hydroxymethyl-chlorin **10**.* Similarly to the synthesis of **6**, zinc metalation of 3-ethyl-7-hydroxymethyl-chlorin gave **10** (89%) after HPLC purification (pyridine/H_2O/MeOH=1/9/90, 2 ml/min, retention time=14.3 min) and recrystallization (CH_2Cl_2–hexane): VIS (THF) λ_{max}=639 (rel intensity, 0.61), 594 (0.10), 564 (0.06), 515 (0.05) 425 nm (1.0); ^{1}H NMR (3% pyridine-d_5–$CDCl_3$) δ=9.57 (1H, s, 10-H), 9.30 (1H, s, 5-H), 8.24 (1H, s, 20-H), 5.79 (2H, s, 7-CH_2), 5.15, 5.03 (each 1H, d, J=19 Hz, 13^1-CH_2), 4.34 (1H, dq, J=2, 8 Hz, 18-H), 4.15 (1H, m, 17-H), 3.99 (1H, br s, 7^1-OH), 3.82 (2H, q, J=7 Hz, 8-CH_2), 3.71 (1H, m, 3-CH_2), 3.68 (3H, s, 12-CH_3), 3.56 (3H, s, 17^2-CO_2CH_3), 3.19 (3H, s, 2-CH_3), 2.54, 2.36, 2.25, 1.91 (each 1H, m, 17-CH_2CH_2), 1.74 (3H, t, J=7 Hz, 8^1-CH_3), 1.70 (3H, d, J=7 Hz, 18-CH_3), 1.65 (3H, t, J=7 Hz, 8^1-CH_3); HRMS (FAB) m/z 628.2031 (M^+), calcd for $C_{34}H_{36}N_4O_4Zn$: 628.2028.

4.4. Preparation of chlorophyll-aggregate in aqueous micellar solution

A THF solution of pigment and TX-100 was mixed, dispersed in warm water (ca. 50 °C) and incubated at 50 °C for 30 min. Final concentrations of THF and TX-100 were 1.0 and 0.025%, respectively. All the optical spectra were measured after 2-h standing at rt.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.12.029.

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