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# Self-Aggregation of Synthetic Zinc Chlorins Possessing a 13-Ester-Carbonyl Group as Chlorosomal Chlorophyll Models

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We have synthesized zinc $3^1$-hydroxychlorins **1**–**4** possessing a methoxycarbonyl group at the 13-position by modifying naturally occurring chlorophyll-*a*. Synthetic zinc chlorins **1**–**4** have three specific substituents, namely $3^1$-OH, central Zn and 13-C=O moieties, along the Qy axis, and **1**–**3** self-aggregate in an aqueous medium containing Triton X-100, as do natural bacteriochlorophylls in the main light-harvesting antennas (chlorosome) of green photosynthetic bacteria. The 13-methoxycarbonyl group in **1**–**3** is a prerequisite for such self-aggregation, while the other methoxycarbonyl groups at the $15^1$- and/or $17^2$-positions are not. This indicates that such a linear situation of these substituents is significant for chlorosomal self-aggregation of chlorophyllous pigments and also that the 13-methoxycarbonyl group is an alternative to the 13-keto-carbonyl group in natural pigments. Furthermore, the resulting oligomers of **1**–**3** have fluorescence emission peaks at less than 700 nm, which are considerably more blue-shifted than previously prepared self-aggregates of chlorins possessing the 13-keto-carbonyl group fixed onto an *exo* five-membered ring, and are a new class of artificial light-harvesting systems.

## Introduction

Photosynthetic green bacteria have unique light-harvesting antenna systems, the so-called chlorosomes, which are constructed by self-aggregates of composite chlorophyllous pigments enveloped by a lipid monolayer.[1–9] In a chlorosome, bacteriochlorophylls (BChls) *c*, *d*, and *e*[10,11] (see left drawing of Figure 1) are utilized as light-harvesting pigments and self-aggregate using their specific substituents ($3^1$-OH, central magnesium atom and 13-C=O moieties).[1,2,7,9,12–14] The driving forces in the self-aggregation of such BChl molecules are intermolecular coordination ($3^1$-O···Mg) and hydrogen-bonding ($3^1$-O–H···O=C-13), which promote exciton coupling among the most closely packed and well-ordered BChl molecules. The resulting excitonically delocalized supramolecule is suitable for efficient and rapid light-energy harvesting and transferral processes. As compared with the monomeric absorption bands of BChl molecules (typically in coordinating organic solvents such as methanol or THF), self-aggregates of BChls in a chlorosome show red-shifted absorption maxima due to the excitonically delocalized molecular packages, as in J-aggregation. Both natural BChls[2,15–20] and synthetic BChl models[2,9,12,14,21–27] such as **5** and **6** (see right drawing of Figure 1) possess the same three characteristic moieties and easily form such self-aggregated species in nonpolar organic media. Furthermore, in an aqueous solution of a surfactant, self-aggregation of BChls occurs in the hydrophobic environments prepared by self-assembly of the surfactant molecules to give a supramolecular structure that is similar to the natural systems.[28–30] Such a facile self-aggregation of dyes inspired us to apply it to artificial photosynthesis and/or photoactive nanodevices.[31–34]

Many synthetic studies have revealed that the essential requisite for chlorosomal self-aggregation is the presence of OH, a coordinative central metal (Mg, Zn, Cd, etc.),[24] and a C=O moiety (vide supra), and their linear situation along the Qy axis in a molecule (see arrow in the left drawing of Figure 1).[35,36] The strongest transition dipole moment in a chlorin chromophore is on the Qy axis, so parallel and slipped overlapping of the Qy axis in chlorins creates their J-aggregates, which give the above-mentioned red-shifts in the Qy absorption bands. We have previously reported that two representatives of the BChl models, zinc 3-(hydroxymethyl)- and 3-(1-hydroxyethyl)chlorins **5**[12] and **6**,[22] respectively, easily form chlorosomal self-aggregates in an aqueous medium containing Triton X-100 (TX-100) as a surfactant, and that their stability and availability would be suitable for a composite molecule in an artificial light-harvesting system.[30] Both zinc chlorins **5** and **6** have the 13-keto-carbonyl moiety on an *exo* five-membered ring (E-ring) that is generally observed in naturally occurring photosynthetic chlorophyllous pigments.[10] The E-ring in such pigments fixes the conformation of the 13-keto-carbonyl moiety such that it achieves a robust interaction with

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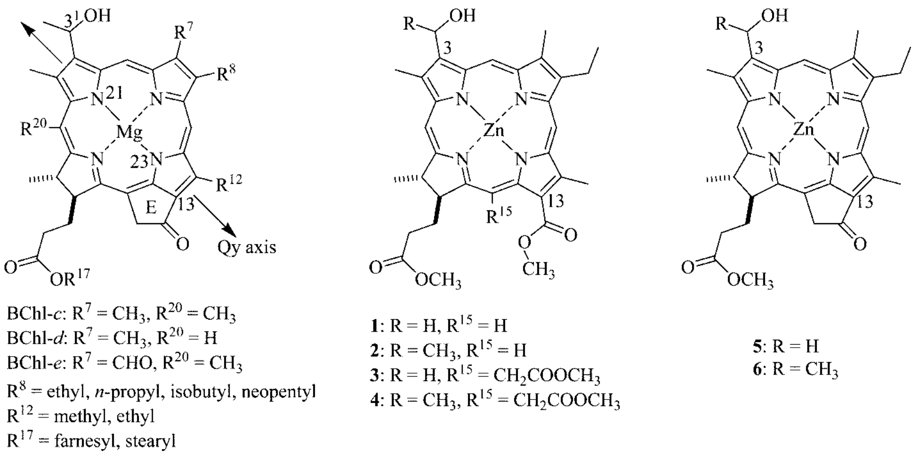


Figure 1. Molecular structures of natural BChls-*c*/*d*/*e* (left), present models **1**–**4** (center), and previous models **5**/**6** (right).

either an amino acid residue in proteins or a functional group in other molecules.[37] Recently, we reported the self-aggregation of zinc chlorins bearing an *exo* six-membered ring (13,15-anhydride/imide, 13-COXCO-15 [X = O, NC$_6$H$_{13}$]),[38] which was modified from purpurin 18 (Fischer nomenclature, 3$^1$,3$^2$-didehydro-15-carboxyrhodochlorin anhydride for IUPAC IUB nomenclature[39]). Such zinc chlorins possessing a 13-carbonyl group on an *exo* six-membered E-ring self-aggregate in an aqueous medium to form chlorosome-like oligomers, thus indicating that the carbonyl groups of the anhydride and imide function on the E-ring are as suitable for constructing hydrogen-bonding networks as the usual 13-keto-carbonyl group on an *exo* five-membered E-ring.

Here we report the synthesis of zinc chlorins **1**–**4** (central drawing of Figure 1), which possess chlorosomal substituents (3$^1$-OH, central Zn, and 13-C=O) by modifying rhodochlorin XV (3$^1$,3$^2$-didehydrorhodochlorin) and chlorin e$_6$ (3$^1$,3$^2$-didehydrorhodochlorin-15-acetic acid). The present models **1**–**4** have a fairly conformationally flexible 13-methoxycarbonyl group instead of the 13-keto-carbonyl group fixed on the E-ring as in **5**/**6**. We describe the chlorosomal self-aggregation of synthetic zinc chlorins possessing the 13-methoxycarbonyl group in an aqueous medium containing TX-100 and compare their self-aggregation behavior with those of reported models **5** and **6**, which possess the 13-C=O moieties fixed on an *exo* five-membered E-ring.

## Results

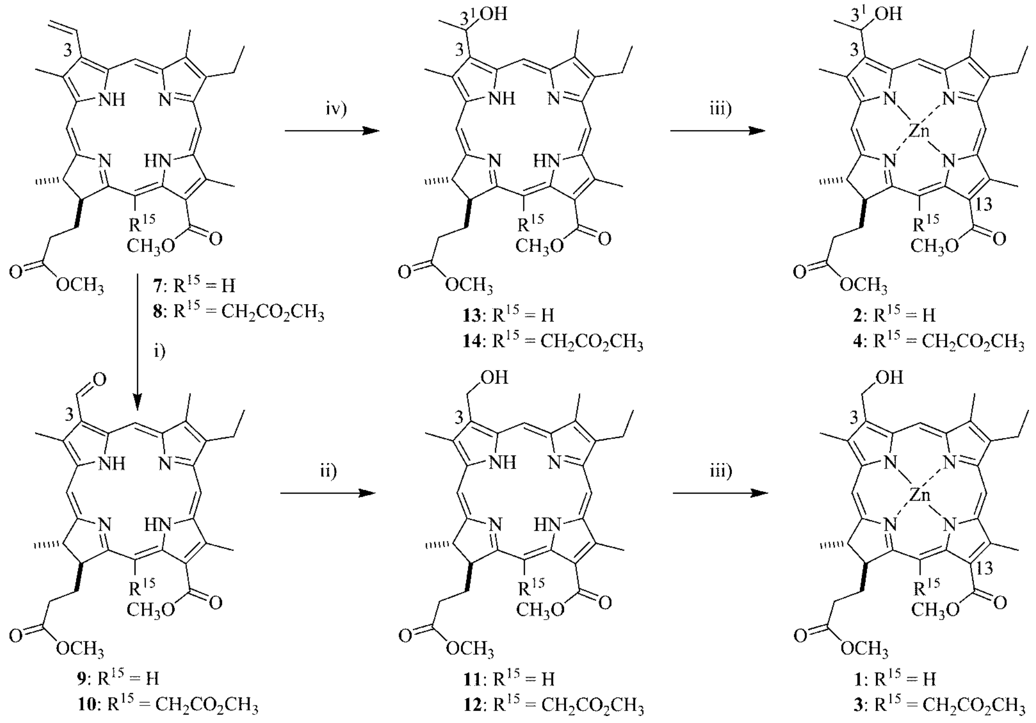
### Synthesis of Zinc 3$^1$-Hydroxy-13-methoxycarbonylchlorins 1–4

Rhodochlorin XV dimethyl ester (**7**) and chlorin e$_6$ trimethyl ester (**8**) were used as starting materials, both of which were prepared from naturally occurring chlorophyll-*a* (Scheme 1). Oxidative cleavage[12,40] of the 3-vinyl group in **7**/**8** gave 3-formylchlorins **9**/**10** (step i of Scheme 1), and this was followed by selective reduction[12] of the 3-formyl group to afford 3-(hydroxymethyl)chlorins **11**/**12** (step ii). Alternatively, 3-(1-hydroxyethyl)chlorins **13**/**14** (a 1:1 3$^1$-epimeric mixture) were prepared by hydration[41] of the 3-vinyl group in **7**/**8** followed by re-esterification (step iv). Metalation[12] of **11**–**14** with zinc, followed by purification by column chromatography, gave the corresponding zinc 3-(hydroxymethyl)- and 3-(1-hydroxyethyl)-13-methoxycarbonylchlorins **1**/**3** and **2**/**4**, respectively. The molecular structures of all the compounds were ascertained by their 1D-$^1$H, 2D $^1$H-$^1$H COSY, and NOESY NMR and FAB mass spectra.

### UV/Vis and Circular Dichroism (CD) Spectra of Zinc Chlorins 1–6 in THF

The UV/Vis spectra of zinc chlorins **1**–**4** in THF show sharp absorption bands and their CD spectra show only weak signals in the region of their Qy and Soret absorption bands (see solid and dotted lines in Figure 2 for 3-(hydroxymethyl)chlorins **1** and **3**). This means that the zinc chlorins **1**–**4** are free from any intermolecular interaction in this polar organic solvent – they are monomers with a THF molecule as an axial ligand, as are natural BChls and the previous models **5**/**6** (see broken lines in Figure 2 for **5**).[12,22] Since the spectral difference between the 3-(hydroxymethyl) (**1**/**3**/**5**) and 3-(1-hydroxyethyl) (**2**/**4**/**6**) compounds is small, only one set of UV/Vis and CD spectra of the former are shown in Figure 2.

The UV/Vis spectra of zinc chlorins **1** and **2**, which possess a hydrogen atom at the 15-position (see solid line in Figure 2 upper part for **1**), show almost the same peak positions and spectral shapes; a similar tendency was observed for zinc chlorins **5** and **6** (see broken line in Figure 2 upper part for **5**). This indicates that the absence/presence of the 3$^1$-methyl group (primary/secondary alcohol) slightly affects their monomeric optical properties.[13] The Qy and Soret absorption peaks of **1**/**2** are situated at 633/632 and 412/411 nm, respectively, and are blue-shifted relative to those of **5**/**6** (646/645 and 424/423 nm). The full widths at half maximum (FWHMs) of the Qy bands in **1**/**2** are almost the same (395/389 cm$^{-1}$) and their Qy/Soret peak intensity ratios are the same (0.56). These values for **1**/**2** are larger and



Scheme 1. Synthesis of zinc 3-(hydroxymethyl)- and 3-(1-hydroxyethyl)-13-methoxycarbonyl-chlorins **1/3** and **2/4**, respectively: i) $OsO_4$/$CCl_4$, $NaIO_4$, 1,4-dioxane/THF/$H_2O$, 53/56% yields for **9/10**; ii) $t$BuNH$_2$·BH$_3$, $CH_2Cl_2$, 88/97% for **11/12**; iii) $Zn(OAc)_2·2H_2O$, $CH_2Cl_2$/$CH_3OH$, 88/81/84/91% for **1/2/3/4**; iv) 30% HBr/AcOH, water, $CH_2N_2$/$Et_2O$, 51/71% for **13/14**.

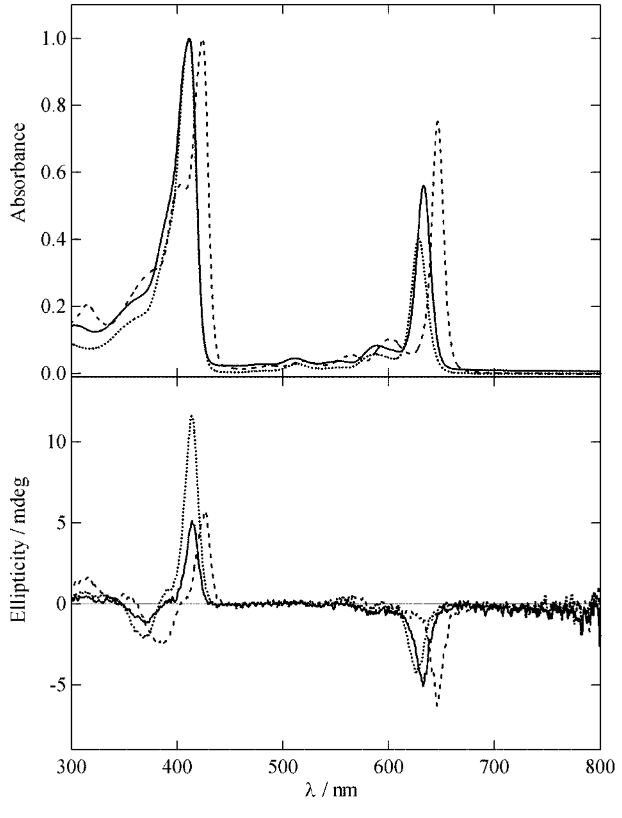


Figure 2. UV/Vis (upper part) and CD spectra (lower part) of zinc chlorins **1/3/5** in THF (solid, dotted, and broken lines for **1**, **3**, and **5**, respectively). The maximal Soret absorption of all THF solutions was equal to 1.0.

smaller, rspectively, than those for **5/6** (316/312 cm$^{-1}$ and 0.75). Transformation of the 13-keto-carbonyl moiety fixed on an E-ring in **5/6** into the conformationally flexible 13-ester-carbonyl moiety in **1/2** causes blue-shifts in both the Qy and Soret absorption peaks and a slight broadening of the Qy band as well as a decrease in its relative intensity. Since the Qy absorption band of chlorophyllous pigments is related to the transition dipole moment along the Qy axis (the arrow in the left drawing of Figure 1) in the molecule, modification of the peripheral substituents on the Qy axis affects the Qy absorption band directly.

The substitution of a hydrogen atom at the 15-position of **1/2** with a (methoxycarbonyl)methyl group, as in **3/4**, affects their absorption spectra slightly: the Qy absorption bands of **3/4** are moved by about 5 nm to shorter wavelength and are broadened (about 1.1-fold increase of FWHM and 1.4-fold decrease of relative intensity) compared to those of **1/2**, while all the Soret bands are similar. Steric repulsions between the 15- and 13/17-substituents distort the chlorin π-conjugation slightly and induce the above difference in the Qy absorption bands. It is noteworthy that 3$^1$-methylation of **3** to **4** induces the same effect in their UV/Vis spectra as those of **1/5** to **2/6**.

The CD spectra of **1**–**4** in THF show small positive and negative CD signals in the Soret and Qy regions, similar to those observed for **5/6**, which are characteristic of monomeric zinc chlorins (Figure 2 lower part). The relative CD intensities of the Qy region of **1**–**6** correspond to the relative intensity of their Qy absorption maxima in the order **3** = **4** < **1** = **2** < **5** = **6**, while those of the Soret regions are different: the relative CD intensities of the Soret region in **3**/**4** are about twice as large as those in **1**/**2** and **5**/**6**.

### UV/Vis and CD Spectra of Zinc Chlorins 1–6 in Aqueous TX-100 Solution

As compared with the above monomeric absorption spectra of **1**–**3** in neat THF, significant differences were observed in an aqueous TX-100 (0.0175, v/v) and THF (1.0, v/v) solution (bold solid, thin solid, and bold dotted lines, respectively, in Figure 3 upper part). When the monomeric THF solution was mixed with TX-100 (1.75, v/v) and diluted with a 99-fold volume of water, the Qy and Soret absorption bands of **1**–**3** shifted to a longer wavelength. The Soret bands were broadened and became less intense, while the Qy bands were mostly enlarged. The CD spectra of **1**–**3** in aqueous solution show intense signals at around the newly appeared absorption bands (Figure 3 lower part). These observations clearly indicate that the zinc chlorins **1**–**3** form J-aggregates characteristic of the chlorosomal self-aggregation seen in natural BChls and models **5**/**6** (bold/thin broken lines in Figure 3).[12,22]

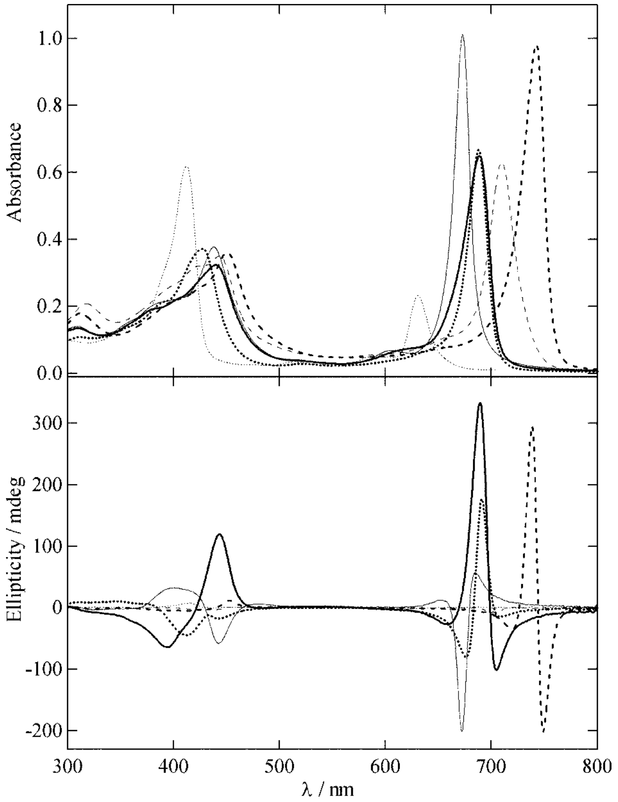


Figure 3. UV/Vis (upper part) and CD spectra (lower part) of zinc chlorins **1**–**6** in an aqueous 0.0175 % (v/v) TX-100 and 1.0 % (v/v) THF solution (bold/thin solid lines for **1**/**2**, bold/thin dotted lines for **3**/**4**, and bold/thin broken lines for **5**/**6**). The concentrations of all the samples were identical to those in Figure 2.

The Qy and Soret absorption bands of **1**/**2** in aqueous solution were red-shifted to 689/673 and 440/438 nm, respectively (bold/thin solid lines of Figure 3 upper part) upon self-aggregation. The FWHMs of the Qy bands of self-aggregated **1** and **2** are 629 and 385 cm$^{-1}$ and their red-shift values upon self-aggregation are 1280 and 960 cm$^{-1}$, respectively. The Qy absorbances in self-aggregated **1** and **2** are larger than the Soret absorbances, and the Qy/Soret peak ratios are 2.0 and 2.7. Self-aggregation of models **5**/**6** (bold/thin broken lines in Figure 3 upper part) causes red-shifts of the Qy and Soret maxima at 743/710 and 450/444 nm, respectively, which is consistent with the absorption spectra of natural chlorosomes.[12,15] Their Qy/Soret ratios are 2.7 and 1.8, and their red-shift values upon self-aggregation are 2020/1420 cm$^{-1}$, which are similar to those of natural BChls and larger than those of **1**/**2**.

The UV/Vis and CD spectra of zinc chlorins **3**/**4**, which possess a sterically large (methoxycarbonyl)methyl group at the 15-position, were measured in aqueous solution (bold/thin dotted lines of Figure 3). Compound **3** self-aggregated similarly to **1**/**2**/**5**/**6**, as seen by the red-shifted Qy and Soret maxima at 688 and 428 nm and the intense CD signals. The red-shift value upon self-aggregation is 1390 cm$^{-1}$, which is similar to that of **1**. In contrast, **4** in aqueous solution shows almost the same Qy and Soret bands as those of monomeric **4** in THF, clearly indicating that **4**, which possesses 3-(1-hydroxyethyl) and 15-(methoxycarbonyl)methyl groups, cannot form chlorosomal self-aggregates.

### Fluorescence Emission Spectra of Zinc Chlorins 1–6 in Aqueous Solution

The fluorescence emission spectra of **1**–**6** in an aqueous TX-100 solution were measured by excitation at 450 nm (Figure 4). The fluorescence emission maxima of self-aggregated zinc chlorins **1**/**2**/**3** are situated at 695/674/694 nm, respectively, with a small Stokes shift about 1–6 nm, and are at higher energy than those of **5**/**6** (747/728 nm), as expected from their Qy absorption maxima. Although the excitation wavelength (450 nm) is well-matched with the Soret bands of the self-aggregated species, relatively small fluorescence bands from their residual monomeric species were observed [obvious monomeric emissions from **3** and **6** at 636 and 657 nm (bold dotted and thin broken lines of Figure 4)]. Zinc chlorin **4** in solution shows an intense emission band (637 nm) due to the monomeric species, as expected from the above UV/Vis spectrum.

### FT-IR Spectral Analysis of Thin Films of Zinc Chlorins 1–4 with or without Pyridine Vapor

Zinc chlorins **1**–**3**, which possess a 13-methoxycarbonyl group, self-aggregate to form large oligomers, as do the previously reported models **5**/**6**, which possess a 13-keto-carbonyl group, as indicated by the red-shifted absorption bands and their induced CD signals. Zinc chlorins **1**–**3** have a methoxycarbonyl group at the 15$^1$- and/or 17$^2$-positions as well. FT-IR spectroscopy is one of the most powerful tools for confirming which carbonyl group forms a hydrogen bond with 3$^1$-OH. Generally, hydrogen bonding in the chlorosomal self-aggregates induces a downshift of the 13-

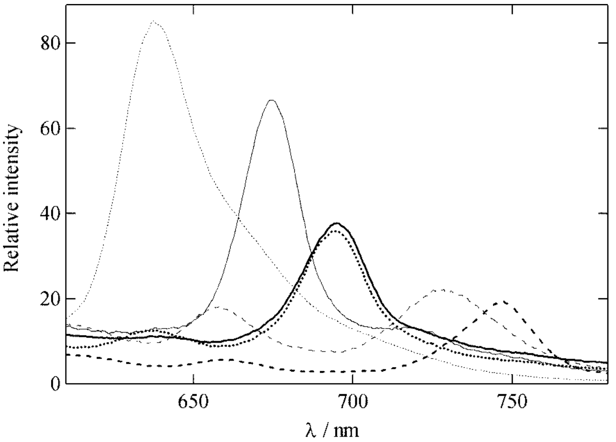


Figure 4. Fluorescence emission spectra of zinc chlorins **1**–**6** in an aqueous 0.0175 % (v/v) TX-100 and 1.0 % (v/v) THF solution, excited at 450 nm (bold/thin solid lines for **1**/**2**, bold/thin dotted lines for **3**/**4**, and bold/thin/broken lines for **5**/**6**). The concentrations of all the samples were identical to those in Figure 2.

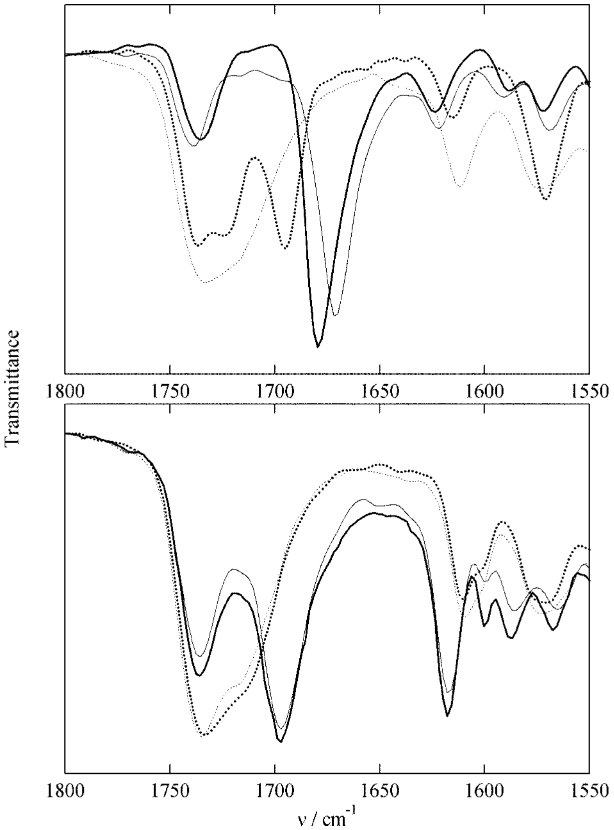


Figure 5. FT-IR spectra of zinc chlorins **1**–**4** in a thin film (upper part), and their corresponding monomeric spectra prepared by treatment with pyridine vapor (lower part). Bold/thin solid lines for **1**/**2** and bold/thin dotted lines for **3**/**4**.

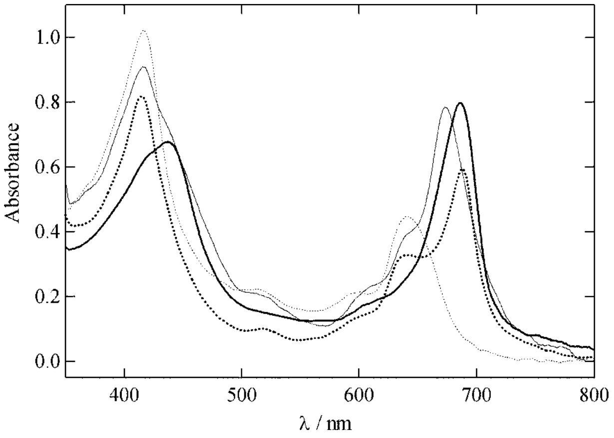


Figure 6. UV/Vis spectra of zinc chlorins **1**–**4** in a thin film-form. Bold/thin solid lines for **1**/**2** and bold/thin dotted lines for **3**/**4**.

C=O vibrational signals of about 30–40 cm$^{-1}$.[12,24] Thin films of **1**–**4**, prepared by dropping the THF solution onto a glass coated with a thin aluminum film followed by air-drying, were therefore examined by FT-IR spectroscopy (Figure 5). The UV/Vis spectra of self-aggregates of **1**–**4** in a thin film (Figure 6) are quite similar to those in aqueous solution, so the supramolecular structures in the thin films are similar to those in the corresponding oligomeric solution.

The bold solid line of Figure 5 (upper figure) shows the FT-IR spectra of zinc chlorin **1** in the solid thin film. In the self-aggregated state, two carbonyl vibrations are observed at 1737 and 1679 cm$^{-1}$. The peak at 1737 cm$^{-1}$ is assigned to the 17$^2$-C=O moiety, based on previous data,[12,24] and the remaining peak can therefore be assigned to the 13-C=O stretch in oligomeric **1**. After treatment with pyridine vapor to induce dissociation to monomeric **1** (bold solid line of Figure 5 lower part), the peak at 1679 cm$^{-1}$ moves to 1697 cm$^{-1}$ (+18 cm$^{-1}$), while the peak at 1737 cm$^{-1}$ is shifted by only +1 cm$^{-1}$. This spectral change before and after pyridine treatment indicates that zinc chlorin **1** forms hydrogen bonds in the oligomeric state through 13-C=O, which is characteristic of chlorosomal self-aggregation. It is noteworthy that no 17$^2$-C=O group is included in the hydrogen-bonding network of oligomeric supramolecules as were those of models **5**/**6**.[12]

Similar results were obtained for zinc chlorin **2**, which possesses methoxycarbonyl groups at the 13- and 17$^2$-positions (see thin solid lines in Figure 5). However, the downshift of the 13-C=O moiety upon self-aggregation of **2** (26 cm$^{-1}$) is larger than that of **1** (18 cm$^{-1}$). The FT-IR spectra of zinc chlorin **3**, which possesses three methoxycarbonyl groups at the 13-, 15$^1$-, and 17$^2$-positions, show complex signals in the carbonyl vibrational region (1650–1750 cm$^{-1}$) due to a combination of three vibrational signals, of which one carbonyl stretch shifts to 1695 cm$^{-1}$ in the self-aggregated state. The lack of apparent change in the FT-IR spectra of **4** upon treatment with pyridine (thin dotted lines in Figure 5) shows that **4** cannot self-aggregate in the solid state or in aqueous solution (vide supra). Although compounds **1**–**3** contain two or three C=O groups in the same molecule, only the 13-ester-carbonyl group acts as the chlorosomal substituent, as did the 13-keto-carbonyl groups in **5**/**6**.

## Discussion

### Monomeric States of Zinc Chlorins 1–6

The Qy and Soret peak-positions of **1**–**4** (627–633 and 410–412 nm) are blue-shifted relative to those of **5/6** bearing the E-ring (646/645 and 424/423 nm). These spectral differences between the present synthetic models **1**–**4** and previous semi-natural models **5/6** in their monomeric states are easily traced to their different molecular structures (with or without the E-ring). Rotation of the C13–C13$^1$ bond in zinc chlorins **1**–**4** is free, so it has various conformations (rotamers), while that in **5/6** is restricted because of its fixation to the E-ring, which is characteristic of natural chlorophyllous pigments. Furthermore, the dihedral angles C12–C13–C13$^1$–O13$^2$ and C14–C13–C13$^1$–O13$^2$ in **1**–**4** and **5/6** are different from each other. The energy-minimized molecular structures of **1/3/5** obtained by MM+/PM3 calculations[42] show that the 13-methoxycarbonyl group in **1/3** deviates slightly from the chlorin π-plane (1.20/6.79° for C12–C13–C13$^1$–O13$^2$ and –178.94/–175.56° for C14–C13–C13$^1$–O13$^2$), while the 13-keto-carbonyl group in **5** is almost planar with it (–0.09° for C12–C13–C13$^1$–O13$^2$ and 179.30° for C14–C13–C13$^1$–O13$^2$) due to fixation of the E-ring. The conformational variation and the slightly deviated situation of the 13-methoxycarbonyl group of **1**–**4** should alter their π-conjugated systems and shift their absorption bands to lower wavelength. As compared with **5/6**, the broadened FWHMs of the Qy bands and the decrease of the Qy/Soret ratio for **1**–**4** must also be due to the altered π-conjugate systems in the absence or presence of the E-ring.[43,44] As compared to **1/2** ($R^{15}$ = H), zinc chlorins **3/4**, which possess a 15-(methoxycarbonyl)methyl group, have slightly blue-shifted Qy and Soret bands due to the steric effects around the 15-position. The 15-$CH_2COOCH_3$ group in **3/4** interacts sterically with both the 13- and 17-substituents to further distort the chlorin π-plane, as seen by the greater deviation of the 13-methoxycarbonyl group. It cannot be ruled out, however, that the difference between methoxycarbonyl and keto groups at the 13-position induces the above electronic absorption properties of **1**–**4** and **5/6**.

### Oligomeric States of Zinc Chlorins 1–3: The 13-Methoxycarbonyl Group in 1–3 as a Chlorosomal Substituent

As described above, zinc chlorins **1**–**3** form self-aggregates in aqueous TX-100 solution in a similar manner to natural chlorosomal BChls and previous models **5/6**. Recently, we reported the synthesis of zinc 3-(hydroxymethyl)-purpurin-18 and its imide derivative as novel chlorosomal chlorophyll models.[38] These chlorins bear an anhydride or imide group fixed to an expanded *exo* six-membered E-ring instead of a keto-carbonyl group (13-$COCH_2$) fixed to an *exo* five-membered E-ring and also self-aggregate to form chlorosome-like oligomers, thus indicating that the presence of 13-COX [X = OCO, N($C_6H_{13}$)CO] is vital as the chlorosomal substituent. Moreover, chlorosome-like self-aggregation of synthetic porphyrins possessing three chlorosomal moieties has also been reported,[36,45] where the 13-formyl- (or keto)-carbonyl group in synthetic zinc 3$^1$-hydroxyporphyrin acts as a chlorosomal substituent without the E-ring, thus suggesting that conformationally free 13-COR (R = H, $CH_3$) is also acceptable for the formation of such self-aggregates. Furthermore, our FT-IR experiments have indicated that the zinc chlorins **1**–**3** self-aggregate using only the 13-methoxycarbonyl group, in a similar manner to natural BChl-*e* (7-CHO)[18] and previously reported (bacterio)-chlorins,[42,46,47] where an additional C=O moiety at the 7-, 8-, or 13$^2$-position is excluded from the hydrogen-bonding network. Thus, the 13-$COOCH_3$ group in the zinc chlorins **1**–**3** is sufficient to induce chlorosomal self-aggregation.

The self-aggregation behavior of zinc chlorins **1**–**6** is discussed below from the following two structural points: (1) the 3$^1$-methylation [3-(hydroxymethyl) (**1/3/5**) vs. 3-(1-hydroxyethyl) (**2/4/6**)] and (2) the molecular structure around the 13-C=O moieties [13-methoxycarbonyl (**1**–**4**) without the E-ring vs. natural 13-keto-carbonyl (**5/6**) with the E-ring].

Generally, the self-aggregation of zinc chlorins possessing a 3-hydroxymethyl group is stronger than those bearing a 3-(1-hydroxyethyl) group because the sterically less hindered primary alcohol at the 3-position favors the coordination to the zinc atom of another chlorin and also the hydrogen bonding with 13-carbonyl group of the third chlorin more than a secondary alcohol.[12,13] The red-shift values upon self-aggregation of zinc chlorins behave similarly to the self-aggregation and are affected by the 3$^1$-methylation − those of zinc 3-(hydroxymethyl)chlorins **1** and **5** are about 1.3–1.4-times larger than those of zinc 3-(1-hydroxyethyl)chlorins **2** and **6**. The fact that **4** fails to self-aggregate is due to the prevention of hydrogen-bond formation between the sterically hindered 3$^1$-OH and 13-C=O, which is bound to the bulky 15-(methoxycarbonyl)methyl group.

The red-shift values of **1/3** and **2** are smaller than the corresponding values for **5** and **6**, respectively, which suggests that a change in substitution from the 13-keto-carbonyl group in **5/6** (with the E-ring) to the 13-methoxycarbonyl group in **1**–**3** (without the E-ring) affects their self-aggregation. The alkyl group (R) of an ester (COOR) is generally oriented in the same direction as its carbonyl oxygen atom (as shown in Figure 1), so the sterically less hindered 13-keto-carbonyl group in natural models **5** and **6** is positioned favorably to form hydrogen bonds with 3$^1$-OH group of another chlorin, whereas this is not the case for **1/3** and **2**. It is noteworthy that a similar steric effect has been observed in the 13$^2$-methoxycarbonylated derivative of **5**.[46] As shown in the FT-IR experiments (Figure 5), zinc chlorins **1**–**3** form hydrogen bonds in their oligomeric state, as indicated by the down-shifted 13-C=O vibrational signals (16–26 $cm^{-1}$), which are smaller than those of **5/6**. These results indicate that although hydrogen bonds are formed in oligomeric **1**–**3**, their strength is inferior to those of **5/6**.

An angle between 13-C=O and the Qy axis (N21–N23 line in Figure 1) in the molecule would significantly affect the resulting supramolecular structure of the chlorosomal self-aggregates (natural BChls as well as **5**/**6** are precisely ordered along the Qy axis). Two zinc porphyrins possessing an OH and a C=O group at the 3/13- and 3/12-positions, respectively, have been investigated previously.[36] The former possesses a linear order of the chlorosomal moieties and self-aggregates, whereas the latter is bent slightly and forms no self-aggregates. The presence of a 13-C=O moiety in chlorosomal chlorin is therefore significant for such self-aggregation, and the orientation of this C=O moiety is also important for the formation of strong intermolecular interactions. The angle formed between the Qy axis (N21–N23) and C$13^1$=O$13^2$ in energetically minimized **5** is 14.6° in a clockwise direction, while those in **1** and **3** are –25.8° and –28.2°, respectively. The present zinc chlorins **1**–**3** have the direction of their 13-C=O moiety altered by 40–43° compared to the natural-types **5**/**6**, which reduces their self-aggregation. The molecular packages of the self-aggregated **1**–**3** would contain slightly loose π-π interactions between the molecules, leading to their less red-shifted values (decrease of about 30–50% compared with those of **5**/**6**). The 13-methoxycarbonyl group is suitable for the chlorosomal substituents but the steric effect of the $13^1$-methoxy group and the altered direction of the 13-C=O moiety to the Qy axis decrease the molecular packing of chlorosomal self-aggregation, i.e., the steric effect of their 13-methoxycarbonyl groups is observed for such chlorosomal self-aggregation.

### Oligomeric States of Zinc Chlorins 1–3: Absorption and Emission Properties of Self-Aggregated 1–3

Green photosynthetic bacteria regulate their electronic absorption properties by modifying peripheral substituents in the molecular structure of composite chlorosomal chlorophylls (left drawing of Figure 1). On the basis of BChl-*c* having its oligomeric Qy band at around 745–760 nm (in living cells), its 20-demethylated analog, BChl-*d* affords a slightly blue-shifted band at 725–745 nm and its $7^1$-oxidized BChl-*e* (7-CHO) yields a blue-shifted band at around 715–725 nm.[1] The electronic absorption and emission properties of synthetic chlorosomal chlorins have been systematically investigated. Since most of the synthetic models prepared mimic the molecular structure of natural BChls by possessing the E-ring, their absorption and emission properties are similar to natural BChls. The self-aggregated porphyrin[23,48] and bacteriochlorin molecules[23,42,49] reported previously have their oligomeric Qy maxima at shorter (640–650 nm) and longer wavelength regions (780–880 nm), respectively, compared with the typical chlorin self-aggregates. These variations are accomplished by modifying the π-conjugated systems of the composite molecules. Self-aggregated synthetic porphyrins have their absorption and emission bands at higher energy than chlorin aggregates, but their less intense Q-bands derived from their symmetrical porphyrin π-conjugate system are unfavorable to achieve efficient energy harvesting. As compared with the oligomeric Qy absorption and emission bands of the natural chlorosome and previous models **5**/**6**, those of self-aggregated **1**–**3** move to a shorter wavelength region situated at less than 700 nm, although with a relatively large Qy absorption intensity, because the red-shift values upon self-aggregation of the present models are small (960–1390 $cm^{-1}$) in addition to the blue-shifted Qy absorption peaks of the monomeric states (320–470 $cm^{-1}$). The present self-aggregated zinc chlorins **1**–**3** bring a variety of absorption and emission properties of chlorosomal self-aggregation without changing their π skeleton.

## Conclusion

We have prepared a series of zinc $3^1$-hydroxychlorins **1**–**4** that possess 13-methoxycarbonyl groups as chlorosomal chlorophyll models. Their syntheses were carried out by modification of rhodochlorin XV dimethyl ester and chlorin $e_6$ trimethyl ester, both of which lack the *exo* five-membered E-ring that is generally present in photosynthetic chlorophyllous pigments. Monomeric zinc chlorins **1**–**4** (13-$COOCH_3$) in THF show blue-shifted Qy and Soret absorption maxima relative to with those of **5**/**6**, which possess a 13-keto-carbonyl group on the *exo* five-membered E-ring (see Table 1). Despite the absence of the E-ring, zinc chlorins **1**–**3** in aqueous 0.0175 % (v/v) TX-100 solution self-aggregate to form large oligomers in a manner similar to natural BChls and synthetic models **5**/**6**, all of which possess the E-ring. The 13-$COOCH_3$ group of **1**–**3** has been demonstrated to function as a hydrogen-bond acceptor to the $3^1$-OH in the supramolecule, while chlorosomal chlorophylls use a keto-carbonyl group at the 13-position. The Qy absorption and fluorescence emission peaks of self-aggregated **1**–**3** are situated at a lower wavelength than those of natural BChls and **5**/**6** and constitute a new class of artificial light-harvesting systems which could transfer their absorbing light energy to various acceptors having energetically higher singlet excited states. Moreover, the 13-methoxycarbonyl groups in the present zinc chlorins are distinguished from the 13-keto-carbonyl group in natural BChls in their reactivity. The easily modifiable ester function could be useful for providing various model compounds of chlorosomal chlorophylls.

## Experimental Section

**General Remarks:** UV/Vis and CD spectra in solution were measured with a Hitachi U-3500 spectrophotometer and a Jasco J-720W spectropolarimeter, respectively. UV/Vis spectra of zinc chlorins in solid states were measured with a System Instruments SIS-50 spectrometer. Fluorescence emission spectra were recorded with a Hitachi F-4500 spectrophotometer. $^1$H NMR spectra in deuterated chloroform were recorded with a JEOL ECA-600 instrument; TMS was used as an internal standard. For NMR measurements of zinc complexes, 1 % (v/v) [D$_5$]pyridine was added to ensure the formation of monomers. $^1$H-$^1$H COSY and NOESY ($\tau_m$ = 400 ms) techniques were used to confirm the molecular structures. FT-IR spectra were recorded with a Shimadzu FTIR-8600 spectrophotometer; films of samples prepared on a glass coated

Table 1. Soret and Qy absorption maxima [nm] of zinc chlorins **1**–**6** and their relative intensity ratio in monomeric[a] and oligomeric states,[b] red-shift values $\Delta$ [$cm^{-1}$] of Qy peaks upon self-aggregation,[c] and fluorescence emission maxima [nm] in their oligomeric form.[d]

| Compound | Soret maximum | | Qy maximum (FWHM)[e] | | Qy/Soret intensity ratio | | $\Delta$ | Emission maximum |
|---|---|---|---|---|---|---|---|---|
| | monomer | oligomer | monomer | oligomer | monomer | oligomer | | |
| **1** | 412 | 440 | 633 (395) | 689 (629) | 0.56 | 2.0 | 1280 | 695 |
| **2** | 411 | 438 | 632 (389) | 673 (385) | 0.56 | 2.7 | 960 | 674 |
| **3** | 411 | 428 | 628 (428) | 688 (458) | 0.40 | 1.8 | 1390 | 694 |
| **4** | 410 | 412[f] | 627 (425) | 631 (564)[f] | 0.40 | 0.38[f] | –[f] | 637[f] |
| **5** | 424 | 450 | 646 (316) | 743 (468) | 0.75 | 2.7 | 2020 | 747 |
| **6** | 423 | 444 | 645 (312) | 710 (598) | 0.75 | 1.8 | 1420 | 728 |

[a] In THF. [b] In an aqueous 0.0175 % (v/v) TX100 and 1.0 % (v/v) THF solution. [c] Red-shift value upon self-aggregation: $\Delta = (1/\lambda_{max}[\text{monomer}] - 1/\lambda_{max}[\text{oligomer}]) \times 10^7$. [d] Excited at 450 nm. [e] In $cm^{-1}$. [f] In an aqueous TX-100 solution (see footnote b), **4** was a monomer.

with a thin aluminum film were examined by reflection mode with a Shimadzu AIM-8000R microscope. Mass spectra ionized by FAB were obtained with a JEOL GCmate II spectrometer; samples were dissolved in chloroform (chloroform/methanol for zinc complexes), and *m*-nitrobenzyl alcohol was added as a matrix. FCC was carried out on silica gel (Merck Kieselgel 60, 9358). THF and dichloromethane for UV/Vis, CD, and fluorescence spectroscopy were purchased from Nacalai Tesque (Kyoto, Japan, grade for spectroscopy). All procedures, including syntheses and spectral measurements, were performed at room temp. in the dark.

Zinc methyl 3-devinyl-3-(hydroxymethyl)pyropheophorbide-*a* (**5**)[12] and zinc methyl bacteriopheophorbide-*d* (**6**)[41] were synthesized according to the reported procedures. Both rhodochlorin XV dimethyl ester (**7**)[39,50] and chlorin $e_6$ trimethyl ester (**8**)[39,51] were prepared from methyl pheophorbide-*a* in several steps.

**Oxidation of a 3-Vinyl to a 3-Formyl Group:**[12,40] A catalytic amount of $OsO_4$ in a small amount of $CCl_4$ was added to a THF/1,4-dioxane solution (5:2, 50 mL) of 3-vinylchlorin (ca. 180 μmol) and the mixture stirred under nitrogen. After stirring for 10 min, aq. $NaIO_4$ (150 mg in 5 mL) was added to the solution and heated at 50 °C for 3 h. The reaction mixture was poured into water, washed with aq. 4% NaOAc and water, dried with $Na_2SO_4$, and the solvents evaporated to dryness. The residue was purified by FCC (0–2% $Et_2O$/dichloromethane) and recrystallized from dichloromethane/hexane to give the corresponding 3-formylchlorin in a pure form.

**3-Devinyl-3-formylrhodochlorin XV Dimethyl Ester (9, 3-Deethyl-3-formylrhodochlorin Dimethyl Ester):** 50.4 mg (53% yield). Brown solid. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 693 (relative intensity, 0.71), 635 (0.06), 545 (0.10), 509 (0.11), 416 nm (1.00). $^1H$ NMR ($CDCl_3$): $\delta$ = 11.58 (s, 1 H, 3-CHO), 10.39 (s, 1 H, 5-H), 9.90 (s, 1 H, 15-H), 9.77 (s, 1 H, 10-H), 8.94 (s, 1 H, 20-H), 4.52–4.58 (m, 2 H, 17-, 18-H), 4.37 (s, 3 H, 13-$COOCH_3$), 3.84 (s, 3 H, 12-$CH_3$), 3.81 (s, 3 H, 2-$CH_3$), 3.80 (q, *J* = 8 Hz, 2 H, 8-$CH_2$), 3.63 (s, 3 H, $17^2$-$COOCH_3$), 3.37 (s, 3 H, 7-$CH_3$), 2.72–2.80, 2.58–2.65, 2.43–2.52, 2.35–2.42 (m, each 1 H, 17-$CH_2CH_2$), 1.91 (d, *J* = 7 Hz, 3 H, 18-$CH_3$), 1.74 (t, *J* = 8 Hz, 3 H, $8^1$-$CH_3$), –1.81 (br. s, 2 H, NH × 2) ppm. MS (FAB): *m*/*z* 568.5 [$M^+$] (calcd. for $C_{33}H_{36}N_4O_5$: 568.3).

**3-Devinyl-3-formylchlorin $e_6$ Trimethyl Ester (10, 3-Deethyl-3-formylrhodochlorin-15-acetic Acid Trimethyl Ester):** 58.5 mg (56% yield). Dark-brown solid. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 691 (rel., 0.58), 634 (0.05), 547 (0.11), 542 (0.10), 416 nm (1.00). $^1H$ NMR ($CDCl_3$): $\delta$ = 11.37 (s, 1 H, 3-CHO), 9.98 (s, 1 H, 5-H), 9.53 (s, 1 H, 10-H), 8.94 (s, 1 H, 20-H), 5.48, 5.36 (d, *J* = 19 Hz, each 1 H, 15-$CH_2$), 4.54 (m, 1 H, 18-H), 4.51 (m, 1 H, 17-H), 4.37 (s, 3 H, 13-$COOCH_3$), 3.88 (s, 3 H, $15^1$-$COOCH_3$), 3.73 (s, 3 H, 2-$CH_3$), 3.72 (s, 3 H, 12-$CH_3$), 3.61 (s, 3 H, $17^2$-$COOCH_3$), 3.52 (q, *J* = 8 Hz, 2 H, 8-$CH_2$), 3.09 (s, 3 H, 7-$CH_3$), 2.67–2.73, 2.24–2.36, 1.76–1.83 (m, 1 H + 2 H + 1 H, 17-$CH_2CH_2$), 1.83 (d, *J* = 7 Hz, 3 H, 18-$CH_3$), 1.63 (t, *J* = 8 Hz, 3 H, $8^1$-$CH_3$), –1.43, –1.81 (s, each 1 H, NH × 2) ppm. MS (FAB): *m*/*z* 640.4 [$M^+$] (calcd. for $C_{36}H_{40}N_4O_7$: 640.3).

**Reduction of a 3-Formyl to a 3-Hydroxymethyl Group:**[12] $tBuNH_2{\cdot}BH_3$ (45 mg) was added to a dichloromethane solution (40 mL) of 3-formylchlorin (ca. 100 μmol) and the solution was stirred for 2 h under nitrogen. The reaction mixture was poured into water, washed with aq. 2% HCl and water, dried with $Na_2SO_4$, and the solvents evaporated to dryness. The residue was purified by FCC (5–8% $Et_2O$/dichloromethane) and recrystallized from dichloromethane/hexane to give the corresponding 3-(hydroxymethyl)chlorin in a pure form.

**3-Devinyl-3-(hydroxymethyl)rhodochlorin XV Dimethyl Ester (11, 3-Deethyl-3-(hydroxymethyl)rhodochlorin Dimethyl Ester):** 44.9 mg (88% yield). Green solid. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 660 (rel., 0.38), 604 (0.03), 524 (0.02), 496 (0.08), 398 nm (1.00). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.83 (s, 1 H, 15-H), 9.75 (s, 1 H, 10-H), 9.59 (s, 1 H, 5-H), 8.74 (s, 1 H, 20-H), 5.87 (s, 2 H, 3-$CH_2$), 4.47–4.54 (m, 2 H, 17-, 18-H), 4.35 (s, 3 H, 13-$COOCH_3$), 3.80 (s, 3 H, 12-$CH_3$), 3.77 (q, *J* = 8 Hz, 2 H, 8-$CH_2$), 3.62 (s, 3 H, $17^2$-$COOCH_3$), 3.43 (s, 3 H, 2-$CH_3$), 3.29 (s, 3 H, 7-$CH_3$), 2.70–2.78, 2.56–2.63, 2.43–2.51, 2.33–2.40 (m, each 1 H, 17-$CH_2CH_2$), 2.04 (br. s, 1 H, $3^1$-OH), 1.89 (d, *J* = 7 Hz, 3 H, 18-$CH_3$), 1.72 (t, *J* = 8 Hz, 3 H, $8^1$-$CH_3$), –1.79 (br. s, 2 H, NH × 2) ppm. MS (FAB): *m*/*z* 570.6 [$M^+$] (calcd. for $C_{33}H_{38}N_4O_5$: 570.3).

**3-Devinyl-3-(hydroxymethyl)chlorin $e_6$ Trimethyl Ester (12, 3-Deethyl-3-(hydroxymethyl)rhodochlorin-15-acetic Acid Trimethyl Ester):** 56.3 mg (97% yield). Dark-green solid. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 658 (rel., 0.31), 603 (0.03), 525 (0.02), 496 (0.08), 398 nm (1.00). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.70 (s, 1 H, 10-H), 9.55 (s, 1 H, 5-H), 8.75 (s, 1 H, 20-H), 5.89 (s, 2 H, 3-$CH_2$), 5.35, 5.24 (d and br. d, *J* = 19 Hz, each 1 H, 15-$CH_2$), 4.44 (m, 1 H, 18-H), 4.40 (m, 1 H, 17-H), 4.26 (s, 3 H, 13-$COOCH_3$), 3.77 (s, 3 H, $15^1$-$COOCH_3$), 3.77 (q, *J* = 8 Hz, 2 H, 8-$CH_2$), 3.63 (s, 3 H, $17^2$-$COOCH_3$), 3.57 (s, 3 H, 12-$CH_3$), 3.45 (s, 3 H, 2-$CH_3$), 3.28 (s, 3 H, 7-$CH_3$), 2.52–2.60, 2.14–2.24, 1.65–1.80 (m, 1 H + 2 H + 1 H, 17-$CH_2CH_2$), 2.06 (br. s, 1 H, $3^1$-OH), 1.75 (d, *J* = 7 Hz, 3 H, 18-$CH_3$), 1.70 (t, *J* = 8 Hz, 3 H, $8^1$-$CH_3$), –1.52, –1.63 (br. s, each 1 H, NH × 2) ppm. MS (FAB): *m*/*z* 642.4 [$M^+$] (calcd. for $C_{36}H_{42}N_4O_7$: 642.3).

**Hydration of a 3-Vinyl to a 3-(1-Hydroxyethyl) Group:**[41] 3-Vinylchlorin (ca. 160 μmol) was dissolved in a 30% HBr/AcOH mixture and stirred for 3 h at 55 °C. The reaction mixture was then poured into ice-chilled water and stirred for a further 10 min. The resulting pigments were extracted with chloroform, washed with water twice, and dried with $Na_2SO_4$. After evaporation in vacuo, the residue was treated with ethereal diazomethane and the solvents evaporated. The desired hydrated chlorin (as a 1:1 $3^1$-epimeric mixture) was obtained after FCC separation (4–7% $Et_2O$/dichloromethane) and recrystallization from dichloromethane/hexane.

**3-Devinyl-3-(1-hydroxyethyl)rhodochlorin XV Dimethyl Ester (13, $3^1$-Hydroxyrhodochlorin Dimethyl Ester):** 43.1 mg (51% yield). Green solid. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 657 (rel., 0.37), 602 (0.03), 523 (0.02), 497 (0.08), 398 nm (1.00). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.88/87 (s, 1 H, 5-H), 9.82 (s, 1 H, 15-H), $9.77_4/77_1$ (s, 1 H, 10-H), 8.72 (s, 1 H, 20-H), 6.39–6.47 (m, 1 H, 3-CH), 4.47–4.53 (1 H+1 H, m, 17-, 18-H), 4.35 (s, 3 H, 13-$COOCH_3$), 3.82 (s, 3 H, 12-$CH_3$), 3.79 (q, $J$ = 8 Hz, 2 H, 8-$CH_2$), 3.62/61 (s, 3 H, $17^2$-$COOCH_3$), $3.45_5/4_8$ (s, 3 H, 2-$CH_3$), 3.31 (s, 3 H, 7-$CH_3$), 2.69–2.77, 2.54–2.62, 2.43–2.51, 2.31–2.39 (m, each 1 H, 17-$CH_2CH_2$), 2.62 (br. s, 1 H, $3^1$-OH), 2.15/14 (d, $J$ = 7 Hz, 3 H, $3^1$-$CH_3$), 1.89/88 (d, $J$ = 7 Hz, 3 H, 18-$CH_3$), 1.72 (t, $J$ = 8 Hz, 3 H, $8^1$-$CH_3$), –1.75 (br. s, 2 H, NH×2) ppm. MS (FAB): $m/z$ 584.6 [$M^+$] (calcd. for $C_{34}H_{40}N_4O_5$: 584.3).

**3-Devinyl-3-(1-hydroxyethyl)chlorin $e_6$ Trimethyl Ester (14, $3^1$-Hydroxyrhodochlorin-15-acetic Acid Trimethyl Ester):** 65.7 mg (71% yield). Dark-green solid. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 655 (rel., 0.30), 601 (0.03), 524 (0.02), 496 (0.08), 398 nm (1.00). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.78 (s, 1 H, 5-H), 9.70 (s, 1 H, 10-H), $8.71_6/71_3$ (s, 1 H, 20-H), 6.37–6.43 (m, 1 H, 3-CH), 5.34, 5.24 (d and br. d, $J$ = 19 Hz, each 1 H, 15-$CH_2$), 4.40–4.47 (m, 1 H, 18-H), 4.37–4.42 (m, 1 H, 17-H), 4.25 (s, 3 H, 13-$COOCH_3$), 3.78 (q, $J$ = 8 Hz, 2 H, 8-$CH_2$), 3.77 (s, 3 H, $15^1$-$COOCH_3$), $3.63_0/62_5$ (s, 3 H, $17^2$-$COOCH_3$), 3.57 (s, 3 H, 12-$CH_3$), 3.45/44 (s, 3 H, 2-$CH_3$), 3.29 (s, 3 H, 7-$CH_3$), 2.58 (br. s, 1 H, $3^1$-OH), 2.51–2.58, 2.14–2.25, 1.69–1.77 (m, 1 H + 2 H + 1 H, 17-$CH_2CH_2$), 2.13 (d, $J$ = 7 Hz, 3 H, $3^1$-$CH_3$), 1.75/74 (d, $J$ = 7 Hz, 3 H, 18-$CH_3$), 1.70 (t, $J$ = 8 Hz, 3 H, $8^1$-$CH_3$), –1.42, –1.54 (br. s, each 1 H, NH×2) ppm. MS (FAB): $m/z$ 656.5 [$M^+$] (calcd. for $C_{37}H_{44}N_4O_7$: 656.3).

**Zinc Metallation:**[12] A methanol solution (1 mL) saturated with zinc acetate dihydrate was added to a chloroform solution (20 mL) of the chlorin (ca. 25 µmol) and the mixture stirred for 2 h under nitrogen. The reaction mixture was poured into water, washed with aq. 4% $NaHCO_3$ and water, dried with $Na_2SO_4$, and the solvents evaporated to dryness. The residue was purified by FCC (10–15% $Et_2O$/dichloromethane) and recrystallized from chloroform/hexane to give the corresponding zinc chlorin in a pure form.

**Zinc Complex of 3-Devinyl-3-(hydroxymethyl)rhodochlorin XV Dimethyl Ester (1, Zinc 3-Deethyl-3-(hydroxymethyl)rhodochlorin Dimethyl Ester):** 13.1 mg (88% yield). Green solid. UV/Vis (THF): $\lambda_{max}$ = 633 (rel., 0.54), 590 (0.07), 553 (0.02), 511 (0.03), 412 nm (1.00). $^1H$ NMR (1%, v/v, [$D_5$]pyridine/$CDCl_3$): $\delta$ = 9.68 (s, 1 H, 10-H), 9.53 (s, 1 H, 5-H), 9.52 (s, 1 H, 15-H), 8.47 (s, 1 H, 20-H), 5.88 (s, 2 H, 3-$CH_2$), 4.35–4.41 (m, 2 H, 17-, 18-H), 4.29 (s, 3 H, 13-$COOCH_3$), 3.82 (d, $J$ = 8 Hz, 2 H, 8-$CH_2$), 3.76 (s, 3 H, 12-$CH_3$), 3.58 (s, 3 H, $17^2$-$COOCH_3$), 3.37 (s, 3 H, 2-$CH_3$), 3.34 (s, 3 H, 7-$CH_3$), 2.54–2.61, 2.35–2.49, 2.11–2.18 (m, 1 H + 2 H + 1 H, 17-$CH_2CH_2$), 1.76 (d, $J$ = 7 Hz, 3 H, 18-$CH_3$), 1.70 (t, $J$ = 8 Hz, 3 H, $8^1$-$CH_3$) ppm. MS (FAB): $m/z$ 632.4 [$M^+$] (calcd. for $C_{33}H_{36}N_4O_5{}^{64}Zn$: 632.2).

**Zinc Complex of 3-Devinyl-3-(1-hydroxyethyl)rhodochlorin XV Dimethyl Ester (2, Zinc $3^1$-Hydroxyrhodochlorin Dimethyl Ester):** 12.4 mg (81% yield). Green solid. UV/Vis (THF): $\lambda_{max}$ = 632 (rel., 0.57), 589 (0.07), 553 (0.02), 510 (0.03), 411 nm (1.00). $^1H$ NMR (1%, v/v, [$D_5$]pyridine/$CDCl_3$): $\delta$ = 9.74/71 (s, 1 H, 5-H), 9.66 (s, 1 H, 10-H), 9.50 (s, 1 H, 15-H), 8.42/41 (s, 1 H, 20-H), 6.38–6.45 (m, 1 H, 3-CH), 4.34–4.40 (m, 2 H, 17-, 18-H), 4.28 (s, 3 H, 13-$COOCH_3$), 3.81 (d, $J$ = 8 Hz, 2 H, 8-$CH_2$), 3.75 (s, 3 H, 12-$CH_3$), $3.57_1/56_8$ (s, 3 H, $17^2$-$COOCH_3$), 3.37/36 (s, 3 H, 2-$CH_3$), 3.33 (s, 3 H, 7-$CH_3$), 2.98 (br. s, 1 H, $3^1$-OH), 2.52–2.60, 2.34–2.49, 2.09–2.17 (m, 1 H + 2 H + 1 H, 17-$CH_2CH_2$), 2.16/2.15 (d, $J$ = 7 Hz, 3 H, $3^1$-$CH_3$), 1.75/73 (d, $J$ = 8 Hz, 3 H, 18-$CH_3$), 1.71 (t, $J$ = 8 Hz, 3 H, $8^1$-$CH_3$) ppm. MS (FAB): $m/z$ 646.4 [$M^+$] (calcd. for $C_{34}H_{38}N_4O_5{}^{64}Zn$: 646.2).

**Zinc Complex of 3-Devinyl-3-(hydroxymethyl)chlorin $e_6$ Trimethyl Ester (3, Zinc 3-Deethyl-3-(hydroxymethyl)rhodochlorin-15-acetic Acid Trimethyl Ester):** 13.5 mg (84% yield). Green solid. UV/Vis (THF): $\lambda_{max}$ = 628 (rel., 0.42), 587 (0.06), 513 (0.03), 411 nm (1.00). $^1H$ NMR (1%, v/v, [$D_5$]pyridine/$CDCl_3$): $\delta$ = 9.52 (s, 2 H, 5-, 10-H), 8.39 (s, 1 H, 20-H), 5.86 (s, 2 H, 3-$CH_2$), 5.24 (br. s, 2 H, 15-$CH_2$), 4.22–4.27 (m, 2 H, 17-, 18-H), 4.21 (s, 3 H, 13-$COOCH_3$), 3.76 (s, 3 H, $15^1$-$COOCH_3$), 3.73–3.79 (m, 2 H, 8-$CH_2$), 3.61 (s, 3 H, $17^2$-$COOCH_3$), 3.45 (s, 3 H, 12-$CH_3$), 3.31 (s, 3 H, 2-$CH_3$), 3.29 (s, 3 H, 7-$CH_3$), 2.42–2.49, 1.96–2.09, 1.53–1.59 (m, 1 H + 2 H + 1 H, 17-$CH_2CH_2$), 1.67 (t, $J$ = 8 Hz, 3 H, $8^1$-$CH_3$), 1.57 (d, $J$ = 7 Hz, 3 H, 18-$CH_3$) ppm. MS (FAB): $m/z$ 704.4 [$M^+$] (calcd. for $C_{36}H_{40}N_4O_7{}^{64}Zn$: 704.2).

**Zinc Complex of 3-Devinyl-3-(1-hydroxyethyl)chlorin $e_6$ Trimethyl Ester (4, Zinc $3^1$-Hydroxyrhodochlorin-15-acetic Acid Trimethyl Ester):** 14.9 mg (91% yield). Green solid. UV/Vis (THF): $\lambda_{max}$ = 627 (rel., 0.42), 585 (0.06), 512 (0.03), 410 nm (1.00). $^1H$ NMR (1%, v/v, [$D_5$]pyridine/$CDCl_3$): $\delta$ = 9.70/65 (s, 1 H, 5-H), 9.50 (s, 1 H, 10-H), 8.35/34 (s, 1 H, 20-H), 6.32–6.39 (m, 1 H, 3-CH), 5.15–5.27 (m, 2 H, 15-$CH_2$), 4.18–4.24 (m, 2 H, 17-, 18-H), 4.20 (s, 3 H, 13-$COOCH_3$), 3.75 (s, 3 H, $15^1$-$COOCH_3$), 3.71–3.79 (m, 2 H, 8-$CH_2$), 3.60/59 (s, 3 H, $17^2$-$COOCH_3$), 3.44 (s, 3 H, 12-$CH_3$), 3.30/29 (s, 3 H, 2-$CH_3$), 3.30 (s, 3 H, 7-$CH_3$), 2.99 (br. s, 1 H, $3^1$-OH), 2.42–2.48, 1.94–2.08, 1.53–1.59 (m, 1 H + 2 H + 1 H, 17-$CH_2CH_2$), 2.10–2.15 (m, 3 H, $3^1$-$CH_3$), 1.66 (t, $J$ = 8 Hz, 3 H, $8^1$-$CH_3$), 1.55 (m, 3 H, 18-$CH_3$) ppm. MS (FAB): $m/z$ 718.4 [$M^+$] (calcd. for $C_{37}H_{42}N_4O_7{}^{64}Zn$: 718.2).

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