Aggregation of Synthetic Zinc Complexes of Cyclotetrapyrroles

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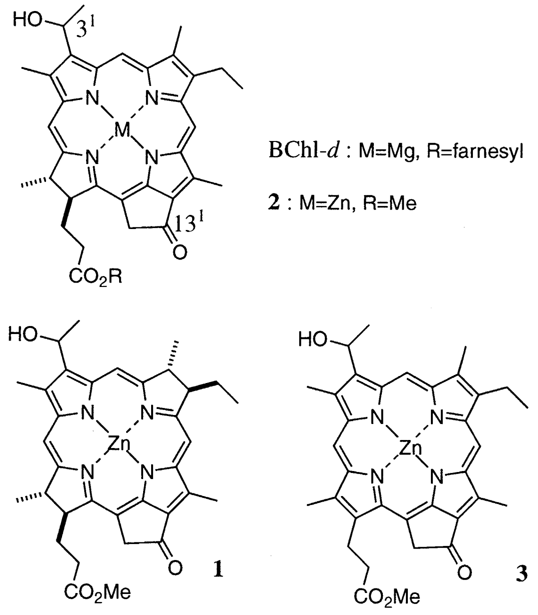
Zinc complexes of cyclotetrapyrroles possessing 3^1-hydroxyl and 13^1-keto carbonyl groups were prepared. The electronic and circular dichroism absorption spectra showed that these compounds self-aggregated in less polar organic solvents to form oligomers, which are good models for natural aggregates of bacteriochlorophyll-*d* in photosynthetic antennae.

Zinc 13^1-oxochlorins possessing a 3^1-hydroxyl group are good models for bacteriochlorophyll(=BChl)-*d* (see Figure 1) as the main light-harvesting pigments of photosynthetic green bacteria.[1-3] These complexes self-aggregate to form oligomers *in vivo* (in chlorosomes) and *in vitro* (in less polar organic solvents).[4] Recent works showed that zinc or magnesium as the central metal and hydroxyl and carbonyl groups at the 3^1- and 13^1-positions, respectively, are necessary for the self-aggregation of metallochlorins.[2] Only metallochlorins have been studied for the model systems. Here we report on the synthesis of zinc bacteriochlorin **1** and zinc porphyrin **3** and self-aggregation of these complexes as well as zinc chlorin **2**[3] (see Figure 1).

Methyl bacteriopyropheophorbide-*a*[5] derived from BChl-*a* (extracted from cultured *Rhodobacter sphaeroides*), was metallated with zinc acetate,[2] subsequently the 3-acetyl group of the zinc complex was reduced by $NaBH_4$ to give zinc bacteriochlorin **1** possessing a 3-(1-hydroxyethyl) group.[6] Zinc methyl bacteriopheophorbide-*d* (**2**) was prepared according to the reported procedures.[3] Hydration of the 3-vinyl group of methyl 3^1,3^2-didehydrophytoporphyrin[7] (derived from Chl-*a*) by HBr–AcOH[8] afforded the corresponding metal-free porphyrin possessing a 3-(1-hydroxyethyl) group, which was zinc-metallated to give zinc porphyrin **3**.[6] All the zinc complexes **1**–**3** have a chiral center at the 3^1-position and epimeric mixtures ($3^1R/3^1S$ = 1/1) were used for the following measurements.



BChl-*d* : M=Mg, R=farnesyl

2 : M=Zn, R=Me

1

3

Figure 1. Metallocyclotetrapyrroles.

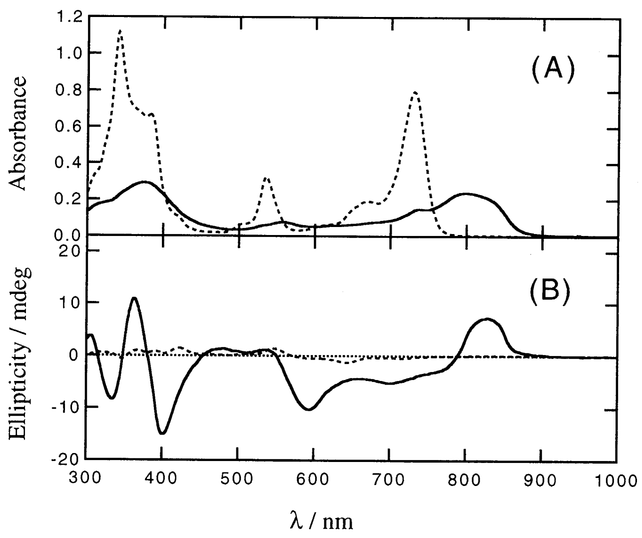


Figure 2. UV-VIS-NIR (A) and CD (B) spectra of **1** in THF (---) and 1% (*v*/*v*) CH_2Cl_2-cyclohexane (—).

A THF solution of zinc bacteriochlorin **1** showed an ultraviolet-visible (UV-VIS) spectrum characteristic of monomeric species (the broken line of Figure 2A).[9] When zinc bacteriochlorin **1** was dissolved in 1% (*v*/*v*) CH_2Cl_2–cyclohexane, all the peaks of **1** were red-shifted and broadened (the solid line of Figure 2A), indicating that **1** aggregates to give oligomers in the less polar organic solvents. Oligomeric **1** absorbed up to 900-nm wavelengths of the near-infrared region (NIR). The circular dichroism (CD) spectrum of the THF solution was almost flat (the broken line of Figure 2B) and that of the less polar solvents showed big peaks around the new red-shifted bands (the solid line of Figure 2B). These Cotton effects are ascribed to exciton coupling of **1** in the oligomers. Zinc bacteriochlorin **1** self-aggregates to form longer-wavelength absorbing oligomers in spite of the lesser planarity of the more saturated bacteriochlorin ligand than the chlorin ligand of **2**. These optical features of synthetic zinc bacteriochlorin **1** are similar to those of natural bacteriochlorophylls-*d* and artificial metallochlorins (including zinc chlorin **2**) reported so far.[2-4] Instead of a chlorin moiety, a bacteriochlorin ligand can also serve as a model system for chlorosomal aggregates.

UV-VIS spectra showed that zinc porphyrin **3** was a monomeric species with sharp bands in THF[9] and an oligomeric species with broad and red-shifted bands in 1% (*v*/*v*) THF–cyclohexane (Figure 3).[10] The monomeric Q_y-bands (the longest wavelength peak, λ_{max}(monomer)) in THF were shifted to longer wavelengths (**3** < **2** < **1**) with decreasing the number of

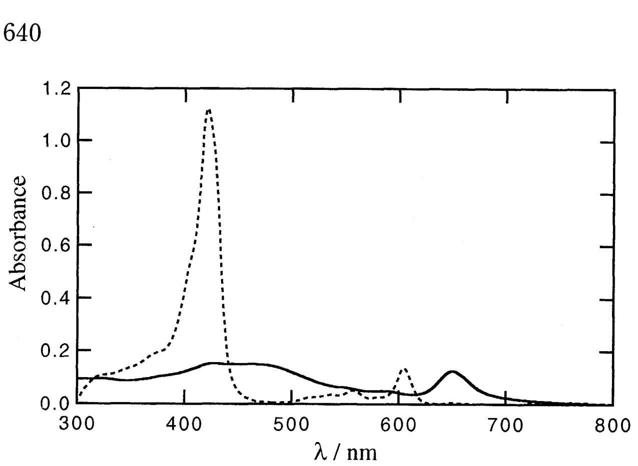


Figure 3. UV-VIS spectra of **3** in THF (---) and 1% (*v*/*v*) THF-cyclohexane (—).

double bonds of cyclotetrapyrrole ligands (see Table 1). The oligomeric Q_y-maxima (λ_{max}(oligomer)) in less polar organic solvents increased with decrease of the π-conjugation similarly to monomeric ones. The value of red-shift ($\Delta\lambda = 1 / \lambda_{max}$(monomer) – $1 / \lambda_{max}$(oligomer)) in Q_y-band of **3** was 1070 cm^{-1} and comparable with those values of **1** (≈1150 cm^{-1}) and **2** (1300 cm^{-1}) as well as BChl-*d* (1240 cm^{-1})[11] (see Table 1), indicating that zinc porphyrin **3** self-aggregates to form oligomers in a similar manner to zinc (bacterio)chlorins **1** and **2**.

In natural chlorosomes, magnesium complexes of chlorin possessing a hydroxyl group at the 3^1-position and a keto-carbonyl group at the 13^1-position as in BChl-*d* are used for sunlight-absorbing pigments. The present results show that more reduced bacteriochlorins and more oxidized porphyrins can similarly function as a ligand for self-aggregates as chlorins. A chlorin moiety is not essential for such aggregation. Requirements for the self-aggregates are 1) central metal (magnesium and zinc), 2) 3^1-hydroxyl group, 3) 13^1-carbonyl group and 4) cyclic tetrapyrroles ligand incorporated in bacteriochlorin, chlorin and porphyrin chromophores. These self-aggregates should serve as a new model for light-harvesting antenna systems.

Table 1. Maxima λ_{max} and red-shift $\Delta\lambda^a$ of Q_y-bands

Pigments	λ_{max} / nm		$\Delta\lambda$ / cm^{-1}
	Monomer	Oligomer	
1 (Zn bacteriochlorin)	731^b	$\approx 798^c$	≈1150
2 (Zn chlorin)	645^b	704^c	1300
3 (Zn porphyrin)	607^b	649^d	1070
BChl-*d* (Mg chlorin)	656^e	714^e	1240

[a] $\Delta\lambda = 1 / \lambda_{max}$(monomer) – $1 / \lambda_{max}$(oligomer). [b] In THF. [c] In 1% (*v*/*v*) CH_2Cl_2–cyclohexane. [d] In 1% (*v*/*v*) THF–cyclohexane. [e] Monomer in CH_2Cl_2–MeOH and *in-vivo* aggregates, see Ref. 11.

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6 All the synthetic compounds were purified by silica gel flash column chromatography, reverse phased HPLC, and/or recrystallization and identified by ^{1}H NMR, UV-VIS, IR, and MS spectra. **1**: MS (FAB) *m*/*z* 630 (M^+, for ^{64}Zn); **2**: MS (FAB) *m*/*z* 628 (M^+, for ^{64}Zn); **3**: MS (FAB) *m*/*z* 626 (M^+, for ^{64}Zn).

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