Self-Assembly of Synthetic Zinc Chlorins in Aqueous Microheterogeneous Media to an Artificial Supramolecular Light-Harvesting Device

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Self-assembled aggregates of a synthetic zinc chlorin in an aqueous suspension with either α-lecithin or *Triton X-100* exhibit unique structural and functional properties. Absorption, circular dichroism, fluorescence, and resonance *Raman* spectra indicate that the supramolecular structure in an aqueous microheterogeneous medium is very similar to that of the bacteriochlorophyll *c* aggregates in non-polar organic solvents and in chlorosomes, the main light-harvesting antennae of green photosynthetic bacteria. The nature of the aggregates is controlled by structure and/or concentration of the added surfactants. When a small amount of metal-free bacteriochlorin is present it acts as an efficient energy acceptor from the aggregated zinc chlorins. Thus, self-assembly of synthetic zinc chlorins, doped with appropriate energy acceptors and surrounded with surfactants, affords an artificial supramolecular light-harvesting device in aqueous environment.

1. Introduction. – Supramolecular self-assemblies play an important role in natural systems. The double helix of DNA, higher-order structures of proteins, and biomembranes are examples of self-organization of supramolecular structures where a number of molecules are suitably organized in order to perform biofunctions. Biomimetic replication of such systems not only helps to elucidate their structure and function, but it can open the access to building artificial systems with novel functions [1].

In photosynthetic organisms, chlorophyll molecules are appropriately organized in antennae to efficiently collect sunlight [2]. While such antennae most often consist of protein-pigment complexes, green photosynthetic bacteria possess a unique alternative system, the so-called chlorosomes [3]. These organelles are composed of self-aggregates of bacteriochlorophyll (BChl[1])) *c*, *d*, and *e* (*Fig. 1*), surrounded by a lipid monolayer of glycolipids and a so-called baseplate containing protein-BChl *a* complex which acts as an energy acceptor. Within the chlorosomes, oligomers of the BChl molecules, consisting of several thousand monomers, form rod-like features with diameters of 5–10 nm – depending on the substitution at C(8) and C(12) – and up to 300 nm in length [3][4].

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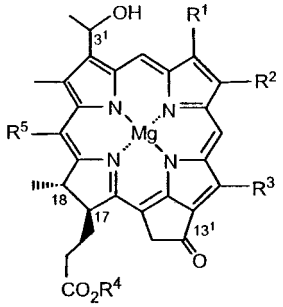
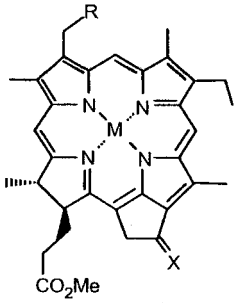
[1]) *Abbreviations:* BChl: bacteriochlorophyll, CD: circular dichroism, RR: resonance *Raman*, DLS: dynamic light scattering, *TX-100: Triton X-100*.



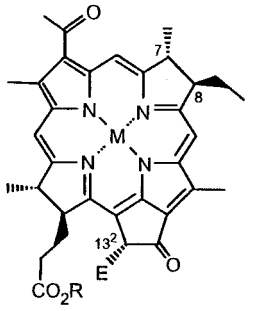
BChl	*c*	*d*	*e*
R^1	Me	Me	CHO
R^5	Me	H	Me

R^2,R^3 =Me, Et, Pr, *i*-Bu, *neo*-pentyl

R^4=stearyl, farnesyl, *etc.*



1 M=Zn, R=OH, X=O
2 M=Zn, R=Me, X=O
3 M=Zn, R=OH, X=H,H
4 M=H,H, R=OH, X=O



BChl *a* M=Mg, R=phytyl, E=CO_2Me

5 M=H,H, R=Me, E=H

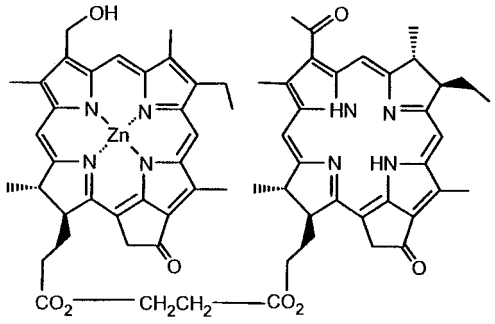


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Fig. 1. *From the top, structures of BChl* a, c, d, *and* e *of natural chlorosomes, synthetic model compounds* **1**–**4**, *metal-free bacteriochlorin* **5**, *and the donor-acceptor dyad* **6**

Since *in vitro* BChl *c* aggregates first have been reported by *Bystrova et al.* [5], a number of synthetic metallochlorins have been studied for the modelling of chlorosome-type aggregates [6]. Recent reports show that BChl *c* aggregates are also formed in water and in aqueous suspensions of lipids or detergents [7][8]. For example, when a MeOH solution of protein-free pigment-lipid extract of natural chlorosomes is injected into H_2O, the optical properties and the particle size of the BChl *c* oligomers formed are similar to those of the rod-like features of intact chlorosomes. Furthermore, purified BChl *c* in the presence of monogalactosyl diglyceride and various detergents forms chlorosome-like oligomers in H_2O [8].

Towards designing an artificial self-assembled antenna device, the use of synthetic bacteriochlorins has been shown to be a promising approach. Thus, zinc chlorins possessing 3^1-hydroxy and 13^1-keto groups, such as **1**, self-aggregate in non-polar organic solvents to form oligomers in a similar manner as does natural BChl *c* [6b,e]. Spectroscopic studies of native chlorosomes and model systems have shown conclusively that C=O···H–O···M (= Mg, Zn) bonding between the 3^1-hydroxy and 13^1-keto groups of two chlorins and the central metal of a third chlorin are the basic structural building blocks of such oligomers [6d,e][9]. Nonetheless, the precise supramolecular structure of chlorosome-type BChl *c* aggregates is still debated [10][11].

Several time-resolved spectroscopic analyses have been carried out on the energy transfer in chlorosomes [3][12]. The experiments with native chlorosomes indicate that excitation energy is efficiently and rapidly transferred (within tens of ps) from the BChl *c* aggregates to the BChl *a* acceptors associated with proteins in the baseplate. Recently, we have reported on singlet energy transfer from self-aggregates of synthetic zinc chlorin (**1**) to a metal-free bacteriochlorin moiety covalently linked to a zinc chlorin (**6**), which constitutes the first biomimetic example of an artificial self-assembled light-harvesting antenna [13]. Several modifications of this principle appear to be promising for building improved artificial antenna devices. Increased chemical stability and energy-transfer efficiency, ease of handling, and simplicity of the building blocks are among the important aspects to be further improved. A particular aim should be a device that can be formed and handled in an aqueous environment.

In this paper, we report on self-aggregates of synthetic **1** in an aqueous suspension with either L-α-phosphatidylcholine (=α-lecithin, a phospholipid) or *Triton X-100* (*TX-100*, a non-ionic detergent). The optical properties of the artificial aggregates in such environments indicate that their supramolecular structure is very similar to that of native chlorosomal aggregates. Furthermore, in the presence of a small amount of the metal-free bacteriochlorin **5**, efficient singlet energy transfer occurs from the donor aggregate **1** to the acceptor **5**. In contrast to our earlier model device formed in hexane solution [13], the new artificial light-harvesting system functions in an aqueous microheterogeneous medium even *without* covalent linkage between the zinc chlorin donor and the bacteriochlorin acceptor.

2. Results. – 2.1. *Absorption Spectra.* Aggregates of **1** with α-lecithin showed absorption maxima at 735 and 449 nm (solid line in *Fig. 2,a*), which are strongly red-shifted compared to those of monomeric **1** in THF solution (λ_{max} = 647 and 424 nm). These bathochromic shifts are typical for the oligomerization of such metallochlorins

[6b,e], and the spectrum of the artificial aggregate is similar to that of isolated natural chlorosomes (broken line in *Fig. 2,a*). The spectra of these aggregates remained unchanged for many hours. Only after days of standing at room temperature was a slight further red shift observed; this change was accelerated by heating (see below). When a MeOH solution of **1** was injected into an aqueous buffer solution without any surfactant, a weak and broad absorption band around 650–760 nm (*Fig. 2,b* and *c*) appeared and a precipitate was formed. Thus, surfactants prevent precipitation, and they also afford a high yield of stable oligomers absorbing at long wavelengths. In an aqueous *TX-100* solution, the Q_y peak (742 nm; dotted line in *Fig. 2,a*) was red-shifted by 7 nm compared to the α-lecithin aggregates.

Compounds **2**, **3** and **4** (lacking the 3^1-hydroxy group, the 13^1-keto group, and the central Zn-atom, respectively) in aqueous α-lecithin and *TX-100* solutions show

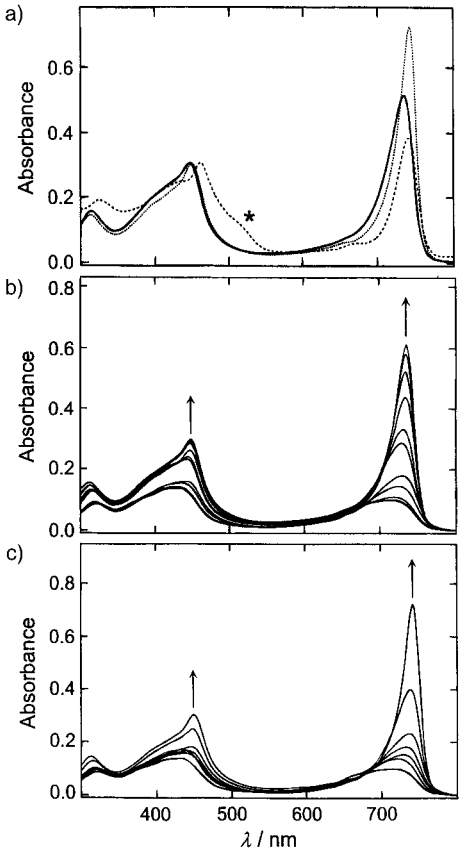

Fig. 2. *Absorption spectra of* a) *zinc chlorin* **1** *in 10 m*M Tris-*HCl buffer* (pH 7.5) *containing* α*-lecithin* (10^{-3}% [2]), solid line) *and with* TX-100 ($2 \cdot 10^{-2}$%, dotted line), *and isolated chlorosomes from a non-sulfur green bacterium*, Chloroflexus aurantiacus, *in 20 m*M Tris-*HCl buffer* (pH 8.0, broken line). All spectra are normalized to the *Soret* band peaks. The shoulder marked by * is due to carotenoids. b), c) *Hyperchromic effect on visible bands of the aggregates* **1** (8 μM) *with increasing concentrations of* α*-lecithin* (b: 0, 0.025, 0.1, 0.25, 0.4, 0.6, 1, 2, 4, $6 \cdot 10^{-3}$%) *and* TX-100 (c: 0, 0.025, 0.1, 0.25, 0.5, 1, $2 \cdot 10^{-2}$%).

absorption spectra corresponding to their monomeric forms, as in hexane solution [6b,e], indicating that the three functional groups are necessary for oligomer formation in both aqueous and hexane solutions.

The hyperchromic effect on the aggregate Q_y absorption at $[\mathbf{1}] = 8\ \mu M$ with increasing α-lecithin and *TX-100* concentrations, and the accompanying decrease of the half-width are plotted in *Fig. 3*. The greatest change in λ_{max} (from 726 to 735 nm) occurred at α-lecithin concentrations of $\leq 10^{-3}\%$ (w/v)[2]), while the values remained almost constant at higher concentrations. A similar concentration effect was also reported for BChl *c* aggregates in aqueous medium with monogalactosyl diglyceride [8a]. In aqueous *TX-100* solution, the concentration independence of λ_{max} and half-width values was reached only at surfactant concentrations of $> 2 \cdot 10^{-2}\%$, *i.e.*, the minimum molar concentration for chlorosomal-type oligomer formation is *ca.* 23-fold smaller for α-lecithin than for *TX-100*. When lower concentrations of **1** ($< 8\ \mu M$) were used for the initial solution, a correspondingly lower concentration of α-lecithin was required to form the oligomer absorbing at 735 nm.

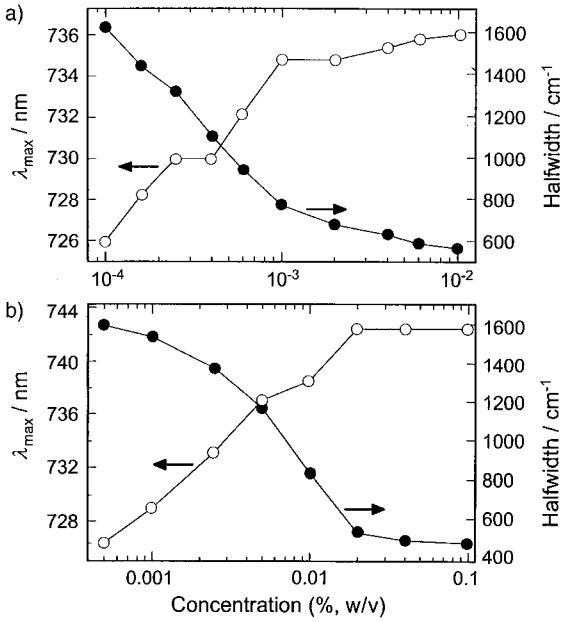

Fig. 3. *Dependence of the absorption wavelength* (λ_{max}; open circles) *and full-width half-maximum* (closed circles) *of the* Q_y *band of aggregated* **1** *on the concentration of* α*-lecithin* (a) *and* TX-100 (b) *in 10 mM* Tris-*HCl buffer* (pH 7.5)

A further difference between α-lecithin and *TX-100* was observed when an excess of surfactant was added to the aqueous aggregate. While increasing amounts of α-lecithin ($> 2 \cdot 10^{-2}\%$) turned the initially clear aqueous solution into turbid suspensions without affecting the λ_{max} value, addition of excess *TX-100* to **1** in H_2O, either in the presence of α-lecithin or without, decomposed the aggregates into monomers. All

[2]) Unless specified otherwise, all percentage concentrations are in *w/v*.

pigment-pigment interactions of **1** were essentially disrupted at 8 mM *TX-100* (= 0.5%), as judged from absorption spectra.

2.2. *CD Spectra*. Aggregates of **1** in aqueous α-lecithin solution show intense CD signals in the near-IR region. The spectral form depends on the concentration of α-lecithin (*Fig. 4,a*). At $4 \cdot 10^{-4}$ to 10^{-3}% an inverse S-shaped signal, with a positive band at 730 nm and a negative band at 747 nm (= type $(+/-)$[3])) accompanied by a minor negative component at 701 nm, was observed (solid line in *Fig. 4,a*). At higher α-lecithin concentrations ($> 4 \cdot 10^{-3}$%), an S-shaped signal appeared, negative at 721 nm and positive at 742 nm (= type $(-/+)$; broken line in *Fig. 4,a*). At intermediate concentrations ($4 \cdot 10^{-3}$ to 10^{-3}%), the CD spectrum (dotted line in *Fig. 4,a*) was accordingly mixed, corresponding to a linear combination of the basic spectra (43% type $(+/-) + 63\%$ type $(-/+)$). At extremely low α-lecithin concentrations ($< 4 \cdot 10^{-4}$%), only a weak $(-/+)$-type CD (694/732 nm) was observed. This behavior of the CD reveals a far-reaching control of the supramolecular aggregate structure by the α-lecithin concentration.

For the aggregates in aqueous *TX-100* solution different spectral changes were observed. The CD spectrum of **1** in the presence of 0.02% *TX-100* was of type $(+/-)$ (735/748 nm; solid line in *Fig. 4,b*). At higher *TX-100* concentration (0.1%), an additional $(+/-)$-type CD signal grew in (704/722 nm; broken line in *Fig. 4*), rather than changing from $(+/-)$ to $(-/+)$. This short-wavelength component is not clearly identifiable in the absorption spectrum. It might originate from trace amounts of a smaller aggregate possessing a relatively high CD intensity.

Particularly striking changes in the CD spectra are brought about upon heating the α-lecithin samples (*Fig. 5*). When the $(+/-)$-type aggregate was warmed to 55° for two days and then cooled again to room temperature, the intensity of the CD band had increased about sixfold[4]). Under the same conditions, the $(-/+)$-type aggregates changed to $(+/-)$, again with a simultaneous increase in spectral intensity. Both spectral changes were accompanied by slight red shifts of the Q_y absorption bands from 734–735 to 737 nm.

2.3. *Fluorescence Spectra*. The fluorescence spectrum of aggregated **1** in the presence of α-lecithin in H_2O has a 745-nm band (solid line in *Fig. 6*) which was independent on excitation wavelength. The fluorescence excitation spectrum (broken line in *Fig. 6*) agreed well with the absorption spectrum. The shape of the 745-nm emission band was independent on the α-lecithin concentration unlike the intensity, which increased sharply with the α-lecithin concentration up to $4 \cdot 10^{-4}$% where it levelled off.

The 745-nm emission intensity was enhanced threefold, furthermore, upon addition of sodium dithionite, and quenched to 1/3 upon addition of benzoquinone, while no

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[3]) The '$(-/+)$-type' and '$(+/-)$-type' CDs correspond to 'type-I' and 'type-II' CDs of BChl *c* aggregates, as defined by *Griebenow et al.* [14]. We prefer here the former connotation and reserve 'type I' and 'type II' as a structural terminology for aggregates exhibiting Q_y maxima at shorter wavelengths (typically 700–710 nm), attributed to aggregates of closed dimers as building blocks, and for aggregates absorbing at longer wavelengths (typically 740–750 nm), attributed to chlorosome-type aggregates, respectively [9].

[4]) This apparent restructuring of the aggregate at 55° is noteworthy also in view of the fact that this is the optimum temperature for culturing the non-sulfur green bacterium *Chloroflexus aurantiacus* where it is most abundant.

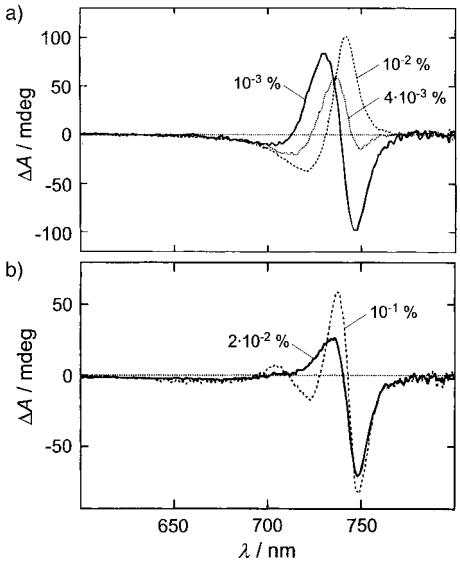

Fig. 4. *CD Spectra of zinc chlorin* **1**: a) *Aggregates in the presence of α-lecithin* (10^{-3}%[2]), type $(+/-)^3$), solid line; $4\cdot10^{-3}$%, mixed type, dotted line; 10^{-2}%, type $(-/+)^3$), broken line) *in 10 mM aqueous* Tris-*HCl buffer* (pH 7.5). b) *Aggregates in the presence of* TX-100 ($2\cdot10^{-2}$%, solid line; 10^{-1}%, broken line) *in 10 mM aqueous* Tris-*HCl buffer* (pH 7.5). All spectra are normalized to the Q_y maximum, $\Delta A = (A_L - A_R)/A_{max}$.

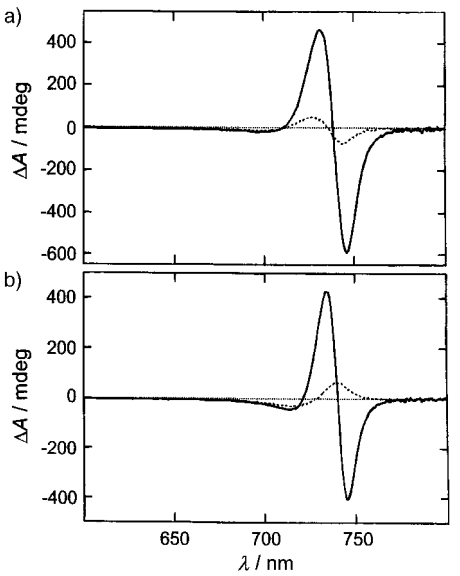

Fig. 5. *Heating effect on the CD spectra of* **1** *aggregate in aqueous solutions of* 10^{-3}%[2]) (a) *and* $5\cdot10^{-3}$% *α-lecithin* (b). Both samples were heated to 55° for 2 d and then cooled to room temperature. The spectra were measured at room temperature (– – –: before heating; ——: after heating) and are normalized to the Q_y maximum, $\Delta A = (A_L - A_R)/A_{max}$.

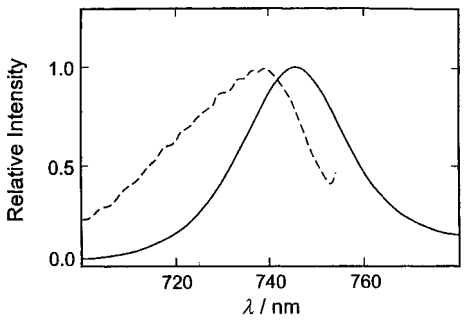

Fig. 6. *Fluorescence* ($\lambda_{exc} = 450$ nm; solid line) *and fluorescence excitation spectra* ($\lambda_{em} = 780$ nm; broken line) *of zinc chlorin* **1** *aggregates in aqueous α-lecithin* (10^{-3}%^{2})) *solution*. Both spectra are normalized to the maxima.

change at all in the absorbance of aggregated **1** was observed. The decrease in the emission of the aggregate in the presence of benzoquinone was reversed by addition of sodium dithionite, and *vice versa*. The effects of reductant and oxidant on the fluorescence intensities have also been reported for BChl *c* aggregates in aqueous monogalactosyl diglyceride solution [8a] and in isolated chlorosomes [15]. Hence, these redox effects might be a common property of metallochlorin aggregates.

The emission of the aggregate in the presence of *TX-100* in H_2O appeared at 748 nm. It exhibited concentration and redox effects similar to those of the aggregates in aqueous α-lecithin solution.

2.4. *Resonance* Raman *Spectroscopy.* In contrast to the variations in absorption, CD and fluorescence, the RR spectra (λ_{max} 456.9 nm) of the diverse aggregates of **1** in the aqueous media are independent on concentration and nature of the surfactant. Thus, the RR spectra of **1** in the presence of α-lecithin (10^{-3} nd 10^{-2}%) and *TX-100* ($2.5 \cdot 10^{-2}$%) were indistinguishable. Moreover, they exhibited, as in non-polar organic solvents [6d], a 1650-cm^{-1} band attributable to the strongly H-bonded 13^1-keto group in the C=O$\cdots$H$-$O$\cdots$Zn building block, and marker bands at 1623 and 1562 cm^{-1} indicative of a pentacoordinated zinc chlorin. Hence, the local structure of the aggregates of **1** in an aqueous microheterogeneous medium is the same as in non-polar organic solvents, independent of the preparation procedure.

2.5. *Singlet Energy Transfer in Zinc Chlorin Aggregates.* Since the aggregates of **1** in aqueous microheterogeneous preparations adequately reproduce the supramolecular structure of the BChl *c* aggregates in chlorosomes, an access to a self-assembled light-harvesting device in an aqueous environment appeared feasible. This should provide a simultaneously simplified and improved version of our first example in this series [13]. When a 50:1 mixture of the potential excitation energy donor (the zinc chlorin **1**) and the potential energy acceptor (the metal-free bacteriochlorin) **5** [6g][16], respectively, was injected into aqueous *Tris*-HCl-buffer-containing α-lecithin, a small absorption band appeared at around 800 nm, next to the intense 735-nm band of the aggregates of **1** (solid line of *Fig. 7,a*). The fluorescence of the aggregate of **1** at 745 nm had decreased significantly, and a new emission band had emerged at 825 nm (*Fig. 7,b*). The fluorescence excitation spectrum shows that the 825-nm emission was indeed sensitized by the excited aggregates of **1** (*Fig. 7,c*).

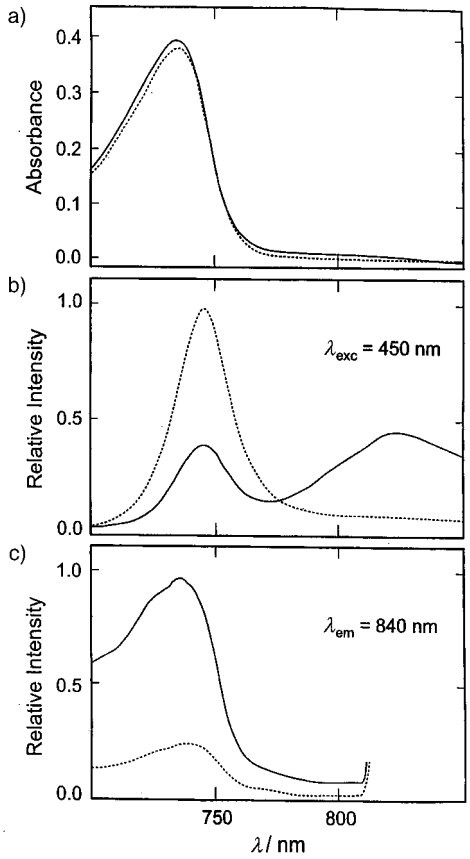

Fig. 7. a) *Absorption*, b) *fluorescence, and* c) *fluorescence excitation spectra of* **1** (broken line) *and of a 50:1 mixture of* **1** *and* **5** (solid line) *in an aqueous solution of α-lecithin* (10^{-3}% [2])

Interestingly, monomeric bacteriochlorin **5** has a 755-nm absorption maximum and a 763-nm fluorescence peak in dichloromethane. *Fig. 7* shows that both are considerably red-shifted to 800 and 825 nm, respectively, when **5** is added to aggregated **1** in α-lecithin/H_2O, as it has also been observed for the heteroaggregate of **1**+**6** in hexane [13].

3. Discussion. – When embedded in the hydrophobic core of surfactants dispersed in water, zinc chlorins such as **1** form supramolecular aggregates. As judged by their absorption, CD, fluorescence, and RR properties, these aggregates possess the same key structural features as both the BChl *c* aggregates constituting the rods in the core of natural chlorosomes and the artificial aggregates formed by BChl *c* when dissolved in the non-polar organic solvents. Aggregate structure and size in the low-polarity solvents are largely controlled by concentration and the type and polarity of the medium, ranging, *e.g.*, from open and closed dimers, and oligomers in CH_2Cl_2 to higher aggregates in hexane [17]. The associative processes are governed by equilibria which

are established relatively slowly and, in hexane, ultimately lead to large chlorosome-type aggregates (type-II aggregates[3])). The latter most likely possess a tubular rod structure [10]. The specific aggregate state of solutions of BChl *c* and structurally related metal chlorins is readily recognized by characteristic spectral patterns.

The *Table* gives an overview of the assignments of the oligomeric structures at several α-lecithin concentrations. Aggregation at its various stages is readily recognized by intensified strongly red-shifted Q_y absorption and fluorescence as well as S-shaped CD spectra (*cf. Figs. 4* and *5*). Raising initially low surfactant concentrations from $<10^{-3}$% α-lecithin and $<2\cdot10^{-2}$% *TX-100* is accompanied by a marked increase in intensity and by narrowing of the weak and broad absorption of **1** (*Figs. 2*,*b* and *c*, and *3*), an indication that populations of several different oligomer structures are transformed to a more uniform composition of larger aggregates. Large chlorosome-type-II aggregates start to appear at $\geq4\cdot10^{-4}$% of α-lecithin, and they predominate at around 10^{-3}%, corresponding to a [surfactant]/[**1**] ratio of *ca*. 1.6. A much higher ratio, *ca*. 38, is required for *TX-100*, which corresponds closely to the critical micellar concentration of this detergent ($1.5\cdot10^{-2}$%). We may, therefore, confidently assume that the aggregates of **1** are formed within the hydrophobic core of the α-lecithin and *TX-100* micelles. Thereby, specific properties of the surfactant affect the supramolecular architecture and/or size of the aggregates of **1**. Hence, the Q_y bands shift slightly to the red when going from α-lecithin to *TX-100* aggregates (*Fig. 2*). Moreover, α-lecithin concentrations higher than $2\cdot10^{-3}$% favor metastable type-II aggregates while excess *TX-100* ($>2\cdot10^{-2}$%) causes some deaggregation to monomeric **1** similar to the action of alcohols on isolated chlorosomes [18], aggregates of BChl *c* [7b][8b], and zinc analogs [6b][17] (presumably, *TX-100* micelles more readily dissolve small BChl *c* oligomers and even monomers).

Table 1. *Spectral and Structural Features of* **1** (8 μM) *in Aqueous Microheterogeneous Medium as a Function of α-Lecithin Concentration*

α-Lecithin concentration [$\cdot10^{-4}$% (*w*/*v*)]	0	4	10	20	40	100
VIS-absorption	weak and broad		735-nm maximum			
CD	weak	(+/−) type		(+/−) and (−/+)	(−/+) type	
Fluorescence	weak	745-nm maximum				
Oligomeric structure assignment	labile		stable		metastable	
	type-I aggregates		chlorosome-type (type II) aggregates			

Monitoring the effects of surfactant concentration by CD reveals further details of the aggregation dynamics in the micellar phases. The change in absorption with surfactant concentration is paralleled by a concomitant transition of the CD from type (+/−) to (−/+). Such a sign inversion has also been observed with isolated chlorosomes [14][19][20] and reconstituted BChl *c* aggregates [8a]. Furthermore, we

have reported recently that the (−/+)-type CD of synthetic zinc chlorins changes to (+/−) with increasing alkyl-ester chain lengths [6f]. This variation of the CD is not yet understood on a molecular level [21]. The large rotatory strength has been attributed to strong excitonic interaction [6i] and a superimposed effect [22] of the polymer-and-salt-induced(psi)-type CD similar to that found for macroscopic chiral domains of DNA aggregates [23]. Since CD is obviously a sensitive characteristic of the supramolecular structure, the similarity of the CD spectral features between natural and artificial aggregates strongly suggests that the pigments self-organize in a similar manner in both systems.

The intensification of the (+/−)-type CD of the artificial aggregates of **1** upon heating to 55° and the conversion from (−/+) and mixed types to (+/−) (*Fig. 5*) is especially remarkable, and certainly very significant in structural terms. It is consonant with a restructuring of the supramolecular aggregate architecture, and with evidence by *Ma et al.* [19] that chlorosomal (type II) BChl *c* aggregates exhibiting a (+/−) CD have a higher structural order than aggregates with a (−/+) CD.

The α-lecithin and *TX-100* aggregates exhibit some spectral differences which are pertinent to the surfactant organization. In H_2O, α-lecithin, in general, forms bilayer and lamellar structures, whereas *TX-100* forms micelles. It is interesting that the aggregates of **1** with α-lecithin in H_2O are in several ways spectrally more similar to the natural chlorosomes. Quite similar CD changes are encountered, and particles of an estimated 100–200 nm in diameter were found in preliminary DLS measurements, with no significant dependence on α-lecithin concentration. Such particle dimensions are similar to those of intact chlorosomes and of chlorosomes reconstituted from crude extracts of *C. aurantiacus* [7b]. In contrast, the *TX-100* aggregates gave exclusively (+/−)-type CD spectra, and the micelles were too small (< 10 nm) to be detected by DLS. It is conceivable that the alkyl chains of α-lecithin promote the formation of aggregate structures related to the tubular inverted-micellar arrangements of BChls which are presumed to exist in the chlorosomes [10]. In the presence of other surfactants, *e.g.*, *TX-100* at micellar and higher concentrations, smaller aggregate structures of BChl, such as type I, are possibly dissolved in the micelles and therefore prevail, while, at submicellar concentrations, *TX-100* may form an enveloping layer around the aggregates.

The independence of the RR spectra on the mode of aggregate preparation, unlike the absorption, CD, and fluorescence spectra of **1**, suggests that the local structural building blocks based on the C=O···H−O···M bonding network [6d,e][9] are retained irrespective of any supramolecular characteristics of the aggregate architecture, when exchanging non-polar organic solvents for either a non-polar lipid (α-lecithin) or detergent (*TX-100*) in H_2O, in agreement with molecular modelling studies (see [10] and unpublished work by *Holzwarth et al.*).

At this point it seemed obvious that a self-assembly of functional units for heterogeneous energy transfer should prove as efficient as described previously for the heteroaggregate of **1** and **6** (see *Fig. 1*) in both hexane and aqueous preparations [13]. Indeed, the energy transfer from aggregated **1** to **5** appears to be quite analogous and of comparable efficiency [13]. For such an efficient energy transfer to occur, it is necessary that the donor-acceptor distance is small, *i.e.*, the acceptor must be included in the same lipid portion containing also the donor aggregate (see *Fig. 8*). Our result, therefore,

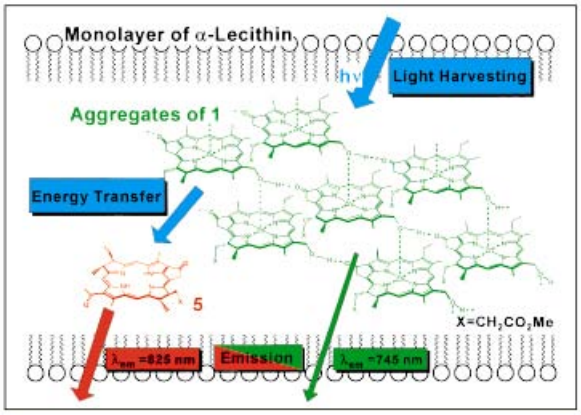

Fig. 8. *Proposed singlet energy transfer from the aggregates of* **1** *to bacteriochlorin* **5** *within hydrophobic areas of organized aqueous α-lecithin structures*

demonstrates that a covalent linkage between zinc chlorin and bacteriochlorin moieties is not a prerequisite for efficient energy transfer from aggregated donor to metal-free bacteriochlorin acceptor in an aqueous microheterogeneous medium.

The non-covalent (metallo)chlorin-bacteriochlorin couple used in this work proved to be an efficient energy acceptor for an artificial light-harvesting system based on self-assembled zinc chlorins. This assembly is even more simple than the covalently linked dyad acceptor used previously [13]. We, therefore, believe that such a system should also be suitable to be incorporated into an efficient artificial light-harvesting/electron transfer device. At present, the energy arriving at the acceptor is not being used further. Comparison with data from our previous work [13] suggests that, in the present situation, energy transfer leads to an equilibrium situation between the donor and the acceptor moiety where efficient back energy transfer occurs. This means that the presently estimated energy-transfer efficiency of $\geq 60\%$ (based on the fluorescence intensities) represents only the lower limit to the possible maximal transfer efficiency, if the energy arriving at the acceptor could be converted rapidly into some other form of energy reservoir, *e.g.*, a radical pair. Therefore, the coupling of the present supramolecular energy donor/acceptor unit with an energy-using process, *e.g.*, a photoinduced electron transfer, should result in an efficient artificial photoactive device that could mimic the function of a natural antenna/reaction center system.

Experimental Part

Preparation of Aggregates in Aqueous Media. Methyl 3-desvinyl-3-hydroxymethylpyropheophorbide *a* zinc complex (**1**) [6e] and L-α-phosphatidylcholine (*Sigma*, USA; from frozen egg yolk, purified chromatographically by elution with $MeOH/CH_2Cl_2$ 1:4 from a silica gel column) were dissolved in MeOH. The soln. was injected into 10 mM *Tris*-HCl buffer (pH 7.5) and shaken vigorously (final MeOH concentration was 1% (*v*/*v*) and [**1**] = 8 μM). The aggregates with aq. *Triton X-100* (*Nacalai tesque*, Kyoto, Japan) soln. were prepared in a similar way.

Spectroscopic Techniques. Absorption and fluorescence spectra were measured with *Hitachi U-3500* and *F-4500* fluorescence spectrophotometers, respectively, and CD spectra with a *Jasco J-720W* spectropolarimeter. RR Spectra were measured with the 457.9-nm line of an Ar^+ laser (*NEC GLG-3460*, < 10 mW) and a *Jobin-*

Yvon Raman System T 64000 with 4-cm^{-1} resolution. The DLS was recorded with a light scattering spectrometer *DLS-600* (*Otsuka Electronics*) upon irradiation with a 5-mW He–Ne laser at 24° at a scattering angle of 90°.

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