Self-aggregation of Synthetic Zinc Chlorophyll Derivatives Possessing Fluoroalkyl Chains in Liquid Carbon Dioxide as Models of Green Photosynthetic Bacterial Antennae

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Zinc chlorophyll derivatives possessing (multi)-perfluoroalkyl chain(s) in the 17-propionate residue were dissolved in liquid carbon dioxide to form their oligomers (=J-aggregates), while the alkyl-type analog was insoluble in the medium. These results indicated solubilization and stabilization of their supramolecules by an interaction between the perfluoroalkyl substituents and liquid carbon dioxide.

Green photosynthetic bacteria have unique light-harvesting antennae called chlorosomes. The chlorosomes are composed of self-aggregates of chlorophyll (Chl) pigments without any assistance of proteins.[1] These chlorosomal Chls having hydroxy, keto carbonyl groups and central magnesium (see Figure 1a) are chemically programmed to form well-ordered aggregates. Their self-aggregates are constructed by specific hydrogen and coordination bonds through the functional groups as well as π–π interaction among chlorosomal Chls.[2] All chlorosomal Chls have a long hydrocarbon chain as R_{17}, which is assumed to stabilize their self-aggregates by interaction with the surrounding environment.[3] However, the detailed role of the hydrocarbon chain has not been unraveled. To elucidate the function of the hydrocarbon chain, various Chl derivatives were synthesized and their self-aggregates were examined in organic and aqueous media.[4]

Recently, we have synthesized zinc Chl derivatives possessing perfluoroalkyl chains in the 17-propionate residue as models of chlorosomal Chls and reported their self-aggregative properties in fluorous solvents.[5] In general, CH-type organic compounds cannot be dissolved in fluorous solvents and a fluorine content of over 60% total molecular weight is necessary for dissolution of CF-type compounds in fluorous solvents. Such fluorinated compounds have a high affinity to liquid and supercritical carbon dioxide.[6] Here, we report the visible absorption properties of zinc Chl derivatives possessing perfluoroalkyl or alkyl chains in liquid carbon dioxide (liq. CO_2), and discuss the effect of the 17-substituents upon the self-aggregation of the synthetic Chl molecules.

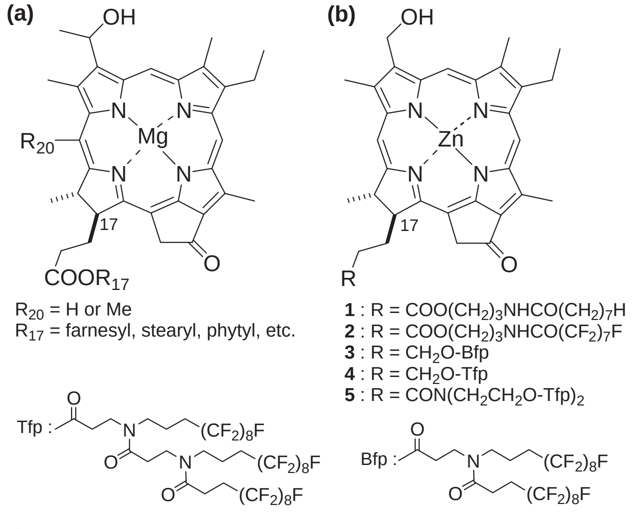

Figure 1. Molecular structures of naturally chlorosomal Chls (a) and their synthetic zinc chlorins **1**–**5** (b).

Zinc Chl derivatives possessing alkyl **1** or perfluoroalkyl chains **2**–**5** shown in Figure 1b were synthesized from naturally occurring Chl-*a* as described previously.[5] Their electronic absorption properties were investigated under two different environments for self-aggregation: one was a nonpolar organic solvent and the other was liq. CO_2.

In neat THF (3 µM), all compounds **1**–**5** were the monomeric state, where a THF molecule was an axial ligand of their central zinc atom.[7] These compounds gave sharp electronic absorption peaks at the Soret/Q_y maxima = 424/646 or 648 nm (see Figure S1).[8] When the THF solution was diluted with hexane (THF/hexane = 0.4/99.6 (v/v), ca. 4 µM), each peak was broadened and red-shifted (see Figure S2)[8] due to formation of self-aggregates as seen in natural chlorosomes (=J-aggregates).[7] Compound **1**, an alkyl-type analog, showed exclusively the most red-shifted Q_y maximum, whereas less red-shifted Q_y bands in self-aggregates of compounds **2**–**5** possessing perfluoroalkyl chain(s) were accompanied by their residual monomeric peak at around 650 nm whose intensity enlarged with the increasing number of chains (see Figure S2).[8] Moreover, the red-shifted Q_y bands were greatly broadened and the peaks moved to a shorter wavelength as the number of perfluoroalkyl chains increased from 0 to 3 in **1**–**4** (see Table 1). These results showed that self-aggregates of compound **1** possessing an alkyl chain were the most stable in a hexane solution.

Carbon dioxide is gas at room temperature and atmospheric pressure, and becomes liquid above 6.4 MPa.[6] Liq. CO_2 is recognized as one of the ideal nonpolar solvents because of nonpolarity of its molecule.[9] Similarly with the above hexane-based

Table 1. Visible absorption spectral data of zinc chlorins **1**–**5**

	λ_{max}/nm (0.4% THF–hexane)		FWHM[a] /cm^{-1}	λ_{max}/nm (0.4% THF–liq. CO_2)		FWHM[a] /cm^{-1}
	Soret	Q_y		Soret	Q_y	
1	448	742	783	—	—	—
2	447	738	893	450	736	1006
3	449	733	1060	452	738	966
4	444	731	1163	452	737	857
5	437	735	1070	417	649	—

[a]A full-width at half-maximum of red-shifted Q_y band.

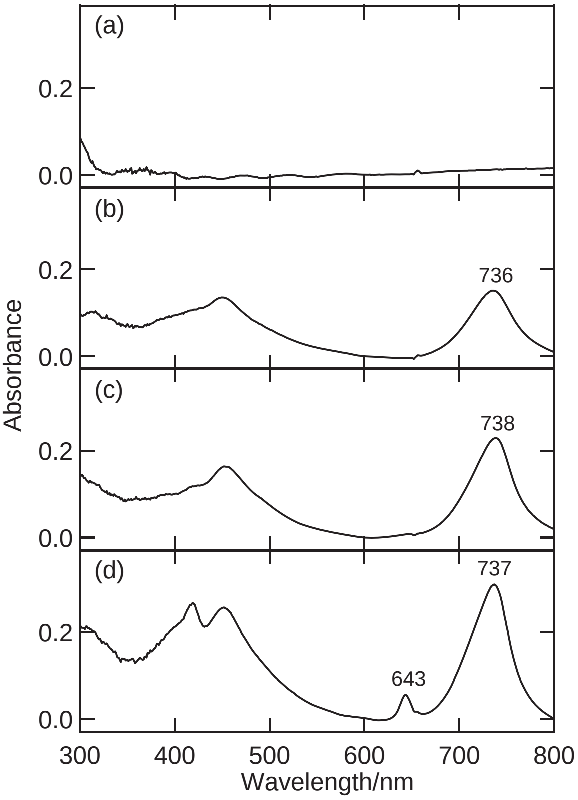

Figure 2. Visible absorption spectra of synthetic zinc chlorins **1** (a), **2** (b), **3** (c), and **4** (d) in 0.4% (v/v) THF–liq. CO_2.

system, a THF solution of zinc Chls was diluted with liq. CO_2 (THF/liq. $CO_2 = 0.4/99.6$ (v/v), ca. 3 µM). For compound **1** possessing an alkyl chain, no absorption peak was observed as shown in Figure 2a, indicating that **1** was not dissolved in liq. CO_2. On the other hand, compounds **2**–**4** possessing one to three perfluoroalkyl chain(s) were soluble in the liq. CO_2 system to show red-shifted Q_y bands as seen in a hexane solution (vide supra). The results showed that the fluoroalkylated Chls self-aggregated in liq. CO_2 (Figures 2b–2d) to give similar oligomers as in chlorosomal J-aggregates. Interestingly, no absorption peak originating from the monomer was observed in cases of **2** and **3** (Figures 2b and 2c). Compound **4** gave a small peak of the monomer absorbing at 643 nm (Figure 2d): the remained monomer was estimated to be about 3%. Moreover, compound **5** gave exclusively a Q_y peak of the monomer at 649 nm, not the self-aggregates (see Figure S3).[8] Therefore, compound **5** possessing six perfluorooctyl chains in the 17-substituent was highly soluble in liq. CO_2, and could not self-aggregate in the medium owing to its higher affinity with liq. CO_2. In contrast to a hexane solution, the red-shifted Q_y bands in liq. CO_2 were sharpened as the number of perfluoroalkyl chains increased (see Table 1 as well as Figures 2 and S4):[8] narrowing the band width indicates formation of well-ordered oligomers.

These self-aggregates prepared by the synthetic fluorinated Chls were assumed to be fairly unstable, since absorption peaks decreased during standing in liq. CO_2 and finally disappeared within 20 min at room temperature (see Figure S5).[8,10] Removal of all the liq. CO_2 and successive addition of new liq. CO_2 led to the recovery of the original absorption peaks. Thus, the self-aggregates of moderately fluorophilic **2**–**4** were temporarily prepared in liq. CO_2, and much higher fluorophilicity due to the presence of a large number of perfluoroalkyl chains in a molecule disturbed such a chlorosomal self-aggregation. Matching of the 17-substituents with the surrounding environment is effective for construction of well-ordered self-aggregates.

We investigated chlorosomal self-aggregation of synthetic Chl pigments possessing perfluoroalkyl chains at the 17-propionate residue under compressed liq. CO_2 conditions. This is the first report on the dissolution and self-aggregation of such Chl molecules in liq. CO_2.

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10 We measured the absorption spectra in supercritical CO_2 (40 °C, 9.8 MPa), but the peak intensities of those self-aggregates were substantially suppressed. During the heating of aggregated solutions from room temperature to 40 °C for a change from liquid to supercritical phase, precipitates of self-aggregates were gradually produced.

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