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Self-aggregation of synthetic zinc perfluoroalkylated bacteriopheophorbide-*d* in fluorous organic solvents

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Introduction

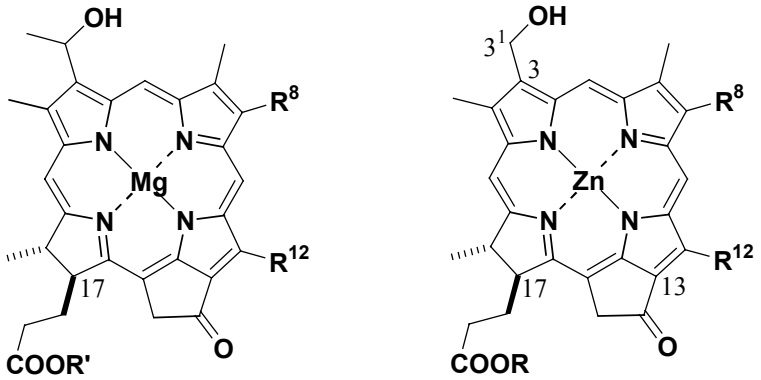
Bacteriochlorophyll(=BChl)s-*d* (left drawing of Fig. 1) and the model compounds self-aggregated in less polar organic solvents, aqueous organic solvents and aqueous micellar solutions as well as in chlorosomes, major light-harvesting antenna systems of green photosynthetic bacteria (Tamiaki 1996). Here we report synthesis of zinc 3^1-demethyl-bacteriopheophorbides-*d* **1** possessing perfluorooctyl groups at the 17-propionate (right drawing of Fig. 1) and their self-aggregation in fluorous organic solvents.

Results and discussion

Pyropheophorbide-*d* was prepared by modification of chlorophyll-*a* and the resulting acid was esterified with perfluoroalkylated alcohols (carbodiimide–dimethylamino-pyridine), followed by reduction of the 3-formyl group and zinc-metallation to give desired compounds **1** (Tamiaki et al. 1996a). Zinc complex **1** was monomeric in neat THF and the solution was mixed with perfluoro-2-butyltetrahydrofuran (FC-75). After stirring, the solution was separated into two phases: the upper THF phase was blue and the lower FC-75 phase was colorless. This observation indicates that monomeric **1** remained in THF. In 0.4%(*v*/*v*)THF–hexane, **1** self-aggregates to form oligomers. When the green solution was shaken with FC-75, the oligomeric **1d** completely moved to the lower fluorous FC-75 phase and could be solvated in FC-75: a reversed S-shaped CD signal at the region of red-shifted Q_y absorption band (λ_{max} = 734 nm). In 7%(*v*/*v*)THF–hexane, **1d** partially self-aggregated to form oligomers and the rest of **1d** remained to be monomeric. After extraction of the solution with FC-75, the blue hexane layer contained only monomeric species and the aggregates were observed exclusively in the green fluorous layer. Such a selective extraction shows that self-aggregates **1** consist of a core part of chlorin π-conjugates (by a special bonding, 13-C=O···H-O(3^1)···Zn, and π-π interaction (Tamiaki et al. 1996b)) and outer sphere of perfluoroalkyl groups. In other fluorous solvents, e.g., perfluoro-octane and tris(perfluorobutyl)amine, similar extraction was observed. The visible and circular dichroism spectra showed that the artificial self-aggregates of **1** in fluorous solvents resembled to natural chlorosomal BChl aggregates. The oligomeric **1** in fluorous solvents would be a good structural model of chlorosomal BChl aggregates.

BChls-*d* self-aggregate to form rod structures in a chlorosome. Supramolecular structure of the rod elements is still in debate and several structures were proposed. The major difference is the direction of the long chain group (R' in left of Fig. 1, e.g., farnesyl group) at

the 17-propionate in the self-aggregates: the long chains self-assembly in the inner sphere like a normal micelle (Matsuura et al. 1993), the chains situate at the outer sphere like a reverse micelle (Holzwarth and Schaffner 1994), and they occupied both the sides like a bilayer (Nozawa et al. 1994; Steensgaard et al. 2000; Van Rossum et al. 2001). The present model system showed that the normal micelle-type model is less favorable and the reverse micelle-type model is more promising for the supramolecular structure of rod elements formed by self-aggregation of 8-ethyl-12-methyl-BChl (R^8=Et and R^{12}=Me in left of Fig. 1), i.e., *Chloroflexus* chlorosomal rods with a 5-nm diameter (Miyatake et al. 2001).



Bacteriochlorophyll-*d* (BChl-*d*)

Model compounds **1**

1a: R = Rf
1b: R = $CH(CH_2ORf)_2$
1c: R = $CH(CH_2ORf)CH_2OCH(CH_2ORf)_2$
1d: R = $CH(CH_2ORf)CH_2OCH(CH_2ORf)CH_2OCH(CH_2ORf)_2$
(Rf = $CH_2CH_2(CF_2)_8F$)

Fig.1. Molecular structures of BChl-*d* and the model compounds **1**

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