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Diastereoselective Control of Aggregation of 3^1-Epimeric Zinc Methyl Bacteriopheophorbides-*d* in Apolar Solvents

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Visible absorption spectra of the *in-vitro* oligomers of the 3^1-epimeric zinc methyl bacteriopheophorbides-*d* are different in apolar organic solvents. This indicates structural differences between these oligomers which are controlled by the configuration of the 1-hydroxyethyl group at C-3.

Chlorosomes are the main light-harvesting complexes of green photosynthetic bacteria.1) It has been shown2,3) that in the chlorosomes of *Chloroflexus aurantiacus*, strain OK-70-fl, *ca.* 2:1 mixtures of the (3^1R) and (3^1S) epimers of several bacteriochlorophyll(BChl)s-*c*4) are self-organized in aggregates without direct assistance of proteins. BChl-*c* molecules are known to self-aggregate in a similar fashion *in vitro* in apolar organic solvents.2d,5) It has been proposed that the C-3^1 configuration may affect the size of the *in-vivo* BChl-*c* oligomers and/or the type of their intermolecular bonding.4,6) However, Cheng *et al.*7) have recently suggested that the visible absorption spectra of the oligomers of C-3^1 epimeric zinc methyl bacteriopheophorbide(Zn-MBPh)s-*d* (**1a** and **1b**), formed upon addition of hexane to a minimum amount of dichloromethane (λ_{max} = 728 nm at $A_{max} < 0.3$), do not differ from each other. Insofar, zinc chlorins would not be appropriate compounds for model studies of the chlorosomal BChl-*c* aggregates.8) This prompts us to report our own finding that the absorptions of **1a** and **1b** oligomers in fact do differ distinctly in *cyclo*hexane–dichloromethane solutions of approximately thrice the concentrations used by Cheng *et al.*7) when judged from the absorbance at the Q_y maximum.

3^1-Epimeric mixtures of Zn-MBPh-*d* (**1**, see Fig. 1) were prepared according to the literature.5b,7,9) The epimers were separated by single HPLC run.10) The configuration of the C-3^1 position was determined by comparison of reported ^{1}H NMR spectral data9) of epimerically pure MBPh-*d* with those of the metal-free samples derived from separated epimers **1a** and **1b** (stirring in aq 2% HCl–CH_2Cl_2).11)

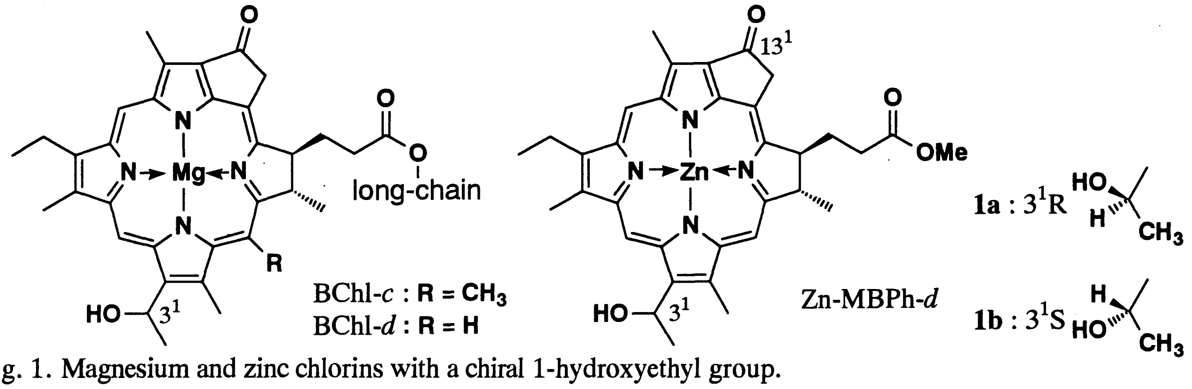

Fig. 1. Magnesium and zinc chlorins with a chiral 1-hydroxyethyl group.

The (3^1R)-epimer **1a** dissolves in dichloromethane as a monomer, characterized by its visible absorption bands (Q_y maximum at 648 nm).7,12) Addition of cyclohexane to the solution induced a red shift of the Q_y band to 705 nm (see Fig. 2). We have already reported that similar zinc chlorins possessing a 3^1-hydroxy and a 13^1-carbonyl substituent readily form oligomers in apolar organic solvents.12) In view of the fact that (3^1R)-BChl-*d* gives a 714-nm oligomer band6) and that substitution of central Mg by Zn induces an about 230-cm^{-1} blue shift in the oligomer band,5b) the 705-nm band of **1a** can be assigned to its oligomeric form. Accordingly, the Qy maxima at 647 and 693 nm of the (3^1S)-epimer **1b** in cyclohexane–dichloromethane (99:1) are attributable to a minor monomer component and to an oligomer, respectively. The oligomers of **1a** and **1b** disintegrated to monomers upon methanol addition, their Q_y absorption bands undergoing the appropriate blue shift. Solution aggregates of **1b** were less stable than those of **1a** on standing and tended to transform into heterogeneous mixtures more easily.

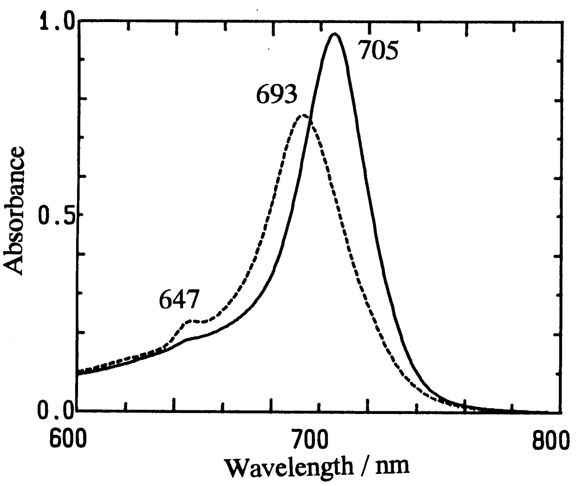

Fig. 2. Visible absorption spectra of **1a** (—) and **1b** (- - -) in 99% (v/v) cyclohexane and 1% dichloromethane.

The diastereoselective control of *in-vitro* aggregation of **1a** and **1b** is thus similar to but more pronounced than that operating for BChl-*c* aggregates.6) In contrast to claims of Cheng *et al.*7) **1a** and **1b** in *dry* hexane–dichloromethane (99:1) gave essentially the same spectra as in Fig. 2; only in *wet* hexane and cyclohexane **1b** gave a broad shoulder around 725 nm, while in **1a** the red shift, albeit present, was much smaller. In summary, the difference between **1a** and **1b** is twofold, *i.e.* with respect to their λ_{max} in dry solvent and their response to water.

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8) Smith *et al.* were first to suggest zinc chlorins as models for BChl-*c* and -*d* aggregates; see Ref. 5b.
9) K. M. Smith, G. M. F. Bisset, and M. J. Bushell, *J. Org. Chem.*, **45**, 2218 (1980).
10) Under the conditions of Cosmosil 5C$_{18}$-AR, 4.6x250 mm, Nacalai Tesque, $CH_3OH:H_2O=7:2$, 1.0 ml/min, (*R*)-**1a** and (*S*)-**1b** were readily separated ($R_s = 2$). The retention times were 27 and 29 min, respectively.
11) After re-zinc metallation, no epimerization could be observed in HPLC analysis.
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