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Theoretical study on the thermodynamic properties of chlorophyll *d*-peptides coordinating ligand

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Abstract

The chlorophyll *d* containing cyanobacterium, *Acaryochloris marina* has provided a model system for the study of chlorophyll replacement in the function of oxygenic photosynthesis. Chlorophyll *d* replaces most functions of chlorophyll *a* in *Acaryochloris marina*. It not only functions as the major light-harvesting pigment, but also acts as an electron transfer cofactor in the primary charge separation reaction in the two photosystems. The Mg-chlorophyll *d*-peptide coordinating interaction between the amino acid residues and chlorophylls using the latest semi-empirical PM5 method were examined. It is suggested that chlorophyll *d* possesses similar coordination ligand properties to chlorophyll *a*, but chlorophyll *b* possesses different ligand properties. Compared with other studies involving theoretical correlation and our prior experiments, this study suggests that the chlorophyll *a*-bound proteins will bind chlorophyll *d* without difficulty when chlorophyll *d* is available.

Keywords: Chlorophyll *d*; Synthetic Peptide; Heats of Formation; Molecular modelling

1. Introduction

The discovery of *Acaryochloris marina* (*A. marina*) [1] reveals the first natural example where chlorophyll (Chl) *d*, instead of Chl *a*, plays an essential role in oxygenic photosynthesis. Here Chl *d* constitutes over 95% of the chlorophyll content, with Chl *a* being present in variable amounts but is generally less than 5% [1,2]. From recent investigations on *A. marina*, it is clear that Chl *d* plays the principal role in both the major light-harvesting complex [3,4] and the special pair in photosystem I (PS I) reaction centre [5,6]. Only in the reaction centre of PS II is it uncertain which Chl (Chl *a* or Chl *d*) acts as the special pair, even though Chl *d* is the major pigment in the reaction center of PS II [7,8]. The challenge of *A. marina* is to carry out O_2-evolving photosynthesis by using the lower energy photons of Chl *d* at longer wavelengths (extended up to 740 nm). The central question of this replacement is how Chl *d* replaces most of the functions of Chl *a* in oxygenic photosynthesis.

The chemical structure of Chl *d* is almost identical to Chl *a* except at the ring A, C-3 position, where a formyl group replaces the vinyl group (Fig. 1). This substitution shifts the maximum absorption (Q_y) of Chl *d* to a longer wavelength, that is about 30 nm red-shifted compared to Chl *a* [1,9]. Therefore, the excited state energy and the redox potential span that can be generated by Chl *d* is less than Chl *a* [5,10]. The substitutions in the peripheral substituents of chlorophylls influence the π-system that is sensitive to the changes in the charge density of the central chelated metal, a Mg atom [11]. It is known that small substitutions in the peripheral groups of chlorophylls will strongly influence the coordinating ligand [12,13]. In the case of Chl *b*, the formyl group at the C-7 position (Fig. 1) increases the Lewis acid strength of the Mg atom (i.e. modulated charge density of Mg) and requires stronger Lewis bases to displace a tightly bound water ligand that is acquired during synthesis [13]. In this respect, Chl *d*, with a formyl group at the C-3 position, provides a particularly interesting case to investigate the interaction influenced by the changes of charge density of the central metal based on their thermodynamic parameters.

Most chlorophyll is bound to hydrophobic proteins located in the thylakoid membranes. There are several different types of

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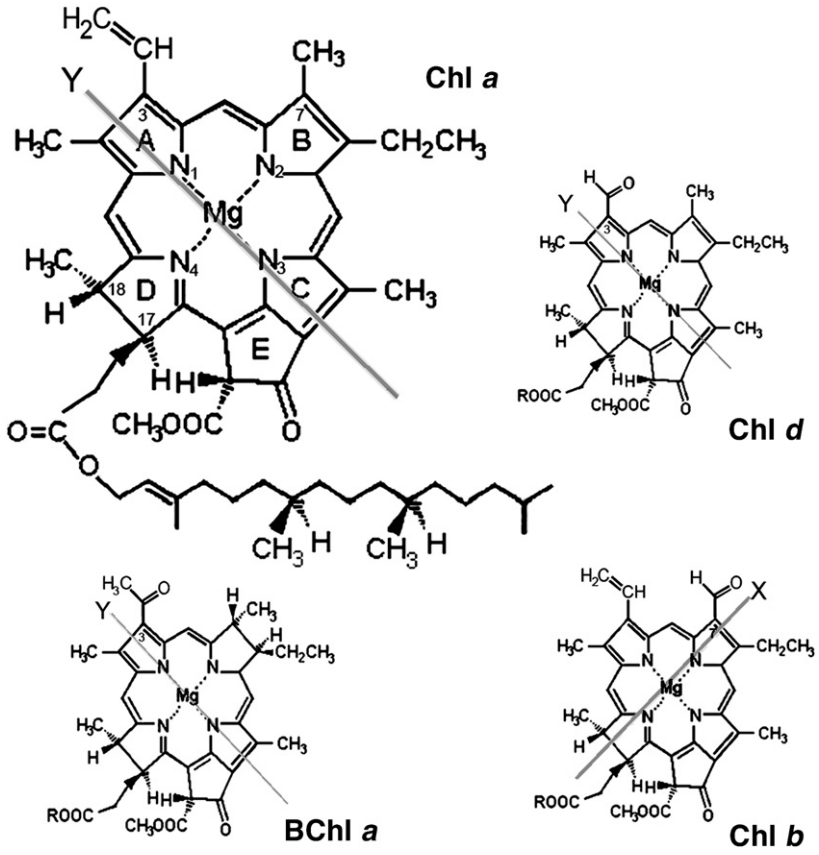

Fig. 1. Chemical structure of chlorophylls. Carbons are numbered according to IUPAC convention see Ref. [49]. Nitrogens in the macrocycle ring are numbered as 1−4 to match the text. Gray lines crossing the molecules indicate the direction of the Q_x and Q_y axes. R is the phytyl chain.

pigment–protein complexes working together to perform photosynthesis, the light-harvesting chlorophyll–protein complexes and reaction centre chlorophyll–protein complexes, where chlorophyll molecules convert the energy of light into electron flow. In considering the function of the pigment–protein complexes, two important aspects are the structure and the organization of the polypeptides, which in turn determine the position, distance, orientation and environment of the pigment molecules. In *A. marina*, the amino acid sequences of the reaction centre (RC) I protein PsaA/PsaB and RC II protein PsbA/PsbD are highly homologous to the analogous proteins of Chl *a*-containing organisms [5,7]. Therefore, it is assumed that no specific sequence of the amino acids is required to bind Chl *d* [14].

The coordinating interactions between amino acids and chlorophylls are important to determine function. The isolated PCP (peridinin–chlorophyll–protein) antenna system can recombine with a range of chlorophylls *in vitro*. This model system provides a hint about the ligand properties involved [15]. The LHCa1 apoprotein of *Porphyridium*, which only binds Chl *a* naturally, can be reconstituted with either Chl *b* or Chl *c* [16]. Satoh et al. [17] introduced the CAO enzyme that converts Chl *a* to Chl *b* into a cyanobacterium and were able to demonstrate the formation of Chl *b* and its functional incorporation in the P700 Chl *a* protein complex (CPI). Scheer and his colleagues have shown that BChl *a* in the special pair of bacterial reaction centers can be substituted by a number of other BChls [18]. They have also demonstrated that various BChls can be substituted, some with metal substituents, in the LH2 region of purple sulphur bacteria [19].

To understand the consequences of replacement of chlorophylls in the assembly of pigment–protein complexes and their functions, the thermodynamic properties of the coordination reaction must be considered. Here we employ the latest semi-empirical PM5 method of molecular modeling to investigate the thermodynamic properties of a chlorophyll–peptide coordinating complex, based on a biomimetic synthetic peptide as well as various other species of chlorophylls. Using a model system [20] a number of theoretical studies involving the calculated heats of formation (ΔH) of chlorophylls binding to the peptide which was built from 16 amino acids were performed. Particular interest was given to the chlorophyll environment surrounding the area where the formyl group substitution occurs.

2. Computational methods

2.1. Model design

A synthetic peptide, NH_2-GLLAWRSHIVELAAGG-$CONH_2$, was folded to form a three-dimensional model by extracting the structure from the crystal structure of the spinach major Light Harvesting Complex II (LHCII) [21]. The prior studies [12,20] using this designed synthetic peptide indicate that two molecules of chlorophylls could bind to this peptide

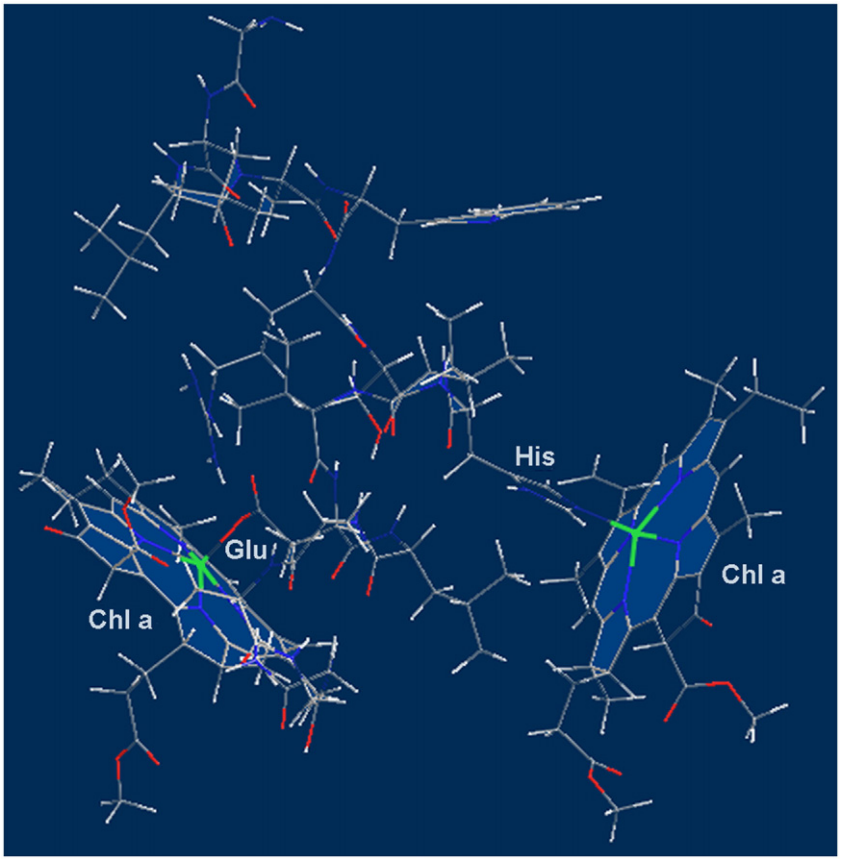

Fig. 2. Model structure of the chlorophyll a-peptide generated by the PM5 optimisation. White, hydrogen bond; gray, carbon bond; purple, nitrogen bond; red, oxygen bond; green, magnesium atom and its coordinating ligands.

through the Glutamic acid (Glu, E)-Arginine (Arg, R) ion-pair and imidazole group of Histidine (His, H). The overall reaction is: Peptide+2Chls ⇆ Peptide·2Chls. The heats of formation of this reaction are calculated by using the PM5 method [22,23] at the optimised model structure.

2.2. Computational details

The PM5 method has been widely used in various environments and successfully predicts excellent molecular properties [24–27]. The PM5 method was performed using the MOPAC 2002 package [28] to optimise the structure of the monomer chlorophyll and to optimise the folded peptide bound chlorophylls that are coordinated to the central Mg atom. The heats of formation were also calculated. The nitrogen of imidazole in His and the oxygen of Glu were chosen as the fifth ligand of the central Mg for the chlorophylls. Since we are only concerned with the chemical bonding between the Mg atom of the chlorophyll and the imidazole of His and the ion pair formed by Glu and Arg, the phytyl chains in the chlorophylls (at C-17 position, Fig. 1) can be replaced by methyl groups. This removal of the phytyl chain aids in the efficiency of the computation without affecting the prediction of the heats of formation.

The optimised structural model of the Chl *a*–Mg–peptide complex is achieved by using the PM5 method searching for a minimum energy on the potential surface. Since the PM5 method can be used to predict good geometries of the chlorin ring in chlorophylls [27], the optimised model of the Chl *a*–Mg–peptide complex can be considered acceptable for additional thermodynamic property calculations. Also, other chlorophyll–peptide model systems, including Chl *b*, Chl *d* and BChl *a*, were first built based on the optimised structure of Chl *a*–Mg–peptide complex, and then were re-optimised by using the PM5 method. The solvent effects were considered by calculating the ΔH. Discussion will also be centred on the

Table 1
Calculated heats of formation (ΔH) of the Chl–Mg–peptide ligand in different environments (with different dielectric constant) using the PM5 method in the model system

Species	Heats of formation (kcal/mol)						Relative stability[a]
	ε=1	ε=2.2	ε=4.3	ε=6.9	ε=12.3	ε=78.4	ε=2.2
BChl *a*-peptide	−892	−1001	−1065	−1093	−1001	−1047	1
Chl d-peptide	−806	−913	−977	−1005	−1027	−949	2
Chl *a*-peptide	−706	−824	−891	−924	−944	−870	3
Chl *b*-peptide	+770	+379	+253	+115	+1	−133	4

*ε is the dielectric constants. Dielectric constant of the gas phase (1.0), benzene (2.2), ether (4.3), aniline (6.9), pyridine (12.3) and water (78.4).
[a] The more negative value, the more thermodynamically stable.

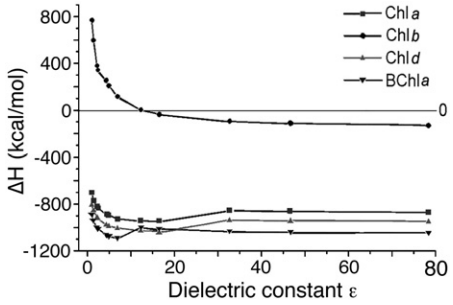

Fig. 3. Comparison of the calculated heats of formation (Δ*H*, kcal/mol) of the Chl–Mg–peptide ligand as a function of the dielectric constant (ε). Square (■) represents Chl *a*; round (●) is Chl *b*; up triangle (▲) is Chl *d* and down triangle (▼) is BChl *a*.

influences relating to the values of the dielectric constant in the protein environment.

3. Results

The optimised structural model of the complex that shows the chemical structure of Chl-*a* binding to the peptide is given in Fig. 2. Our current structural model of chlorophylls included in the complex, retains the macrocycle ring of Chl *a* but the tail of the phytyl chain has been replaced by a methyl group (CH_3) to reduce the number of atoms used in the computation. This structural model is consistent with that generated by the designers [12]. Comparison among the various chlorophylls in the structural model was performed by substituting the Chl *a* by other groups and then re-optimising the resultant structure using the PM5 method.

Table 1 summarizes the results of the heats of formation (Δ*H*) for the coordination interaction between various chlorophylls and the peptide in the gas phase. Various solvents with different values of dielectric constant (ε) were also considered. The ε dependence of the Δ*H* energies for the coordinating reaction between chlorophylls and the peptide is described in Fig. 3.

The calculated values of Δ*H* of the Chl *a*, Chl *d* and BChl *a*-peptides in the model system were determined to be negative, which indicate that the coordination reactions are thermodynamically stable. The range of the values of Δ*H* for the Chl *a*–peptide from −706 kcal/mol at ε=1 to −870 kcal/mol at ε=78.4, Chl *d* from −806 to −949 and BChl *a* from −892 to −1047 kcal/mol, respectively, suggests that the Δ*H* in these three model systems is relatively insensitive to ε (Table 1 and Fig. 3). However, the Δ*H* in the Chl *b*-system showed very different thermodynamic properties from the others. The calculated Δ*H* for the Chl *b*–peptide complex is positive in the gas phase (ε=1) but rapidly decreases to zero as ε was lowered in value to a relatively low-ε region (ε<12). The Δ*H* finally converges to a constant negative value of 100–130 kcal/mol in the high-ε region (Fig. 3). This ε dependence of the Δ*H* indicates that the coordination of the Mg–peptide ligand in the

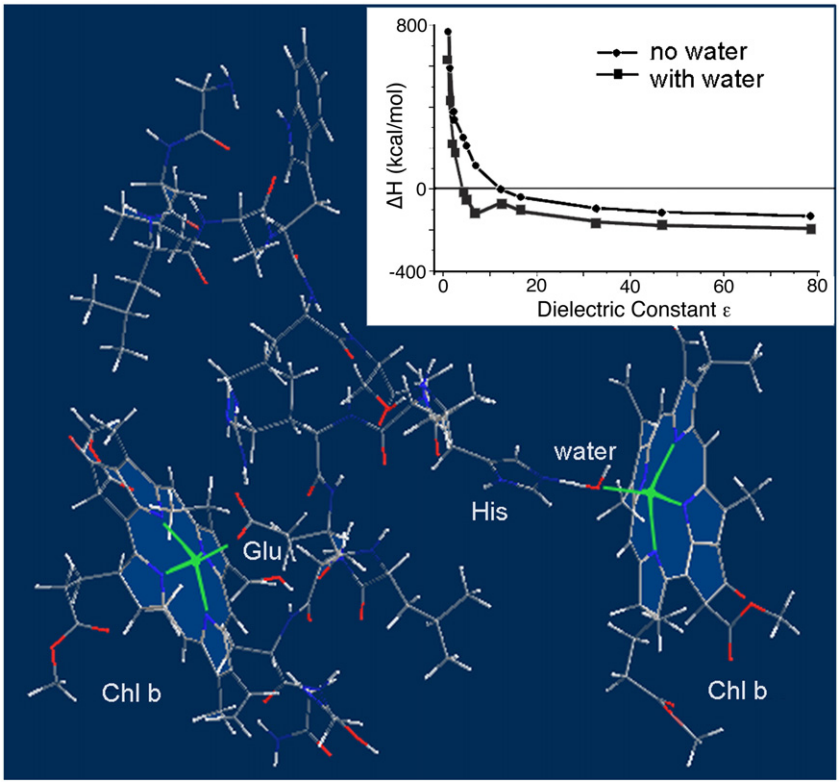

Fig. 4. The model structure of Chl b–peptide complex with one water added between imidazole of His and Chl *b*–Mg. White, hydrogen bond; gray, carbon bond; purple, nitrogen bond; red, oxygen bond; green, magnesium atom and its coordinating ligands. Insert: influence of the water molecule on the heats of formation of the Chl *b*–Mg–peptide ligand as a function of the dielectric constant (ε). The calculated Δ*H* (●) without additive water (Chl *b*–Mg–peptide) in the model functions as the dielectric constant (ε); The calculated Δ*H* (■) with additive water in the His side of the model (Chl *b*–Mg–HOH–peptide) functions as the dielectric constant (ε).

Chl *b*-system is weaker in a non-polar environment (low ε region). The calculated results are consistent with the Fluorescence Resonance Energy Transfer (FRET) analyses of the synthetic peptide [20]. Hence, the imidazole of His and the Glu–Arg charge-compensated ion pair can readily form the fifth coordination bond with the Mg atom in chlorophylls *a* and *d* but do not interact significantly with Mg in chlorophylls *b in vitro* [20]. In other words, Nitrogen (N) of the imidazole group of His in the peptide will form a coordinating bond to chlorophylls *a* and *d* rather than with Chl *b* particularly when there are enough chlorophylls *a* and *d* available. The interaction of Chl *b*–Mg–His may happen if the HOH (water) molecule exists in the model system.

By adding one water molecule between Chl *b*–Mg and imidazole–His (Fig. 4) to the above model, the calculated heats of formation of Chl *b*–Mg–peptide showed a dramatic change (Fig. 4 insert). Addition of one water molecule (Fig. 4) in the model system indicates that the Chl *b* prefers to link to the His via the water bond, but this additive water between Mg of Chl and imidazole of His will not affect the heats of formation for other chlorophylls (Chl *a/d* and BChl *a*) (data not shown). The phenomenon of Chl *b*–Mg–HOH (water) bond preference is consistent with the crystal structure of LHCII [21], where three out of six bound Chl *b* are via HOH ligands to the amino acids and two Chl *b* are coordinated with the peptide backbone carbonyl groups [21].

The PM5 optimised geometry of the monomer Chl *a* indicates that the Mg atom is about 0.045 Å out of the macrocycle ring plane if the N1–N2–N3–N4 of the chlorophyll (Fig. 1) is assumed to be on the same plane. Additionally, the high-level density functional calculations provide similar results. There is not an obvious difference among the monomer chlorophylls. Interestingly, there are obvious different distances of the Mg atom out of the macrocycle ring plane defined by N1–Mg–N3 and N2–Mg–N4 toward the imidazole ligand in the model Chl–peptide complex system (Table 2) although the coordinating bond lengths of Mg–N of the imidazole of His or Mg–O of Glu have similar values among the different species of chlorophyll (Table 2). The central Mg in Chls *a* and *d* is displaced toward the top (out of the macrocycle ring plane) about 0.47 Å in Glu–Arg side and 0.60 Å in the His side (Fig. 2), while the Mg in Chl *b* shows the highest displacement out of the macrocycle ring plane, 0.60 Å in Glu–Arg side and 0.62 Å in the His side (Fig. 4). These results agree well with the hypothesis: Mg of Chl *b* possesses a stronger Lewis acid strength (hardness) that requires stronger Lewis bases, this is comparable to molecules that possess an oxygen dipole (e.g. water, carboxyl and carbonyl groups) [29].

Table 2
Calculated displacement (in Å) of the Mg atom of chlorophylls out of the macrocycle plane and the calculated bond lengths (in Å) between the Mg atoms of chlorophylls to the peptide in the model system

Species	Bond length		Displacement	
	Mg–N	Mg–O	His side	Glu–Arg side
Chl *a*–peptide	2.117	2.031	0.600	0.473
Chl *b*–peptide	2.142	1.893	0.623	0.607
Chl *d*–peptide	2.114	1.978	0.591	0.471
BChl *a*–peptide	2.116	2.027	0.598	0.541

Mg–N, Mg of chlorophylls to the nitrogen of imidazole of His; Mg–O, Mg of chlorophylls to the oxygen atom of glutamic acid in the ion pair of Glu–Arg.

4. Discussion

Chl *d* is the chief photo-pigment performing photosynthesis in *A. marina*. It is known that Chl *d*-bound Pcb protein complexes serve as efficient antennae for both photosystems, PS I and PS II in *A. marina* [30,31]. Hu et al. [5] showed that the primary donor of the PS I reaction centre in *A. marina* consists of Chl *d* rather than Chl *a* and Akiyama et al. [32] have shown that the P740 is a heterodimer of Chl *d* and *d*′. Understanding the influence of the substituents of chlorophylls on the coordinating ligand of the central Mg could shed light on the mechanisms of the chlorophyll replacement in nature and has implications for the understanding of the evolution of chlorophylls.

The calculated ΔH of chlorophylls and peptides indicate that the substitution of peripheral sub-groups can generate significantly different thermodynamic properties of the fifth coordinating ligand of Mg in the chlorophylls. Surprisingly, the Chl *d*–Mg–peptide is more stable than the Chl *a*–Mg–peptide and Chl *b* can form a stable coordinating bond only when water is present. Introduction of the electronegative formyl group on a chlorin ring will reduce the p*K* values of the pyrrole nitrogen and increase the Lewis acid of Mg [13,33]. However, FRET experiments demonstrate the different influence of substitution by a formyl group at different positions of chlorophylls, such as in Chl *b* and Chl *d* (Fig. 1); Chl *b* binds less readily than Chl *d* to the designed peptide [20]. The interpretation suggests that extending the electron distribution along the Q_x axis (in Chl *b*) and Q_y axis (in Chl *d*) changes the charge density of the central Mg in the opposite way (Fig. 1). In the case of Chl *d*, the formyl group at the C-3 position will extend the electron distribution along the Q_y axis and, therefore, only influence electron densities substantially at the two nitrogens near the Mg in the pyrrole centre.

According to theoretical studies by Gouterman [34,35] and others [36,37], the wavelength of the four major electronic transitions in chlorophylls (Q_y, Q_x, B_x and B_y, in order of increasing energy) are determined by the orbital energies. The energies of the orbital HOMO and LUMO also determine the potentials of the ring-centred porphyrin oxidation and reduction, and reflect the charge density of the central Mg [38–41]. Hartwich et al. [42] suggested that the energies of Q_x and B_y have much larger interaction with the central positive charge of the metals in the chlorophylls than that of Q_y and B_x. In the light of these considerations, it is not surprising that Chl *d* possesses similar ligand properties to Chl *a* and BChl *a*. This may be due to the extended electron distribution that can be found along the Q_y axis that is driving the structural modifications associated with the reduction of the C17–C18 double bond in Chl *a*, formyl group at C-3 position of Chl *d*, and with the reduction of C7–C8, C17–C18 double bonds and the electronegative C-3 acetyl group in BChl *a*.

The comparison of the calculated ΔH (Table 1) and the FRET experiments [20] demonstrates that Chl *d*, with red-shifted Q_y, has more stable Chl–Mg–peptide (N-imidazole of His or O–Glu) ligands in the model system, and Chl *a* also prefers the similarly stable Chl–Mg–peptide (N-imidazole of His or O–Glu) ligands. In contrast, the C-7 formyl group of Chl *b* compensates for the reduction of the C17–C18 double bond and generates a spectroscopic blue-shift of Q_y with reduced oscillator strength [43]. Therefore, this formyl group of Chl *b* moves the electrons away from the central pyrrole nitrogens and this results in a stronger positive charge of the central Mg [44]. Therefore such "hardness" of the central Mg will consequently coordinate with a "hard" Lewis base [29]. Also our calculated ΔH of Chl–Mg–peptide ligand showed a positive value. The estimated displacement of the Mg–macrocycle plane in the present study (Table 2) shows that the central Mg in Chl *b* is more out of the plane, which agrees well with the calculated ΔH and the results of FRET experiments. According to the correlation of theoretical studies in the present study with the prior experiments [20,45], we suggest that the Chl *a*-bound proteins will bind Chl *d* without difficulty when the surrounding area is filled by Chl *d*.

It has been demonstrated (see Table 1 and Fig. 2) that the dielectric constant is an important index for the mimetic protein environment, especially at the low region where ($\varepsilon < 5$). This is due to the reorientation of the proteins that are *in situ* which are limited structurally in this particular protein matrix environment. The membrane binding proteins have a substantially lower ε [46] and the chlorophyll binding site is an ideal hydrophobic surrounding area with estimated $\varepsilon = 2$, which is a general value of the optical dielectric constant of organic molecules [46]. It is also suggested by other studies that the ε in the surrounding environment of PS II and LHCII complexes *in situ* is about $\varepsilon = 2$ [47,48]. Using the ε of various organic solvents in the calculation, we suggest that Chl *a*, Chl *d* and BChl *a* can form strong Mg–imidazole ligands in the low ε region which is an important environment of the reaction centres *in vivo*.

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