



Preferential pathways for light-trapping involving β -ligated chlorophylls

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ABSTRACT

The magnesium atom of chlorophylls (Chls) is always five- or six-coordinated within chlorophyll–protein complexes which are the main light-harvesting systems of plants, algae and most photosynthetic bacteria. Due to the presence of stereocenters and the axial ligation of magnesium the two faces of Chls are diastereotopic. It has been previously recognized that the α -configuration having the magnesium ligand on the opposite face of the 17-propionic acid moiety is more frequently encountered and is more stable than the more seldom β -configuration that has the magnesium ligand on the same face [T.S. Balaban, P. Fromme, A.R. Holzwarth, N. Krauß, V.I. Prokhorenko, Relevance of the diastereotopic ligation of magnesium atoms in chlorophylls in Photosystem I, *Biochim. Biophys. Acta (Bioenergetics)*, 1556 (2002) 197–207; T. Oba, H. Tamiaki, Which side of the π -macrocycle plane of (bacterio)chlorophylls is favored for binding of the fifth ligand? *Photosynth. Res.* 74 (2002) 1–10]. In photosystem I only 14 Chls out of a total of 96 are in a β -configuration and these occupy preferential positions around the reaction center. We have now analyzed the α/β dichotomy in the homodimeric photosystem II based on the 2.9 Å resolution crystal structure [A. Guskov, J. Kern, A. Gabdulkhakov, M. Broser, A. Zouni, W. Saenger, Cyanobacterial photosystem II at 2.9 Å resolution: role of quinones, lipids, channels and chloride, *Nature Struct. Mol. Biol.* 16 (2009) 334–342] and find that out of 35 Chls in each monomer only 9 are definitively in the β -configuration, while 4 are uncertain. *Ab initio* calculations using the approximate coupled-cluster singles-and-doubles model CC2 [O. Christiansen, H. Koch, P. Jørgensen, The second-order approximate coupled cluster singles and doubles model CC2, *Chem. Phys. Lett.* 243 (1995) 409–418] now correctly predict the absorption spectra of Chls *a* and *b* and conclusively show for histidine, which is the most frequent axial ligand of magnesium in chlorophyll–protein complexes, that only slight differences (<4 nm) are encountered between the α - and β -configurations. Significant red shifts (up to 50 nm) can, however, be encountered in excitonically coupled β - β -Chl dimers. Surprisingly, in both photosystems I and II very similar "special" β - β dimers are encountered at practically the same distances from P700 and P680, respectively. In purple bacteria LH2, the B850 ring is composed exclusively of such tightly coupled β -bacteriochlorophylls *a*. A statistical analysis of the close contacts with the protein matrix (<5 Å) shows significant differences between the α - and β -configurations and the subunit providing the axial magnesium ligand. The present study allows us to conclude that the excitation energy transfer in light-harvesting systems, from a peripheral antenna towards the reaction center, may follow preferential pathways due to structural reasons involving β -ligated Chls.

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Abbreviations: PS, photosystem; RC, reaction center; CPC, chlorophyll–protein complex; Chl, chlorophyll; LHC, light-harvesting complex; CC2, coupled-cluster singles-and-doubles

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1. Introduction

The vast majority of chlorophylls (Chls), which are ubiquitous natural pigments, are primarily responsible for light-harvesting in photosynthetic organisms. Efficient photon capture of solar radiation is assured by large assemblies of Chl molecules either within chlorophyll–protein complexes (CPCs) or within self-assembled nanoarchitectures [1–3]. Energy transfer steps assure that eventually the radiation is

trapped within reaction centers (RC) formed from a few specialized Chls capable of charge separation and directing subsequent *electron transfer* steps [4]. The RC-CPC is unique for converting light into biochemical energy. The bacterial RC [5] and the plant photosystems PSI [6–8] and PSII [9–13] all present strikingly similar architectures of the specialized RC-Chls, indicating that organisms having less efficient charge separation machines have not survived the evolutionary pressure. In stark contrast is the large variety of light-harvesting (LH) systems. These comprise the elliptical purple bacterial LH1 [14,15] and circular LH2 [16–18] complexes, the phycobilisomes of cyanobacteria and red algae [19] or even the chlorosomes of green photosynthetic bacteria [20–25], all of which are very different from the plant LH complexes, LHCI being associated with PSI [8] and LHCII mainly with PSII [26–28].

An important yet unanswered question is how come light-harvesting is so efficient across a variety of species and habitats? Are there preferential pathways engineered by CPCs for funneling the energy captured by a peripheral antenna to the RC, or is the CPC just an

amorphous conglomeration of pigments with an increased photon capture cross section, so that practically any photon captured will have its energy eventually trapped by an energetic sink?

We were fascinated by CPC architectures which have only very recently become known to atomic resolution [1–19,29,30]. Currently we are trying to understand and further mimic light-harvesting with artificial systems [23,24]. We noted in several CPCs that when the protein ligand coordinates the magnesium atom from the opposite side of the 17-propionyl acid substituent which is esterified by a long chain alcohol, such as phytol in the case of Chls, this leads to more stable structures which are encountered more frequently. This ligation is denoted by α . The alternative β -coordination is uncommon but preferentially occupies positions around the RC in PSI [31].

These stereochemical details of magnesium ligation are pictured in Fig. 1 for Chl *a* or *b* molecules. Chls have several carbon atoms with four different substituents that are stereocenters (indicated by asterisks in Fig. 1) and thus render Chls intrinsically chiral tetrapyrroles. Recently,

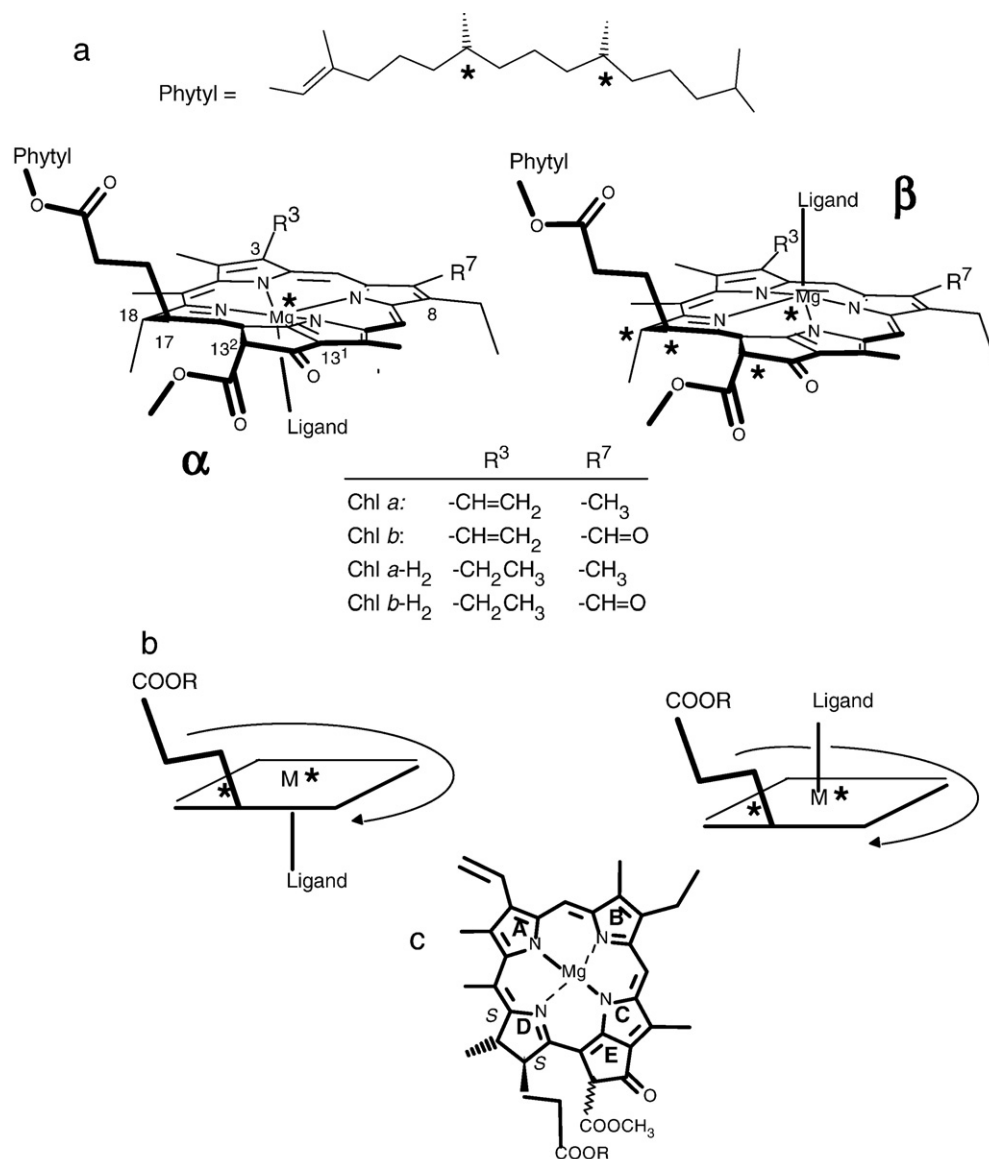


Fig. 1. α/β Nomenclature for describing the diastereotopic ligation of tetrapyrroles. a) Shown are Chl *a* and Chl *b* molecules with the IUPAC clockwise atom numbering (arrows in the cartoons in part b). In the dihydro-Chls, R³ is an ethyl substituent. Asterisks denote chiral atoms. The α -configuration has the ligand below the chiral tetrapyrrolic plane (on the opposite side of the substituent at C17), while the β -configuration has the ligand above this plane. The central metal atom is thus an additional stereocenter. The β -configuration is given by a “left hand rule”: if the fingers point clockwise, then the left thumb points upwards to the metal ligand. Analogously, the α -configuration is given by a “right hand rule”. c) Typical text book formula of Chls *a* showing rings A–E of the chlorin tetrapyrrole. The stereochemistry at C13² in ring E is *R* in Chl *a* and *S* in the epimer Chl *a'*. Note that the magnesium atom in this representation is shown as four coordinate, lacking the fifth ligand. This coordination has never been encountered experimentally as in all crystal structures the magnesium atom in tetrapyrroles is five- or six-coordinate [47]). Figure adapted from reference [33].

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