Biological diversity of photosynthetic reaction centers and the solid-state photo-CIDNP effect

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1 Introduction

Photosynthesis is a light driven process that converts light energy to chemical energy providing almost all the free energy available to living organisms. The origin of photosynthesis on earth can be traced back to at least 3.5 billion years ago (1). The origin of photosynthesis appears to be complex. The photosynthetic apparatus has several components like the reaction center, antenna complexes, electron transfer complexes and carbon fixation machinery, each having its own unique evolutionary history (2). The presence of these components in various combinations in photosynthetic organisms is proposed to have occurred either by selective loss of parts or by genetic fusion (2). The process of photosynthesis takes place in pigment protein complexes that are located in membranes. First, light is captured by an antenna system. The collected light energy is then transferred to the reaction center complex. This RC complex contains a special pigment molecule called the primary electron donor and a chain of cofactors that form the electron transfer chain and serve as electron carriers. The RC complex is composed of different polypeptide chains that lace through the membrane, providing a supporting framework for metal ions and the other cofactors.

Photosynthetic electron transport involves a series of individual electron transfer steps. Upon photon absorption, the primary electron donor undergoes charge separation by releasing an electron to the next electron carrier, called the primary electron acceptor, which is then passed to a final electron acceptor. The initial charge separation is a highly optimized step having a quantum yield close to unity (3, 4). The translocation of the electron results in a difference in the electric potential across the membrane and produces reduced compounds that store chemical energy. Various (bacterio)chlorophylls and (bacterio)pheophytins are found in photosynthetic organisms like BChl *a*, *b*, *c*, *d*, *e*, *g*, Chl *a*, *b*, *c*, *d*, BPhe, Phe as well as carotenoids, iron sulphur clusters and quinones.

The RCs from different groups of photosynthetic organisms are generally divided into two categories, type I and type II (Fig. 1.1), based on the terminal electron acceptor (5):

(i) Type-I RCs contain iron sulphur clusters as the terminal electron acceptors. Photosystem I, heliobacteria and green sulphur bacteria are placed in this category.

(ii) Type-II RCs have quinones as the terminal electron acceptor. Photosystem II, RCs from purple bacteria and green filamentous bacteria (*Chloroflexaceae*) belong to this category. The pigment protein complexes that comprise the antenna system in these diverse organisms can be very different, while the functional structure of the RC core is remarkably conserved over

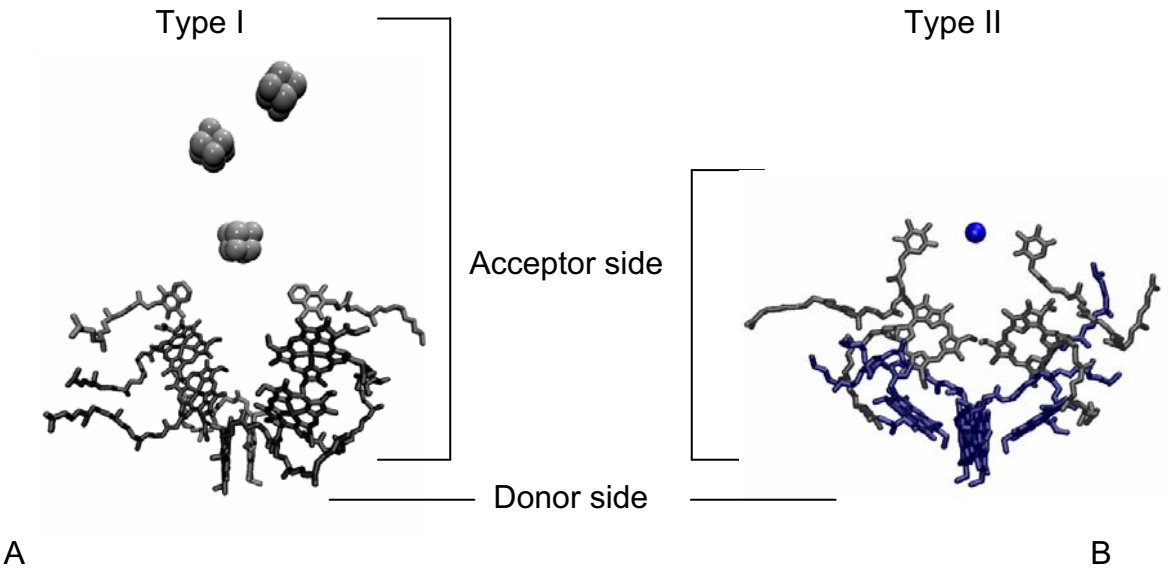

Figure 1.1. The general arrangement of cofactors in the electron transfer chain of type I (A) PSI RC from cyanobacterium *Synechococcus elongatus* (PDB file 1JBO) and type II (B) PSII from cyanobacterium *Thermosynechococcus elongatus* (PDB file 1S5L). The figures were made using the VMD molecular graphic programme (http://www.ks.uiuc.edu/Research/vmd/).

billions of years of evolution, and across many organisms.

This thesis aims to investigate the RC complexes from various organisms by applying solid-state photochemically induced dynamic nuclear polarization techniques in an attempt to explore the variability of the mechanisms of the photo-CIDNP effect in various type I and type II RCs. In addition, by studying diverse RC complexes, further insight may be gained in the functional principles that govern the efficient electron transfer in RCs. The next section gives a brief description of the photo-CIDNP technique in solid-state NMR and its application in the study of photosynthetic RCs. This is followed by a section describing the RCs from various photosynthetic organisms that were investigated.

1.1 Photo-CIDNP MAS NMR

Solid-state NMR spectroscopy is a widely used tool for a variety of applications, ranging from chemical analysis in organic and inorganic chemistry, to structure determination of large molecules like proteins (6-9). In solid-state NMR, magic angle spinning can be applied in order to average the chemical shift anisotropy and dipolar couplings, which improves the spectral resolution. In recent years MAS NMR has developed into a technique for the study of large biological systems like membrane proteins, prions, amyloids and nucleic acids. In addition, with solid-state NMR it is possible to perform a detailed analysis of the dynamics and functional mechanisms of membrane bound protein systems (9, 10).

Chemically induced dynamic nuclear polarization is a non-Boltzmann nuclear spin state

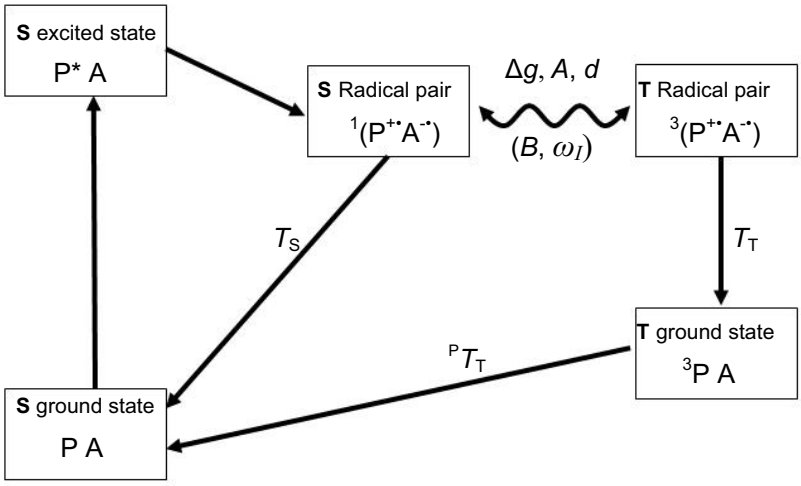

Figure 1.2. General reaction cycle scheme in quinone-blocked RCs. After light-induced electron transfer from P to A, initially the correlated radical pair is formed in a pure singlet state which evolves into a triplet radical pair due to Δ*g*, *d* and hyperfine interactions. In the TSM contribution, the initial coherence in the electron pair is transformed into nuclear polarization by matching with the nuclear Zeeman frequency, ω_I. In the DD mechanism the build up of nuclear polarisation is due to the difference in lifetime (T_S and T_T) of the two radical pair states leading to a difference in contributions from the interconversion process between the radical pair states. The DR mechanism produces net nuclear spin polarization at the triplet branch, due to the long lifetime $^P T_T$ of the donor triplet ^{3}P (23). The oscillating arrow represents coherent evolution, while the solid arrows indicate (incoherent) decay processes towards the electronic ground state.

distribution which is produced in thermal or photochemical reactions. This nuclear spin state can be detected by NMR spectroscopy as enhanced positive or negative signals. Photo-CIDNP was observed for the first time by solution NMR in 1967 (11, 12). In the solid-state, photo-CIDNP is a powerful technique to study the function of light-induced electron transfer in photosynthetic membrane proteins at the atomic level. It was observed in quinone-blocked frozen bacterial RCs of *Rhodobacter sphaeroides* R-26 and subsequently in RCs of *Rb. sphaeroides* wild type (13-18). This resulted in studies of other RCs, like PSII from plants (19, 20, 21). The use of isotope labels is advantageous in strongly enhancing the NMR response. The combination of photo-CIDNP and isotope labelling enables the enhancement of both the intensity and the selectivity of the photo-CIDNP NMR signals (18, 22). The chemical shift provides information about the electronic structure of the ground state after the photo-reaction and recombination, while the intensities relate to the electron spin density distribution in the radical pair (23).

1.1.1 *Photo-CIDNP effect in solids*

After photochemical excitation of the electron donor P (Fig. 1.2), an electron is emitted to the primary acceptor A and a singlet radical pair $^1(P^{+\bullet}A^{-\bullet})$ is formed. Further electron transfer in RCs can be blocked by reducing or depleting the secondary electron acceptor. Under these conditions, the singlet radical pair can either decay to the electronic ground-state (P A) or it

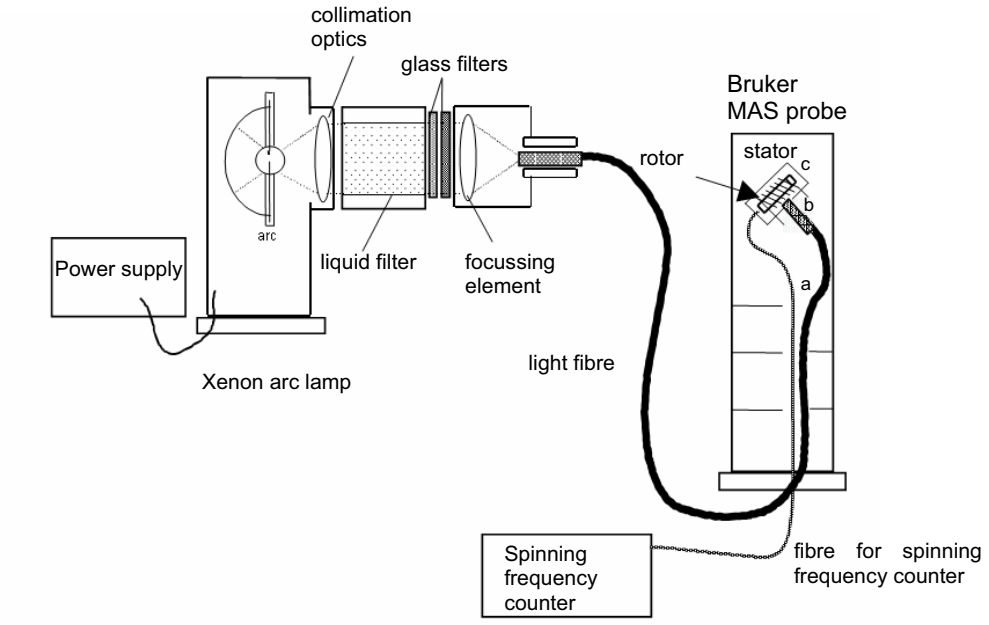

Figure 1.3. Schematic representation of the continuous illumination setup used for photo-CIDNP MAS NMR experiments. The points where modifications were made in the probe are (a) a bore drilled into upper partition plate separating electronics and stator chamber, (b) a small opening in the stator and (c) a thin silver wire coil allowing penetration of light.

can evolve into the triplet radical pair state $^3(P^{+\bullet}A^{-\bullet})$. The lifetime T_T of this triplet radical pair is short due to fast formation of a donor triplet state (^{3}P A). This donor triplet also relaxes to the singlet ground state (P A). During this photo-cycling process, three mechanisms are thought to occur that break the symmetry between the two branches and lead to an imbalance of the population of nuclear spin state distribution which is detected as net nuclear polarization (22, 23).

The spin-correlated radical pair is initially in a singlet state. Due to differences in *g*-value between the two electrons (Δg) and due to hyperfine interactions, the radical pair oscillates between singlet and triplet states (23). In the three spin mixing mechanism the magnitude of the photo-CIDNP effect is at its maximum when matching of the nuclear Zeeman frequency (ω_I) to coupling between the two electrons (d) and hyperfine interaction occurs (25, 26). In the differential decay mechanism, a net photo-CIDNP effect is caused due to the different lifetimes (T_S, T_T) of the two forms of the spin-correlated radical pair (27). This mechanism requires a single matching, of the nuclear Zeeman frequency to the hyperfine interaction. If the lifetime of the donor triplet state ^{3}P is long, the differential relaxation mechanism occurs (28). During this long lifetime, the triplet opens up relaxation channels that can contribute to establish net nuclear polarization.

In bacterial RCs of *Rb. sphaeroides* WT, contributions from both TSM and DD are observed. Emissive (negative) signals in this case arise due to the predominance of TSM over

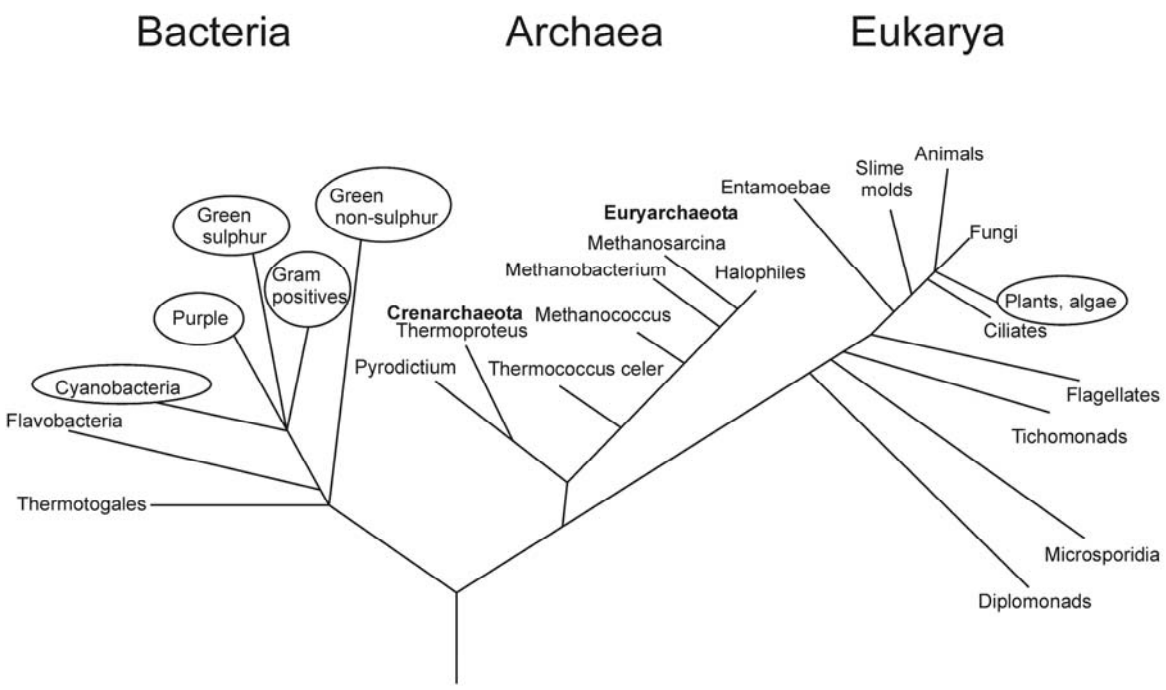

Figure 1.4. Phylogenetic tree based on the small subunit RNA method. Groups containing (B)Chl-based photosynthetic organisms are encircled (ref. 1). Heliobacteria belong to the Gram positive organisms.

DD (29). In RCs of *Rb. sphaeroides* R-26, both absorptive and emissive signals are observed. This difference in the sign change in the photo-CIDNP patterns between R-26 and WT RCs of *Rb. sphaeroides* can be explained by the contribution of the DR mechanism (30).

1.1.2 *Experimental setup*

The setup used for the photo-CIDNP experiments under continuous illumination is designed for a standard Bruker wide bore MAS NMR probe as shown in Fig. 1.3. The points that were modified in the probe are shown in the figure. The setup consists of a 1000-Watt xenon arc lamp containing collimation optics, a liquid filter and glass filters, a focusing element and a light fibre. The light is transported from the xenon arc lamp to the stator inside the probe with a light fibre bundle (16).

1.2 Photosynthetic organisms

Various methods are used for the classification of living organisms, one of which is based on the evolutionary relationships. This approach can be based on the small subunit rRNA method developed by Carl Woese (31). With the availability of more data on photosynthetic organisms, the phylogenetic trees continue to be improved. However, the data interpretation remains controversial. Organisms are placed into three domains, bacteria, archaea (also known as archaebacteria) and eukarya. Photosynthetic organisms that use tetrapyrrole based

photosynthesis are present in two of these domains (Fig. 1.4). Plants, algae and cyanobacteria perform oxygenic photosynthesis which results in the production of oxygen. Anoxygenic photosynthesis is carried out by bacteria that have only one type of photosystem, either type I or type II.

The origin and evolution of photosynthesis has been analysed and discussed over a long time. Phylogenetic and molecular studies on RC core proteins indicate that the two types of RC complexes may have evolved from a common ancestor but the nature of the earliest photosynthetic organisms has not yet been resolved (32-38). The bacteria capable of photosynthesis are purple sulphur bacteria, purple non-sulphur bacteria, green sulphur bacteria, green non-sulphur bacteria, obligate aerobic photosynthetic bacteria, heliobacteria and cyanobacteria. Purple bacteria contain type II RCs while cyanobacteria are the only group of bacteria that is oxygenic and contains both types of RCs. The first X-ray structure of an intrinsic membrane protein complex was determined from purple bacterial RCs (39). The most studied RC from green non-sulphur bacteria or green filamentous bacteria is from *Chloroflexus aurantiacus*. The photosynthetic apparatus in these bacteria is unique as it combines the properties of both the green sulphur bacteria and the purple bacteria (40). The light harvesting system is similar to that of green sulphur bacteria, while they are similar to purple non-sulphur bacteria (*Rhodospirillaceae*) regarding the optical properties of the RC (41).

The proposed hypotheses on the evolution of the RCs can be generalised into two models (2, 42). The selective loss model postulates that a common ancestor of type I and type II RCs was similar to oxygenic cyanobacteria which contained both types of RCs. The various anoxygenic forms of bacteria arose by the loss of one or the other photosystem. The most recent revision of this model suggest that a group termed ‘procyanobacteria’ containing type I RCs was the ancestral prototype from which an evolutionary precursor of type II RCs (37). The fusion model proposes that type I and type II RCs evolved independently. In this scheme the common ancestor gave rise to two separate lines one containing RCI and the other RCII. RC I evolved to form the RCs from heliobacteria and green sulphur bacteria, while RCII led to the formation of RCs from purple bacteria and green filamentous bacteria. The RCs of cyanobacteria were the result of a genetic fusion between an organism containing RCI and an organism containing RCII (2). A more recent version of this hypothesis places purple bacterial RCs as the ancestor which evolved along three different pathways. The first pathway led to the evolution of type II RCs found in green filamentous bacteria. The second led to the development of type II RCs found in cyanobacteria while the third pathway gave rise to type I RCs found in heliobacteria. The heliobacterial RC then further divided into two different pathways, one leading to the type I RC of green sulphur bacteria and the second to the type I RC found in cyanobacteria (2, 43, 44). Recent studies on phylogenetic analysis of the chlorophyll biosynthetic pathway indicate that anoxygenic photosynthetic organisms were the

first to evolve prior to oxygenic photosynthetic organisms (43). These studies also suggest that purple bacterial descendants may be most ancient with respect to the chlorophyll biosynthetic pathway (43) and that heliobacteria are the closest common ancestors of all oxygenic photosynthetic lineages despite their biochemical analysis, which reveals that they contain the most primitive photosynthetic machinery (45, 46).

1.2.1 *Plants and Cyanobacteria*

Plants are considered to be the most complex photosynthetic organisms. Plants, algae and cyanobacteria have a similar basic structure of their photosynthetic membrane. The photosynthetic machinery is embedded into folds of the cell membrane, the thylakoids and contains two photosystems, PSI and PSII. The photosynthetic process in these organisms is oxygenic and PSII oxidizes water to produce oxygen.

The X-ray structures of both cyanobacterial and plant PSI are available and provide information regarding the arrangement of the cofactors in the electron transport chain (47-49). They represent the only available crystal structures of RCs from type I. The cyanobacterial PSI structure is built from twelve protein subunits and 127 cofactors comprising 96 chlorophylls, 2 phylloquinones, three [Fe_4S_4] clusters, 22 carotenoids, four lipids, a putative Ca^{2+} ion and 201 water molecules (47). For higher plants the structure reveals an additional four different light-harvesting membrane proteins assembled in a half-moon shape on one side of the core (48, 49). The positions of chlorophylls in the core complex are found to be conserved between cyanobacterial and plant PSI. The plant RC moiety retains the location and orientation of the electron transfer components and most of the cyanobacterial transmembrane helices. In addition to these retained features, four RC proteins subunits, G, H, N, and O are present exclusively in plants and green algae (50, 51) while two subunits, X and M, are exclusively found in cyanobacteria. The central part of the RC is formed by a heterodimer, comprising the major subunits PsaA and PsaB. The organization of the antenna system in PSI contains a core antenna system surrounding the electron transfer chain. A peripheral antenna system is present on both sides.

The electron transfer chain in PSI comprises of six chlorophylls, two phylloquinones and three iron sulphur [Fe_4S_4] clusters. They are arranged in two branches. The first Chl pair termed as P700 is a heterodimer consisting of one Chl *a* and its epimer, a Chl *a'* molecule (52). The second pair is also Chl *a* and the third pair of Chl *a* molecules in both branches probably represents the primary electron acceptor assigned as A_0. One or both of the phylloquinones could be the secondary electron acceptor A_1. The arrangement of the three Fe_4S_4 clusters in the crystal structure is in agreement with spectroscopic studies and is in the order of F_X, F_A and F_B as shown in Fig. 1.1A on the acceptor side.

PSII is the only RC that has the capability of oxidising water to oxygen. The crystal structure of PSII from cyanobacteria is available with a resolution between 3.8 and 3.2 Å

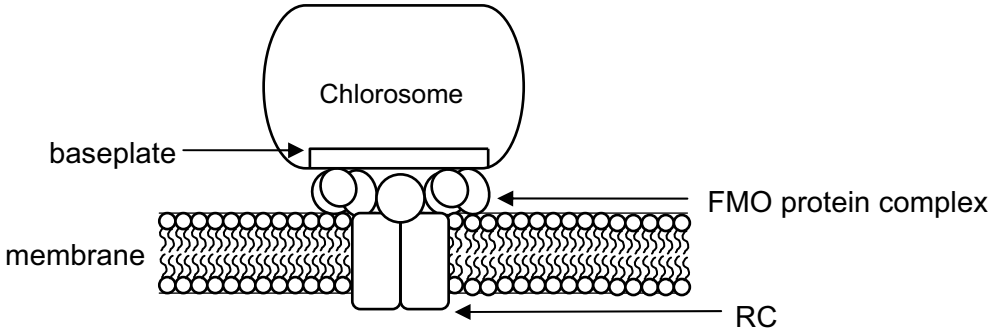

Figure 1.5. Schematic representation of antenna system and RC in green sulphur bacteria associated with the membrane (adapted from ref. 64).

(53-55). The core of the RC complex is a heterodimer, containing the D1 and D2 subunits. The cofactors in the electron transfer chain form two branches, comprising four Chl *a* molecules including a pair of Chl *a* molecules termed P_{D1} and P_{D2}, two Chl *a* molecules, two Phe molecules, $Pheo_{D1}$ and $Pheo_{D2}$ and two plastoquinone molecules. The inner antenna subunits are CP43 and CP47 which are found on adjacent sides to D1and D2, respectively.

Photo-CIDNP observed on PSI is presented in **chapter 2** of this thesis. The magnetic field dependence of photo-CIDNP MAS NMR signals observed in plant PSI and PSII is described in **chapter 3** of this thesis.

1.2.2 *Green sulphur bacteria*

Green sulphur bacteria are exclusively photoautotrophic. They are found in habitats which are anaerobic and abundant in reduced sulphur compounds, like the bottom of stratified lakes where there is low light intensity. They are also found growing below other photosynthetic organisms like algae, cyanobacteria and purple bacteria (56). Due to their habitat, which is characterised by low light intensity, they have large, highly specialised light harvesting complexes called chlorosomes. Recently a stable population of green sulfur bacteria has been isolated from the Black sea chemocline which represents the most extreme low light adapted and slowest growing type of phototroph known to date (57). A previously unknown green sulfur bacterial species has been isolated from a deep-sea hydrothermal vent, where the only source of light is geothermal radiation that includes wavelengths absorbed by photosynthetic pigments of this organism (58).

They belong to the family *Chlorobiaceae*, which is divided into two species, green and brown. The green species contains BChl *c* or *d*, and the carotenoid chlorobactene as a light harvesting pigment (59). The brown species contain BChl *e*, and carotenoids isorenieratene and β isorenieratene as light harvesting pigments (60). The photosynthetic pigment system consists of chlorosomes which are found attached to the inner side of the cytoplasmic membrane, Fenna-Matthews-Olson protein complexes and RC core complexes. The chlorosome is connected with the cytoplasmic membrane via the baseplate (61). The FMO

protein complex is located between the chlorosome and the RC complex. It contains only BChl *a* and is tightly bound to the RC complex. A schematic representation is shown in Fig. 1.5. In **chapter 4** the RCs isolated from the green sulphur bacterium *Chlorobium tepidum* are investigated.

On the basis of functional, structural and genetic data, the RC of green sulphur bacteria is believed to be similar to the RC of PSI (62). The RC core complex of green sulphur bacteria is formed by a homodimeric protein (62). The primary electron donor (P840) is a dimer of BChl *a* (64). The primary electron acceptor absorbs at 670 nm and has been shown to be a Chl *a* which is similar to plant and cyanobacterial Chl *a* except that it is esterified with Δ2,6-phytadienol rather than a phytol (65).

The putative quinone binding site appears to be conserved in PSI, green sulphur bacteria and heliobacteria (34), indicating that the secondary electron acceptor in green sulphur bacteria could be a quinone. On the other hand, experimental evidence shows that electron transport in the RC of green sulphur bacteria and heliobacteria can still function when the quinone is removed (66, 67).

1.2.3 *Heliobacteria*

In **chapter 5** of this thesis, the photosynthetic membrane fragments of the heliobacterium *Heliobacillus mobilis* have been investigated. The organisms belonging to this group are placed in a distinct family, termed *Heliobacteriaceae* (68). They are found in diverse habitats primarily in garden soil, soil from rice fields and in hot springs. Unlike purple and green bacteria, they require high light intensities. Based on 16S ribosomal RNA sequence analysis, they are classified together with Gram positive bacteria (69). All species belonging to this family are characterized by the presence of a unique BChl called BChl *g* (70).

Although the architecture of the photosynthetic system of the heliobacteria resembles the organisation in plant PSI and green sulphur bacteria, it is simpler, having a smaller antenna system associated with the RC. The antenna pigments and RC are bound to a single pigment protein complex (71, 72). This is a homodimer of two 65 kDa proteins (73). The RCs contain around 37 BChl along with six chlorins that constitute the two branches of electron transfer (74). The primary electron donor is called P798 (75) and is probably a dimer of BChl *g* (76, 77) or 13^2-epimer of BChl *g*, BChl *g*′ (78). On the basis of experimental data, the primary electron acceptor is proposed to be 8^1- hydroxy Chl *a* esterified with farnesol, absorbing at 670 nm (79). The electron transport pigment appears to be similar to that found in PSI (46, 80). Membranes of heliobacteria contain menaquinone in the RCs (81). EPR and optical spectroscopic data indicate the presence of iron sulphur centers F_X, F_A and F_B (82, 83).

References

1. Blankenship, R.E. In *Molecular mechanisms of photosynthesis*; Blackwell Science: Oxford, 2002.
2. Olson, J.M.; Blankenship, R.E., *Photosynth. Res.* **2004**, 80, 373-386.
3. Hoff, A.J.; Deisenhofer, J., *Phys. Rep.* **1997**, 287, 2-247.
4. Nelson, N.; Ben-Shem, A., *Nat. Rev. Mol. Cell Bio.* **2004**, 5, 971-982.
5. Golbeck, J.H., *Proc. Natl. Acad. Sci. U. S. A.* **1993**, 90, 1642-1646.
6. Laws, D.D.; Bitter, H.M.L.; Jerschow, A., *Angew.Chem. Int. Ed.* **2002**, 41, 3096-3129.
7. Castellani, F.; Van Rossum, B.J.; Diehl, A.; Rehbein, K.; Oschkinat, H., *Biochemistry* **2003**, 42, 11476-11483.
8. Lange, A.; Becker, S.; Seidel, K.; Giller, K.; Pongs, O.; Baldus, M., *Angew.Chem. Int. Ed.* **2005**, 44, 2089-2092.
9. Zech, S.G.; Wand, A.J.; McDermott, A.E., *J Am Chem Soc* **2005**, 127, 8618-8626.
10. de Groot, H.J.M., *Curr. Opin. Struc. Biol.* **2000**, 10, 593-600.
11. Bargon, J.; Fischer, H.; Johnsen, U., *Z. Naturforsch. C.* **1967**, A 22, 1556-1562.
12. Ward, H.R.; Lawler, R.G., *J. Am. Chem. Soc.* **1967**, 89, 5518-5519.
13. Zysmilich, M.G.; McDermott, A., *J. Am. Chem. Soc.* **1994**, 116, 8362-8363.
14. Zysmilich, M.G.; McDermott, A., *J. Am. Chem. Soc.* **1996**, 118, 5867-5873.
15. Zysmilich, M.G.; McDermott, A., *Proc. Natl. Acad. Sci. U. S. A.* **1996**, 93, 6857-6860.
16. Matysik, J.; Alia; Hollander, J.G.; Egorova-Zachernyuk, T.; Gast, P.; de Groot, H.J.M., *Indian J. Biochem. Biophys.* **2000**, 37, 418-423.
17. Matysik, J.; Alia; Gast, P.; Lugtenburg, J.; Hoff, A.J.; de Groot H.J.M. In *Perspectives on Solid State NMR in Biology*; Kiihne, S., de Groot H.J.M., Eds.; Kluwer: Dordrecht, 2001; p 215-225.
18. Schulten, E.A.M.; Matysik, J.; Alia; Kiihne, S.; Raap, J.; Lugtenburg, J.; Gast, P.; Hoff, A.J.; de Groot, H.J.M., *Biochemistry* **2002**, 41, 8708-8717.
19. Matysik, J.; Alia; Gast, P.; van Gorkom, H.J.; Hoff, A.J.; de Groot, H.J.M., *Proc. Natl. Acad. Sci. U. S. A.* **2000**, 97, 9865-9870.
20. Diller, A.; Alia; Roy, E.; Gast, P.; van Gorkom, H.J.; Zaanen, J.; de Groot, H.J.M.; Glaubitz, C.; Matysik, J., *Photosynth. Res.* **2005**, 84, 303-308.
21. Diller, A.; Roy, E.; Gast, P.; van Gorkom, H.J.; de Groot, H.J.M.; Glaubitz, C.; Jeschke, G.; Matysik, J. ; Alia, A. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, 104, 12767-12771.
22. Matysik, J.; Schulten, E.; Alia; Gast, P.; Raap, J.; Lugtenburg, J.; Hoff, A.J.; de Groot, H.J.M., *Biol. Chem.* **2001**, 382, 1271-1276.
23. Daviso, E.; Jeschke, G.; Matysik, J. In *Biophysical techniques in photosynthesis*; Aartsma, T.J., Matysik, J., Eds.; Springer: Dordrecht, 2007, p 385-399.
24. Jeschke, G.; Matysik, J., *Chem. Phys.* **2003**, 294, 239-255.
25. Jeschke, G., *J. Chem. Phys.* **1997**, 106, 10072-10086.
26. Jeschke, G., *J. Am. Chem. Soc.* **1998**, 120, 4425-4429.
27. Polenova, T.; McDermott, A.E., *J. Phys. Chem. B* **1999**, 103, 535-548.
28. McDermott, A.; Zysmilich, M.G.; Polenova, T., *Solid State Nucl. Magn. Reson.* **1998**, 11, 21-47.

29. Prakash, S.; Alia; Gast, P.; de Groot, H.J.M.; Jeschke, G.; Matysik, J., *J Am Chem Soc* **2005**, 127, 14290-14298.
30. Prakash, S.; Alia; Gast, P.; de Groot, H.J.M.; Matysik, J.; Jeschke, G., *J. Am. Chem. Soc.* **2006**, 128, 12794-12799.
31. Woese, C.R.; Kandler, O.; Wheelis, M.L., *Proc. Natl. Acad. Sci. U. S. A.* **1990**, 87, 4576-4579.
32. Mulkidjanian, A.Y.; Junge, W., *Photosynth. Res.* **1997**, 51, 27-42.
33. Blankenship, R.E.; Hartman, H., *Trends Biochem. Sci.* **1998**, 23, 94-97.
34. Schubert, W.D.; Klukas, O.; Saenger, W.; Witt, H.T.; Fromme, P.; Krauss, N., *J. Mol. Biol.* **1998**, 280, 297-314.
35. Rivera, M.C.; Lake, J.A., *Nature* **2004**, 431, 152-.
36. Nelson, N.; Ben-Shem, A., *BioEssays* **2005**, 27, 914-922.
37. Mulkidjanian, A.Y.; Koonin, E.V.; Makarova, K.S.; Mekhedov, S.L.; Sorokin, A.; Wolf, Y.I.; Dufresne, A.; Partensky, F.; Burd, H.; Kaznadzey, D.; Haselkorn, R.; Galperin, M.Y., *Proc. Natl. Acad. Sci. U. S. A.* **2006**, 103, 13126-13131.
38. Allen, J.F.; Martin, W., *Nature* **2007**, 445, 610-612.
39. Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H., *Nature* **1985**, 318, 618-624.
40. Pierson, B.K.; Thornber, J.P., *Proc. Natl. Acad. Sci. U. S. A.* **1983**, 80, 80-84.
41. Reiner, F.; Shiozawa, J.A.; Ertlmaier, A. In *Anoxygenic photosynthetic bacteria*; Blankenship, R.E., Madigan, M.T., Bauer, C.E., Eds.; Kluwer: Dordrecht, 1995; p 699-708.
42. Xiong, J. *Genome Biol.* **2006**, 7, 245-249.
43. Xiong, J.; Bauer, C.E., *An. Rev. Plant Biol.* **2002**, 53, 503-521.
44. Xiong, J.; Bauer, C.E., *J. Mol. Biol.* **2002**, 322, 1025-1037.
45. Xiong, J.; Fischer, W.M.; Inoue, K.; Nakahara, M.; Bauer, C.E., *Science* **2000**, 289, 1724-1730.
46. Blankenship, R.E., *Trends Plant Sci.* **2001**, 6, 4-6.
47. Jordan, P.; Fromme, P.; Witt, H.T.; Klukas, O.; Saenger, W.; Krauss, N., *Nature* **2001**, 411, 909-917.
48. Ben-Shem, A.; Frolow, F.; Nelson, N., *Nature* **2003**, 426, 630-635.
49. Amunts, A.; Drory, O.; Nelson, N., *Nature* **2007**, 447, 58-63.
50. Scheller, H.V.; Jensen, P.E.; Haldrup, A.; Lunde, C.; Knoetzel, J., *Biochim. Biophys. Acta* **2001**, 1507, 41-60.
51. Knoetzel, H.; Mant, A.; Haldrup, A.; Jensen, P.E.; Scheller, H.V., *FEBS Lett.* **2002**, 510, 145-148.
52. Watanabe, T.; Kobayashi, M.; Hongu, A.; Nakazato, M.; Hiyama, T.; Murata, N., *FEBS Lett*. **1985,** 191, 252-256.
53. Zouni, A.; Witt, H.T.; Kern, J.; Fromme, P.; Krauss, N.; Saenger, W.; Orth, P., *Nature* **2001**, 409, 739-743.
54. Ferreira, K.N.; Iverson, T.M.; Maghlaoui, K.; Barber, J.; Iwata, S., *Science* **2004**, 303, 1831-1838.
55. Biesiadka, J.; Loll, B.; Kern, J.; Irrgang, K.D.; Zouni, A., *Phys. Chem. Chem. Phys.* **2004**, 6, 4733-4736.
56. Vila, X.; Abella, C.A., *Photosynth. Res.* **1994**, 41, 53-65.
57. Manske, A.K.; Glaeser, J.; Kuypers, M.A.M.; Overmann, J., *Appl. Environ. Microbiol.* **2005**, 71, 8049-8060.

58. Beatty, J.T.; Overmann, J.; Lince, M.T.; Manske, A.K.; Lang, A.S.; Blankenship, R.E.; Van Dover, C.L.; Martinson, T.A.; Plumley, F.G., *Proc. Natl. Acad. Sci. U. S. A* **2005**, 102, 9306-9310.
59. Gloe, A.; Pfennig, N.; Brockmann, H.; Trowitzsch, W., *Arch. Microbiol.* **1975**, 102, 103-109.
60. Imhoff, J.F. In *Anoxygenic photosynthetic bacteria*; Blankenship, R.E., Madigan, M.T., Bauer, C.E., Eds.; Kluwer: Dordrecht, 1995; p 665-685.
61. Staehelin, L.A.; Golecki, J.R.; Drews, G., *Biochim. Biophy. Acta* **1980**, 589, 30-45.
62. Feiler, U.; Hauska, G. In *Anoxygenic photosynthetic bacteria*; Blankenship, R.E., Madigan, M.T., Bauer, C.E., Eds.; Kluwer: Dordrecht, 1995; p 665-685.
63. Buttner, M.; Xie, D.L.; Nelson, H.; Pinther, W.; Hauska, G.; Nelson, N., *Proc. Natl. Acad. Sci. U. S. A.* **1992**, 89, 8135-8139.
64. Hauska, G.; Schoedl, T.; Remigy, H.; Tsiotis, G., *Biochim. Biophys. Acta.* **2001**, 1507, 260-277.
65. Kobayashi, M.; Oh-Oka, H.; Akutsu, S.; Akiyama, M.; Tominaga, K.; Kise, H.; Nishida, F.; Watanabe, T.; Amesz, J.; Koizumi, M.; Ishida, N.; Kano, H., *Photosynth. Res.* **2000**, 63, 269-280.
66. Kleinherenbrink, F.A.M.; Ikegami, I.; Hiraishi, A.; Otte, S.C.M.; Amesz, J., *Biochim. Biophys. Acta* **1993**, 1142, 69-73.
67. Frankenberg, N.; Hager-Braun, C.; Feiler, U.; Fuhrmann, M.; Rogl, H.; Schneebauer, N.; Nelson, N.; Hauska, G., *Photochem. Photobiol.* **1996**, 64, 14-19.
68. Beer-Romero, P.; Gest, H., *FEMS Microbiol. Lett.* **1987**, 41, 109-114.
69. Woese, C.R., *Microbiol. Rev.* **1987**, 51, 221-271.
70. Brockmann, H.; Lipinski, A., *Arch. Microbiol.* **1983**, 136, 17-19.
71. Trost, J.T.; Blankenship, R.E., *Biochemistry* **1989**, 28, 9898-9904.
72. van de Meent, E.J.; Kleinherenbrink, F.A.M.; Amesz, J., *Biochim. Biophys. Acta* **1990**, 1015, 223-230.
73. Liebl, U.; Mockensturm-Wilson, M.; Trost, J.T.; Brune, D.C.; Blankenship, R.E.; Vermaas, W., *Proc. Natl. Acad. Sci. U. S. A.* **1993**, 90, 7124-7128.
74. Neerken, S.; Amesz, J., *Biochim. Biophys. Acta.* **2001**, 1507, 278-290.
75. Fuller, R.C.; Sprague, S.G.; Gest, H.; Blankenship, R.E., *FEBS Lett.* **1985**, 182, 345-349.
76. Prince, R.C.; Gest, H.; Blankenship, R.E., *Biochim. Biophys. Acta* **1985**, 810, 377-384.
77. Brok, M.; Vasmel, H.; Horikx, J.T.G.; Hoff, A.J., *FEBS Lett.* **1986,** 194, 322-326.
78. Kobayashi, M.; van de Meent, E.J.; Erkelens, C.; Amesz, J.; Ikegami, I.; Watanabe, T., *Biochim Biophys Acta* **1991**, 1057, 89-96.
79. van de Meent, E.J.; Kobayashi, M.; Erkelens, C.; van Veelen, P.A.; Amesz, J.; Watanabe, T., *Biochim. Biophys. Acta* **1991**, 1058, 356-362.
80. Golbeck, J.H.; Bryant, D.A., *Curr. Top. Bioenerg.* **1991**, 16, 83-177.
81. Muhiuddin, I.P.; Rigby, S.E.J.; Evans, M.C.W.; Amesz, J.; Heathcote, P., *Biochemistry* **1999**, 38, 7159-7167.
82. Neerken, S.; Amesz, J., *Biochim. Biophys. Acta* **2001**, 1507, 278-290.
83. Heinnickel, M.; Golbeck, J.H., *Photosynth. Res.* **2007**, 92, 35-53.