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

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Summary

Photosynthesis is an important biological process that converts light energy into chemical energy which is storable and usable. This process takes place in photosynthetic organisms which have pigment protein complexes located in their membranes. First, light is captured by pigment protein complexes constituting the antenna system and is then transferred to a protein complex termed as reaction center (RC). The RC 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. Photosynthetic electron transport consists of a series of individual electron transfer steps. Upon photon absorption, charge separation occurs in the primary electron donor resulting in the release of an electron to the next electron carrier, called 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 unit (**Chapter 1**). Photosynthesis is performed in plants algae, cyanobacteria, purple bacteria, green sulphur bacteria, heliobacteria and green filamentous bacteria.

Chemically induced dynamic nuclear polarization (CIDNP) is produced in thermal or photochemical reactions and can be detected by NMR spectroscopy as enhanced positive or negative signals. Since the first observation of photo-CIDNP by MAS NMR in frozen bacterial RCs of *Rhodobacter (Rb.) sphaeroides* R-26 in 1994, it has developed as a technique used to study the light-induced electron transfer in photosynthetic membrane proteins at the atomic level. The photo-CIDNP effect in solids is explained by three mechanisms, (a) three spin mixing mechanism (TSM), (b) differential decay mechanism (DD) and (c) differential relaxation mechanism (DR). This thesis investigates photo-CIDNP effect in photosynthetic RCs from diverse photosynthetic organisms, ranging from plants, heliobacteria and green sulphur bacteria (**Chapter 1**).

Photo-CIDNP observed in photosystem I (PSI) of spinach by ^{13}C MAS solid-state NMR under continuous illumination with white light is presented in **chapter 2**. The photo-CIDNP data gives the first tentative set of chemical shifts of the aromatic ring carbons of a single Chl *a* molecule. All light-induced ^{13}C NMR signals appear negative and this is proposed by a predominance of the TSM mechanism over the DD mechanism.

The magnetic field effect observed in PSI and PSII from spinach is significantly different as shown in **chapter 3**. There are contrasting field dependence observed in the light-induced signal pattern of the two photosystems at three different magnetic fields, 17.6, 9.4 and 4.7 Tesla. For PSII the optimal NMR enhancement factor of ~5000 is observed at 4.7 Tesla, while the strongest light-induced signals of PSI are observed at 9.4 T. Since field dependence of

nuclear polarization is related to the magnetic parameters and lifetimes of the intermediate radical species, simulations were performed to examine what parameter changes can explain the experimental observations. The simulations indicate that an increase of the exchange coupling leads to a slight increase in absolute polarization, which can be reconciled with experimental observations. Such a change in the exchange coupling may well be caused by slight rearrangements of the cofactors that lead to an improved overlap between the molecular orbitals of the donor and the accessory chlorophyll (Chl) *a* or between the molecular orbitals of the accessory chlorophyll and the primary acceptor. Hence, this change in the magnetic field dependence of solid-state photo-CIDNP between bacterial RCs and plant PSI can be traced back to an increase of the exchange coupling between the donor and acceptor radical anions.

In **chapter 4** isolated RCs of green sulphur bacteria *Chlorobium tepidum* have been investigated. The light-induced ^{13}C MAS NMR spectra appear negative and can be tentatively assigned to the two bacterio chlorophyll (BChl) *a* molecules of the donor side. The observed doubling of several signals suggests only a slightly asymmetric dimer in both the electronic ground-state and radical-cation state of the donor side. Comparing with other RCs the dimer appears to be similar to the more symmetric donor of PSI rather than the substantially asymmetric special pair of purple bacteria.

Membrane fragments containing RCs of heliobacterium, *Heliobacillus mobilis* are analysed in **chapter 5**. The photo-CIDNP spectral pattern at lower magnetic fields (4.7 Tesla), appear to be both positive and negative, which is similar to the pattern observed in the RCs of plant PSII and purple bacterial reaction centers of *Rb. sphaeroides* R-26. However, unlike the other RCs studied by photo-CIDNP, this system is unique, at high fields of 17.6 Tesla, the positive signals undergo a sign change and the spectra appear negative.

The future outlook of the study of natural RCs by photo-CIDNP is addressed in **chapter 6**. The observation of this effect in all natural photosynthetic RCs from diverse photosynthetic organisms leads to the conclusion that the principles leading to this effect are an inherent property conserved in natural RCs from biologically diverse photosynthetic organisms. This suggests that photo-CIDNP is a good technique which can be used for evaluating the efficiency of artificial photosynthetic systems.