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

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6 Future Outlook

6.1 Introduction

The observation of the photo-CIDNP effect on photosynthetic RCs by solid-state NMR opened a new area for the application of this technique in the study of photosynthetic RCs. However, these studies were mainly from the purple bacteria *Rb. sphaeroides* WT and R-26 followed by PSII from plants which belong to the group of type II RCs as described earlier in chapter 1. The observation of photo-CIDNP signals from plant PSI (Chapter 2), RCs from green sulphur bacteria (Chapter 4) and heliobacteria (Chapter 5) covers the major representative groups of organisms having type I RCs. Green filamentous bacterial RCs are the only group which has not yet been studied. This thesis shows that photo-CIDNP is not restricted to only RCs from purple bacteria and plants but extends to six systems from diverse photosynthetic organisms which have different evolutionary origin. Regarding the evolution of photosynthesis there are various competing concepts at the level of photosynthetic organisms and the various components associated with photosynthesis, for example RC proteins, in the literature. The various unlabelled RCs studied till now show two major photo-CIDNP spectral patterns, with (a) all signals are negative or (b) a mixed pattern of both positive and negative signals. On the basis of this spectral pattern one cannot categorise the RCs, albeit that type II RCs in general show a mixed pattern of both positive and negative signals, with the exception of *Rb. sphaeroides* WT, while type I RCs show only an emissive pattern with the exception of heliobacteria. The RCs of heliobacteria though structurally and functionally related to RCs of green sulphur bacteria and PSI (1) show a photo-CIDNP pattern of positive and negative signals similar to that observed in type II RCs.

6.2 Functional relevance of photo-CIDNP for light-induced electron transfer

Due to the small Zeeman splitting and resulting unfavourable Boltzmann distribution, all magnetic resonance methods have intrinsically low sensitivity. Photo-CIDNP MAS NMR has been shown to be a method to overcome this limitation by production of non-Boltzmann nuclear spin distributions by photochemical reactions in solids and to allow for detailed studies of the photochemical machineries of RCs. Enhancement factors of about 10,000 have been observed in several RCs. The underlying spin-chemical processes producing such high polarization are now better understood (2, 3) and full control over the ruling parameters may allow for enhancement of a factor of more than 100,000 (4).

The window of occurrence of this effect has been shown to be very limited by kinetic and magnetic parameters (4, 5), however, it appears that evolution remained confined on this small area of the infinite parameter landscape. Hence, it appears that the conditions required for the solid-state photo-CIDNP effect in photosynthetic RCs is highly conserved.

6.3 Future experiments

Evolution happens at conditions of the earth magnetic field (50 μ Tesla). However, current theory on the solid-state photo-CIDNP effect would predict a maximum solid-state photo-CIDNP effect at medium fields and decay of the effect at low fields (4, 5). On the other hand, the current theory has been developed for conditions of medium and high fields and does not include cross-relaxation effects and new possibilities occurring at low fields. At low fields (*i.e.*, below 7 mTesla = 0.3 MHz proton frequency = 0.07 MHz ^{13}C frequency), the three triplet states T_+ , T_- and T_0 are degenerate and offer additional options for singlet-triplet mixing which may provide new channels for photo-CIDNP. In liquid-state photo-CIDNP, for example, S-T. mixing is well known to occur at low fields (6). The entire theory on the solid-state photo-CIDNP effect developed until now is based on high-field conditions which are characterized by a complete separation of the three triplet states simplifying the theory since solely T_0 is allowed to mix with the singlet states. In addition, current experiments have been limited to primary radical pairs, while under natural conditions secondary radical pairs may play a much more important role. Their natural lifetime is sufficiently long to allow the build-up of nuclear polarization via hyperfine interaction, and the lower electron-electron coupling parameters may fulfill the matching conditions required at lower fields.

Despite extensive efforts in artificial RC systems, having low quantum yield $<\sim 20\%$, photo-CIDNP has not yet been observed. Therefore, there may be a link between the occurrence of photo-CIDNP in RCs and the conditions of the unsurpassed efficient initial light-induced electron transfer in RCs. There may be some until now unknown fundamental principles ruling the spin-chemistry of photosynthetic charge separation and stabilization. Understanding of the interaction of all four electron-spin states at low magnetic fields may provide the key to these fundamental principles of efficient electron transfer. Knowledge of these principles may help in the synthesis of efficient artificial RCs. The current photo-CIDNP mechanisms may appear just to be the special case of these fundamental principles for high-field conditions. Hence, for future photo-CIDNP solid-state NMR studies a fruitful spin-chemical *terra incognita* may open at low magnetic fields.

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