Towards photo-CIDNP MAS NMR as a generally applicable enhancement method

Thamarath Surendran, S.

Chapter 6

General discussion

In the past, work on the solid-state photo-CIDNP effect received significant attention,[1,2] although its limitation to isolated, frozen, quinone reduced natural photosynthetic RCs has been a concern. Recently, some of this limit has been overcome. In particular, the solid-state photo-CIDNP effect was observed in large non-frozen photosynthetic membrane-complexes.[3] The possibility to observe the effect has also been demonstrated for cells without further isolation.[4,5] In addition, the theory of the solid-state photo-CIDNP-effect at high magnetic fields has been complemented by a low-field analogon, predicting significant nuclear polarization for various electron transfer-systems in the earth's field range.

This thesis is part of the efforts to develop the solid-state-photo-CIDNP effect to a generally applicable method for signal enhancement, similar to other hyperpolarization methods, for example dynamic nuclear polarization (DNP).[6,7] In this thesis, again several borders are addressed, extending previous experimental possibilities and also understanding, leading to a new view on the occurrence of the effect.

Although the pure observation of the effect was already possible in other cellular systems, in Chapter 2, it is demonstrated that photo-CIDNP MAS NMR can be applied as analytical tool to cellular systems. That allows to apply the method also to plenty of less studied photosynthetic systems in which isolation is difficult or unknown. Due to strong light scattering, even optical methods are difficult to apply, however, photo-CIDNP MAS NMR can study this systems in different states (here Braunstoff *vs*. Grünstoff).

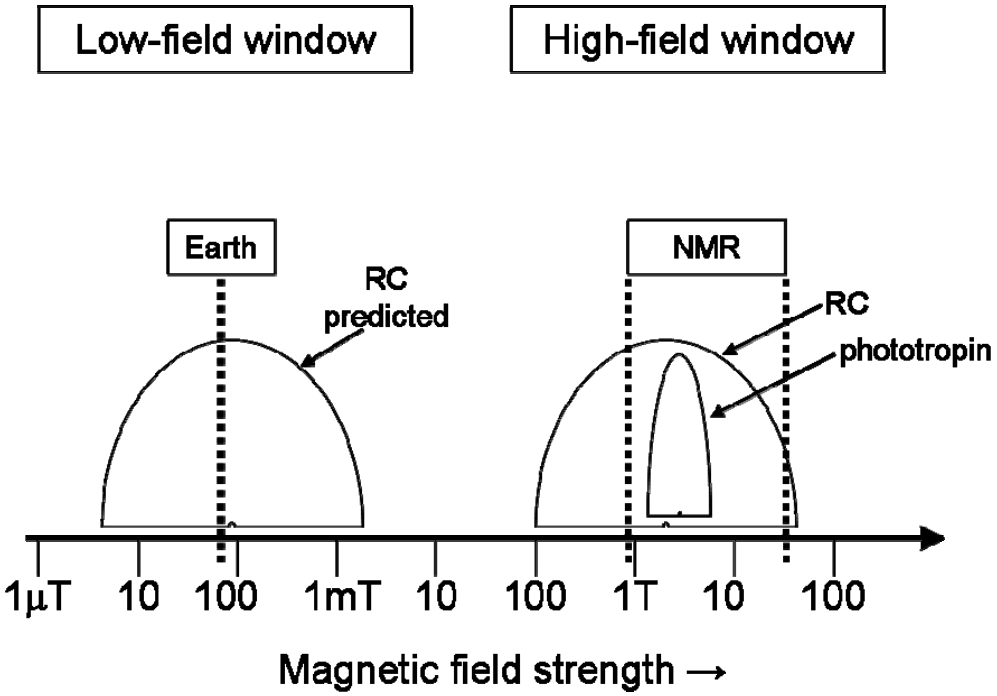

Figure 6.1: The two regimes of the solid-state photo-CIDNP effect. The high-field matching window has been fully experimentally studied in this thesis for two systems (RCs of *Rb. sphaeroides* WT, Chapter 3, and of the C57S-mutant of LOV1-phototropin, Chapter 5). The low-field matching window is theoretically predicted.

Previous experimental possibilities were limited to the magnetic field range of 17.6 to 4.7 T .[4,8] In Chapter 3, this field range is widened to low fields of 2.4 and 1.4 T. Here, for the first time, the high-field matching curve of the solid-state photo-CIDNP effect has been observed, very well in agreement with the high-field theory for RCs of *Rb. sphaeroides* WT.[4,9]

Chapter 4 presents the effect on the first non-photosynthetic system, a blue-light-photoreceptor phototropin LOV1-C57S. Hence, here it has been proven that the effect is not limited to natural photosynthetic systems but can also be observed in other electron-transfer systems. Chapter 5 provides deeper insight by showing the field dependence of the effect. It turns out that the matching window is smaller as in RCs of *Rb. sphaeroides*, inline with the assumption that the radical pair lifetime is correlated to the width of the window (Figure 6.1).

While the occurrence of the high-field matching window is now experimentally well established, observation of the predicted low-field window[10] (for example by using a shuttle system) again would open a new world in spin dynamics. The theory also predicts that this low-field effect is in particular strong for radical pairs having a distance similar to secondary radical pairs.[10] Hence, due to the larger distance, the radical-pair lifetime is in the μs- to -ms range and the matching windows must be very sharp. This selectivity of the conditions might also be the reason, why the effect is so difficult to observe in electron transfer systems as for example artificial reaction centers or cryptochromes.

If these narrow matching windows at and around earth's field could be explored experimentally, it might be possible to get direct access in the spin dynamics of light-dependent bird-navigation[11] or the stability of circadian rhythms in plants and animals.[12,13]

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