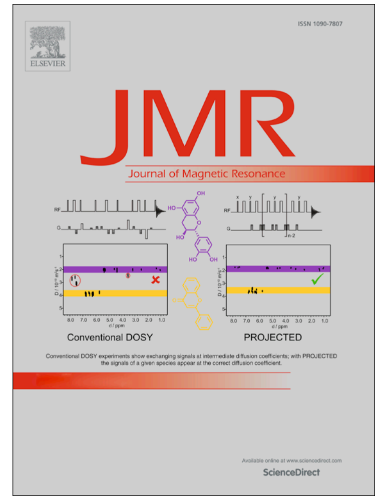
Accepted Manuscript



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PII: S1090-7807(18)30158-7
DOI: https://doi.org/10.1016/j.jmr.2018.06.003
Reference: YJMRE 6315

To appear in: *Journal of Magnetic Resonance*

Received Date: 24 March 2018
Revised Date: 6 June 2018
Accepted Date: 7 June 2018

Please cite this article as: P. Bielytskyi, D. Gräsing, K.R. Mote, K. Babu Sai Sankar Gupta, S. Vega, P.K. Madhu, A. Alia, J. Matysik, $^{13}C \rightarrow {}^{1}H$ transfer of light-induced hyperpolarization allows for selective detection of protons in frozen photosynthetic reaction center, *Journal of Magnetic Resonance* (2018), doi: https://doi.org/10.1016/j.jmr.2018.06.003

$^{13}C \rightarrow {}^{1}H$ transfer of light-induced hyperpolarization allows for selective detection of protons in frozen photosynthetic reaction center

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Keywords: Photo-CIDNP, spin-torch, MAS NMR, HETCOR, hyperpolarization transfer, inverse cross polarization, windowed detection

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Abstract. In the present study, we exploit the light-induced hyperpolarization occurring on ^{13}C nuclei due to the solid-state photochemically induced dynamic nuclear polarization (photo-CIDNP) effect to boost the NMR signal intensity of selected protons via inverse cross-polarization. Such hyperpolarization transfer is implemented into ^{1}H-detected two-dimensional ^{13}C-^{1}H correlation magic-angle-spinning (MAS) NMR experiment to study protons in frozen photosynthetic reaction centers (RCs). As a first trial, the performance of such an experiment is tested on selectively ^{13}C labeled RCs from the purple bacteria of *Rhodobacter sphaeroides*. We observed response from the protons belonging to the photochemically active cofactors in their native protein environment. Such an approach is a potential heteronuclear spin-torch experiment which could be complementary to the classical heteronuclear correlation (HETCOR) experiments for mapping proton chemical shifts of photosynthetic cofactors and to understand the role of the proton pool around the electron donors in the electron transfer process occurring during photosynthesis.

1. Introduction

NMR spectroscopy is one of the most versatile techniques to study the structure and dynamics of both organic and inorganic molecules. However, the main drawback of NMR spectroscopy as an analytical tool lies in its low sensitivity due to unfavorable nuclear Boltzmann polarization at thermal equilibrium and lack of selectivity especially for protons in the solid state. These issues become more apparent when characterizing large biomolecular systems such as membrane proteins, where low sensitivity and low resolution combine to be a great experimental challenge [1]. A range of different methods to increase the NMR sensitivity has been developed over the years in which a non-Boltzmann spin order is induced by physical or chemical means [2]. These methods, often summarized as “nuclear spin-hyperpolarization methods”, despite being extremely effective in a wide range of applications, possess their own weaknesses, whether it is long-lasting hyperpolarization build-up, short lifetime of the produced hyperpolarization, occurrence of hyperpolarization only on specific type of nuclei or its high localization with inability to be used beyond a particular system. In order to take the most advantage of the hyperpolarization method in