Phototropin is a blue light receptor containing flavin mononucleotide (FMN) in its LOV domain. After photoexcitation with blue light, the FMN forms a photoexcited triplet state which in natural occurring LOV domains reacts with a conserved nearby cysteine to form a covalent adduct. By mutation of the cysteine to a serine, the adduct formation is prohibited and the lifetime of the photoexcited \(^3\)FMN is elongated. This induces a one-electron transfer from a tryptophan of the protein matrix (1 nm edge-to-edge distance) which in turn forms a radical pair as an intermediate leading to photochemically induced dynamic nuclear polarization (photo-CIDNP) signal enhancement in NMR which is observable in both solid and liquid states [1]. Here, isotope enrichment of \(^{13}\)C and \(^{15}\)N allows the selective detection of the hyperpolarized signals from both partners involved in the electron transfer.

The measurement time under illumination, however, is limited because of the generation of singlet oxygen by the photoexcited \(^3\)FMN [2] which enhances the photodegradation of the protein. Besides, expensive and not straightforward isotope labelling can prohibit the search for photo-CIDNP in newly discovered proteins and impede further investigations on known ones. Therefore, an increase in stability of the protein under illumination can enable the use of two-dimensional solid-state photo-CIDNP NMR techniques for further investigations.

Here, we present an approach where the protein is embedded into a sugar glass matrix and measured with \(^{13}\)C solid-state photo-CIDNP NMR. This has the advantage that the solid-state experiment can be performed at room temperature while simultaneously prolonging the measurement time to investigate unlabeled protein samples here presented for LOV1 of phototropin C57S.

**References**