

Completing the Picture: A ^{13}C -Hyperfine Mapping of Flavin Semiquinone Radicals by Photo-CIDNP NMR

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In this contribution we present the electronic structure of flavin semiquinone radicals in terms of their ^{13}C hyperfine coupling constants. Photochemically induced dynamic nuclear polarization (photo-CIDNP) spectroscopy was used to study both the neutral and anionic radical species of flavin mononucleotide (FMN) in bulk aqueous solution. Apart from universally ^{13}C labelled FMN, partially labelled isotopologues were used to increase sensitivity for nuclei exhibiting very small hyperfine couplings and to cope with spectral overlap. In addition, experimental findings are supported by quantum chemical calculations and implications for the spin density distribution in free flavin radicals are discussed [1]. A comparison with ^{13}C hyperfine couplings obtained from flavin radicals in protein surroundings will be presented [2].

[1] N. Pompe, B. Illarionov, M. Fischer, A. Bacher, S. Weber. *J. Phys. Chem. Lett.*, submitted

[2] E. Schleicher, S. Rein, B. Illarionov, A. Lehmann, T. Al Said, S. Kacprzak, R. Bittl, A. Bacher, M. Fischer, S. Weber. *Sci. Rep.* **11**, Art. No. 18234 (2021)