# Optically Hyperpolarized Electrons for Dynamic Nuclear Polarization

Matthew W. Dale[1] and Christopher J. Wedge[1,2]

[1] *Department of Physics, University of Warwick, Coventry, UK.*
[2] *Current Address: Department of Chemistry, University of Huddersfield, UK.*

We have recently shown that the large electron spin-polarizations generated optically through the radical-triplet pair mechanism (RTPM) can be transferred to nuclei to enhance sensitivity in solution-state NMR [1]. This optical method offers a new route to Dynamic Nuclear Polarization (DNP) without the need for microwave pumping (Fig. 1). NMR is intrinsically insensitive due to the low thermal spin-polarization of nuclei, limiting both routine applications and development of new methodologies; DNP seeks to overcome this barrier by using the much larger electronic spin polarization to boost nuclear population differences [2]. DNP methods typically involve microwave pumping of thermally equilibrated electron spins, with maximum enhancements limited by the thermal electron spin-polarization. Hyperpolarizing the electron spin by optical pumping could offer much larger enhancements whilst also removing the need for microwave irradiation.

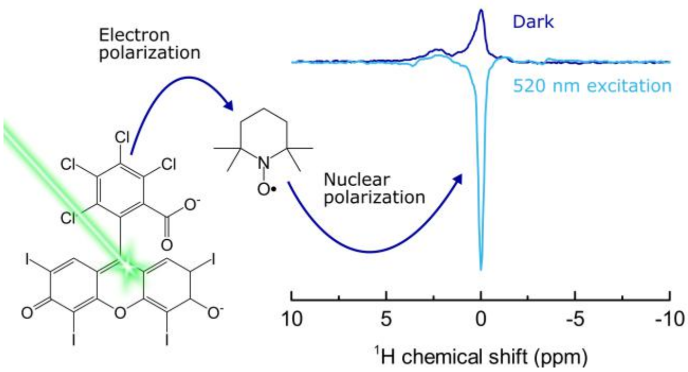


**Figure 1.** Optically generated triplet hyperpolarizes a stable radical via the RTPM, leading to enhanced $^{1}$H NMR sensitivity in aqueous solution (Reproduced from [1]).

Alongside our proof of principle demonstration of RTPM enhanced NMR we report recent progress in optimizing the method. Combining time-resolved EPR investigations with recent kinetic studies [3] we have further developed our understanding of the radical-triplet pair system. Correlating this data with NMR measurements we have identified the requirements to maximise the DNP enhancement, and have exceeded our previous record whilst also removing the requirement for costly solvent deuteration.

*Support*: We thank the Engineering and Physical Sciences Research Council for financial support (EP/N007875/1), and Bruker UK for an equipment loan.

[1] M. W. Dale and C. J. Wedge, *Optically generated hyperpolarization for sensitivity enhancement in solution-state NMR spectroscopy*, Chem. Commun., **2016**, 52, 13221–13224.

[2] J. van Bentum, B. van Meerten, M. Sharma and A. Kentgens, *Perspectives on DNP-enhanced NMR spectroscopy in solutions*, J. Magn. Reson., **2016**, 264, 59–67.

[3] L. Ludvíková, P. Friš, D. Heger, P. Šebej, J. Wirz and P. Klán, *Photochemistry of rose bengal in water and acetonitrile: a comprehensive kinetic analysis*, Phys. Chem. Chem. Phys., **2016**, 18, 16266–16273.