

Novel Metallofullerene Boosts Dynamic Nuclear Polarization

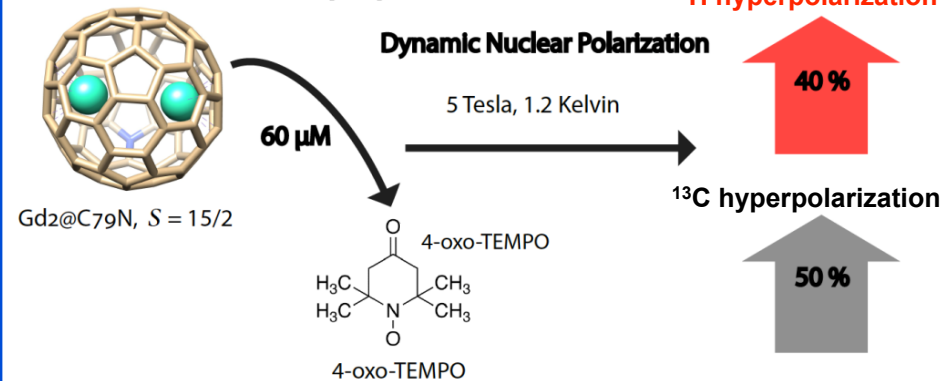
X. Wang¹, J. E. McKay¹, B. Lama², J. van Tol¹, T. Li³, K. Kirkpatrick³, Z. Gan¹, S. Hill^{1,4}, J. R. Long², H. C. Dorn³
1. NHMFL, FSU; 2. Biochemistry & Molecular Biology, UF; 3. Chemistry, Virginia Tech.; 4. Physics, FSU
Funding Grants: G.S. Boebinger (NSF DMR-1157490, NSF DMR-1644779)



Dynamic nuclear polarization (DNP) has gained tremendous popularity in recent years as an effective method to greatly boost the sensitivity of NMR and MRI. Upon application of a magnetic field, DNP is achieved by transferring the large electron spin polarization of a paramagnetic dopant to the NMR-active nuclei of interest. This polarization transfer is mediated by the saturation of electron spin resonance (ESR) transitions (e.g. in an organic radical mixed with the sample) via microwave irradiation of the sample. By combining DNP at low temperatures with rapid dissolution, researchers can achieve nuclear spin polarization enhancements that are as much as 10,000-fold over thermal equilibrium for solutions at room temperature. These DNP enhancements enable novel MRI applications, such as monitoring in vivo metabolism in real time.

In this study, researchers added a low concentration of the endohedral metallofullerene (EMF) $Gd_2@C_{79}N$ to DNP samples, finding that 1H and ^{13}C enhancements increased by 40% and 50%, respectively, at 5 T and 1.2 K. Complementary multi-dimensional pulsed high-field ESR studies of the same sample provide important insights into the enhancement mechanism. While Gd reagents have previously been shown to enhance DNP at low fields, albeit at significantly higher Gd concentrations, this is the first time such increases have been observed at 5 T. Importantly, the encapsulation of Gd in the EMF, along with the need for significantly lower concentrations, contribute to a significant reduction in toxicity of MRI for medical applications.

Endohedral Metallofullerene (EMF)



(Top) A mixture of $Gd_2@C_{79}N$ with the organic radical 4-oxo-TEMPO is shown to boost DNP efficiency, resulting in both 1H and ^{13}C hyperpolarization. (Bottom) State-of-the-art spectrometer (HiPER) employed in this study, which combines expertise from the MagLab's EMR and NMR programs.

Facilities used: W-band HiPER ESR Instrument at EMR, MagLab/FSU and the 5 T Dissolution DNP Polarizer at AMRIS, MagLab/UF.

Citation: X. Wang, J. E. McKay, B. Lama, J. van Tol, K. Kirkpatrick, Z. Gan, S. Hill, J. R. Long, H. C. Dorn, *Gd based endohedral metallofullerene $Gd_2@C_{79}N$ as a relaxation boosting agent for dissolution DNP at high fields*, **Chem. Comm.** **54**, 2425-2428 (2018).