Gd Based Endohedral Metallofullerene as a High-Field DNP Boosting Agent

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Introduction

Dynamic nuclear polarization (DNP) has gained tremendous popularity in recent years as an effective method to address the low nuclear spin sensitivity challenges of NMR and MRI. Upon application of a magnetic field, DNP is achieved through transfer of the much larger electron spin polarization of a paramagnetic dopant (e.g. an organic radical mixed with the sample) to the NMR active nuclei of interest. Importantly, this polarization transfer is mediated by the saturation of electron spin resonance (ESR) transitions via microwave irradiation of the sample. By combining DNP at low temperature with rapid dissolution, nuclear spin polarization enhancements of order 10,000 over thermal equilibrium can be achieved for solutions at room temperature, enabling novel MRI applications monitoring *in vivo* metabolism in real time.

Experimental

Broadband pulsed ESR measurements were performed at W-band (94 GHz) using the HiPER instrument in the EMR facility at Florida State University. DNP experiments were carried out using the 5 T Dissolution Polarizer in the AMRIS facility at the University of Florida. The NHMFL is the only user facility that provides access to the necessary high-field dissolution DNP and pulsed ESR instruments employed in this investigation. This user-driven project also leverages the unique combination of expertise available through the NMR and EMR user programs.

Results and Discussion

In this study, it is shown that by adding a low concentration of the endohedral metallofullerene (EMF) $Gd_2@C_{79}N$ to DNP samples, ^{1}H and ^{13}C enhancements increase by 40% & 50%, respectively, at 5 T & 1.2 K (not shown) [1]. Complementary multi-dimensional pulsed high-field ESR studies of the same sample provide important insights into the enhancement mechanism (**Fig.1**) [1]. 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 for medical applications.

Conclusions

Increased DNP enhancements to ^{1}H & ^{13}C NMR signals are found upon adding a low dosage boosting agent to samples − the $Gd_2@C_{79}N$ endohedral metallofullerene. High-field pulsed ESR measurements additionally provide microscopic insights into the DNP enhancement mechanism.

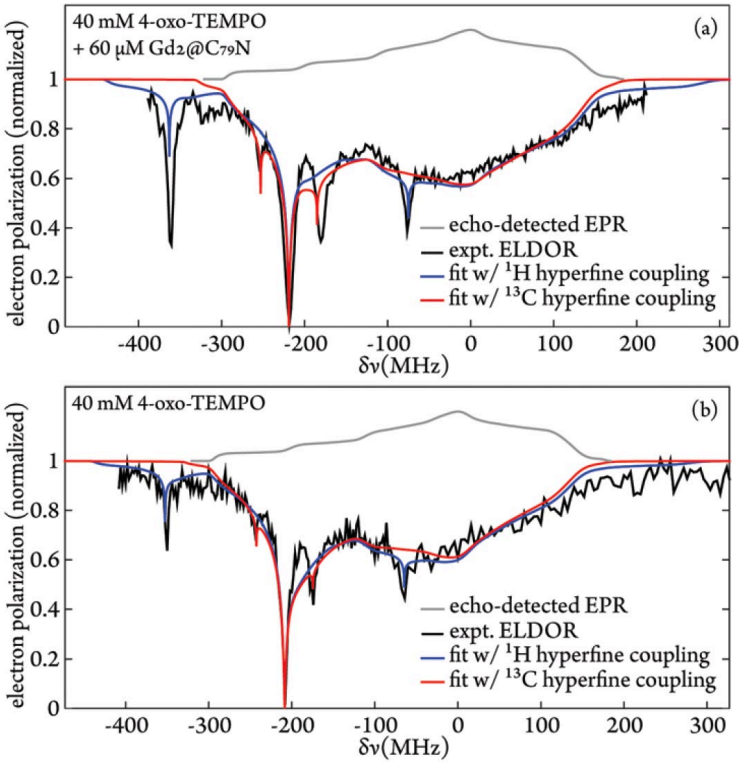

Fig.1 Experimental pulsed electron-electron double resonance (PELDOR) spectra and fits, both with (a) and without (b) the $Gd_2@C_{79}N$ relaxation agent. The fits were performed using a model that considers hyperfine coupling with ^{1}H and ^{13}C nuclear spins. The saturation pulse frequency was swept over a 600 MHz bandwidth (1 MHz steps), followed by Hahn-echo detection sequence at $\delta\nu$ = –219 MHz in (a) and –209 MHz in (b). Electron depolarization by solid effect (SE) polarization transfer is seen at two positions, detuned approximately ±36 MHz and ±143 MHz from the detection frequencies, resulting from hyperfine interactions with the ^{13}C (67% isotope enriched) and ^{1}H nuclei.

Acknowledgements

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References

[1] Wang, X., *et al.*, Chem. Comm., **54**, 2425-2428 (2018).