Understanding BDPA as a Radical Center for Dynamic Nuclear Polarization

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Introduction

Dissolution Dynamic Nuclear Polarization (dDNP) was introduced in 2003 [1], and is moving towards use in clinical diagnostics rapidly [2]. DNP transfers polarization from a highly polarized electron spin bath to nuclear spins via intramolecular dipolar coupling from an exogenous free radical doped into the sample. In general, for DNP carbon-13 enriched samples, matching the electron dipolar linewidth to the nuclear Larmor frequency produces superior polarization. The well-known compound, 1,3-bisdiphenylene-2-phenylallyl (BDPA) has an ESR linewidth that should make it a superior polarization agent compared to the more commonly used trityl radical, but actual enhancements lag that of trityl significantly. We have undertaken a study to understand concentration dependencies and the effect of Ho^{3+} doping on DNP kinetics and absolute polarization levels in BDPA doped samples.

Experimental

All samples were freshly prepared on the same day of DNP experiments. First, stock BDPA sample of either 120 mM or 240 mM were prepared in sulfolane solvent only. Different concentrations of BDPA solutions (15mM, 20 mM, 30 mM, 40 mM, 50 mM, 60 mM and 100 mM; with or without different concentrations of Ho-DOTA) were made by adding appropriate amount of BDPA stock, Ho-DOTA (from 5 mM stock) and 1:1 v/v [1-^{13}C] pyruvic acid:sulfolane, keeping ^{13}C spins number constant in all samples. 25 µL sample volume size was used for all experiments. Microwave sweep spectra in 3.35 T (HyperSense) were acquired at 1.4 K with 100 mW microwave power, polarized for 5 min at each frequency. In the 5 T (NHMFL homebuilt DNP) system, the microwave frequency sweeps were collected with irradiation for 3 min at each time point at 1.2 K temperature. A ~5 degree excitation pulse were applied in both 3.35 T and 5 T system to acquire the buildup curve, using P(+) (maximum positive enhancement) microwave frequency.

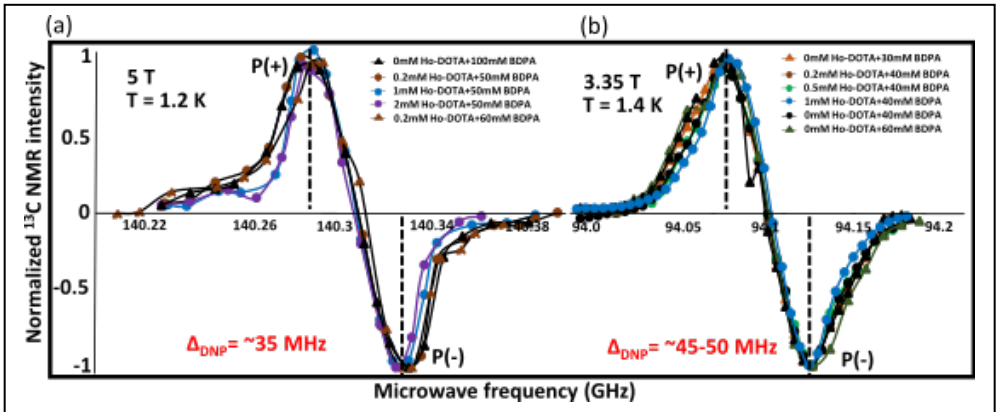

Fig.1 Microwave frequency sweeps for BDPA samples at 3.35 T and 5 T. All data is normalized to 1. Holmium doping provides increased polarization at 3.35 T at increasing concentrations, but at 5 T, only the minimum concentration assayed provided enhanced signal.

Results and Discussion

BDPA produces microwave sweep spectra which are more narrow at 5 T, than at 3.35 T. Increasing concentrations of Ho-DOTA further narrow the enhancement manifold. The Ho-DOTA concentration dependence is different between the two field strengths.

Conclusions

Reducing the electronic T_1 of BDPA is not sufficient to produce polarization in excess of that produced using the trityl radical.

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References

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[2] Kurhanewicz, J., *et al.,* Neoplasia **21**, 1-16 (2018).