Supporting Information

DNP by thermal mixing under optimized conditions yields >60,000-fold enhancement of ^{89}Y NMR signal

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The Borghini model.

At B=3.35 T and T_L=1.4 K, the electron thermal polarization is $P_{th}(e^-)$ is 92 % while ^{89}Y spins have $P_{th}(^{89}Y)$=0.013 %. At this field, the ESR linewidth (full-width at half maximum) for trityl is around 63 MHz. The dependence of the ^{89}Y polarization shown in Figure 1 conforms to the thermal mixing theory. The Borghini model which predicts that, for electronic linewidth D greater than the nuclear Larmor frequency v_n, the position of the maximum positive and negative solid-state NMR enhancements does not depend on the nuclear species but are determined only by the properties of the free radical. The microwave DNP spectrum is obtained by plotting the spin temperature T_s as a function of microwave irradiation frequency for a given electron polarization $P_{th}(e^-)$ using Eq. S1.

$$P_{th}(e-) = \int_{-\infty}^{+\infty} f(\Delta)\tanh((\Delta_0 - \Delta)/2k_B T_s)[(\Delta_0 - \Delta)/\Delta_0]d\Delta \qquad \text{Eq. S1}$$

where $f(\Delta)$ is the ESR lineshape function of the radical, $\Delta_0=\omega_0-\omega_e$, and Δ is the irradiation frequency with respect to central ESR frequency, and T_s is the spin temperature of the electronic dipolar system. Since the spin temperature of electron SSI reservoir and nuclear Zeeman system is equal in thermal mixing, Equation 1 should also describe the dependence of nuclear polarization on the microwave frequency.[1-3]

^{13}C NMR signal as a function of microwave frequency.

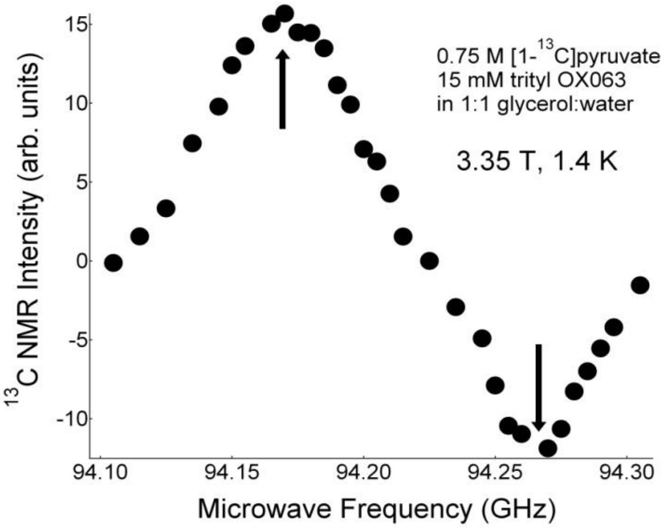


Figure S1. ^{13}C NMR signal from sodium [1-^{13}C]pyruvate (0.75 M in 1:1 glycerol-water) doped with 15 mM trityl OX063 in glycerol water as a function of microwave frequency at 3.35 T and 1.4 K. The datapoints represent solid state polarizations measured with the solid state NMR probe of the polarizer. The separation between the positive and negative polarization peaks is ~70 MHz. The location of the ^{13}C polarization peaks is approximately the same as that of the ^{89}Y polarization peaks which conforms with thermal mixing theory of DNP.

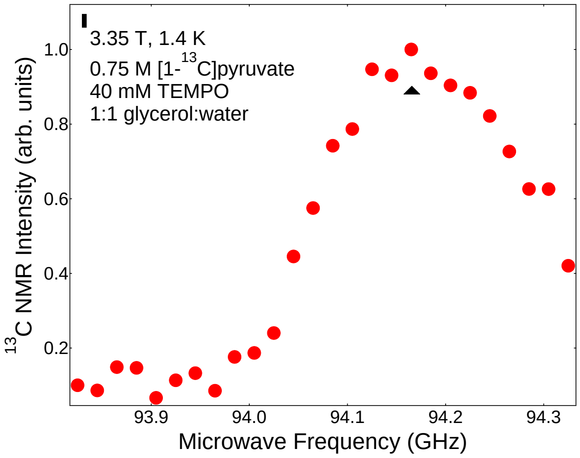


Figure S2: ^{13}C microwave DNP spectrum of TEMPO-doped sodium [1-^{13}C]pyruvate sample. Only the positive polarization peak (~94.17 GHz) of ^{13}C sample could be determined due to the limited bandwidth of the microwave frequency sweep in the HyperSense polarizer; the negative polarization peak is located further upfield.

T_1 Decay of the hyperpolarized ^{89}Y NMR signal for nitroxide doped samples.

Due to higher concentration of paramagnetic species, samples doped with the optimum radical concentration of TEMPO (40 mM) and deuterated TEMPO (40 mM) in the solid-state have slightly lower liquid-state nuclear T_1 values compared to samples doped with samples doped with trityl OX063 (15 mM).

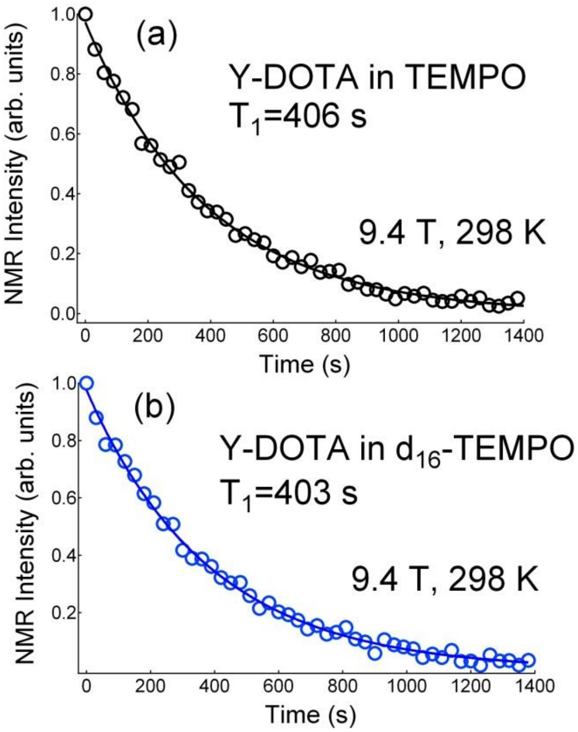
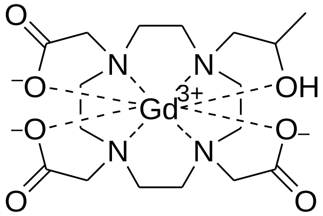


Figure S3. Decay of the hyperpolarized ^{89}Y NMR signal at 298 K and 9.4 T after dissolution of 160 µL hyperpolarized samples containing 0.28 M YDOTA and 40 mM (a) TEMPO and (b) deuterated TEMPO in 1:1 glycerol:water glassing matrix. The dissolution liquid contained 36 mM Y-DOTA and 1.8 mM TEMPO/deuterated TEMPO. The solid lines were obtained by fitting the data to Eq. 2 with 5° flip angle and 30-second repetition time.

Structure of ProHance



ProHance

Chart S1

References

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