

High-Field ^{13}C DNP with a Radical Mixture

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Materials and Methods

a.) Materials

Samples were prepared using $^{13}\text{C}_3$ -glycerol- d_8 , D_2O and H_2O in a 60:30:10 mixture. Trityl (OX-063) and SA-BDPA samples were prepared using 40 mM radical concentration (40 mM electrons), while the mixture was a 20 mM trityl : 20 mM SA-BDPA. Samples were mixed homogeneously at 298 K and packed within 4 mm sapphire rotors equipped with a Vespel drive cap and a Kel-F top cap. Typical fill volumes were between 40 and 50 μL . $^{13}\text{C}_3$ -glycerol- d_8 and D_2O were purchased from Cambridge Isotope Laboratories (Andover, MA) and used without further purification. Trityl was a gift from Jan-Hendrik Ardenkjaer-Larsen and Klaus Golman (Nycomed Inc., Malmo, Sweden).

b.) Methods

Nuclear Magnetic Resonance - Dynamic nuclear polarization magic-angle spinning NMR experiments were performed on a custom home-built instrument, consisting of a 212 MHz (^1H , 5 T) NMR spectrometer (courtesy of Dr. David Ruben, FBML, MIT) and a 140.6 GHz cyclotron maser (gyrotron) generating high power microwaves up to 15 W. Spectra were recorded on a home-built cryogenic 4 mm quadrupole resonance (^1H , ^{13}C , ^{15}N & e^-) DNP NMR probe equipped with a Kel-F stator (*Revolution NMR*, Fort Collins,

CO). Microwaves are guided to the sample via circular overmoded waveguide whose inner surface has been corrugated to reduce mode conversion and ohmic losses. Sample temperatures were maintained below 85 K, with a spinning frequency, $\omega_r/2\pi = 4.8$ kHz. Directly polarized ^{13}C experiments were acquired under continuous microwave irradiation, using a Bloch sequence and high-power TPPM¹ proton decoupling (^1H and $^{13}\text{C} - \gamma B_1/2\pi = 100$ kHz). Recycle delays were determined using a saturation recovery experiment yielding T_B between 167 and 287 seconds. The recycle delay was chosen as $T_B \times 1.26$, yielding optimum sensitivity per unit of time. ^{13}C detected DNP field-profiles were performed by sweeping the main NMR field using a sweep coil between 4974 and 4988 mT (211.8 and 212.3 MHz, ^1H Larmor frequency).

High field Electron Paramagnetic Resonance – SA-BDPA and trityl EPR spectra were obtained at 140 GHz and 80 K, using 1 mM solutions dissolved in 60:40 (v/v) glycerol:D₂O. Spectra were recorded by integration of a Hahn echo at various field points. For SA-BDPA, 131 field points were acquired between 4989 mT and 5002 mT, using a $\pi/2$ - τ - π timing of 30 ns–200 ns–60 ns, and taking 200 shots at each point with a 4-step phase cycle. For trityl, 241 field points were acquired between 4988 mT and 5000 mT, using a timing of 35 ns–200 ns–70 ns, and taking 400 shots at each point with a 4-step phase cycle.

Electron spin-lattice relaxation times (T_{1S}) were recorded using the three DNP samples. These were acquired by saturating the center of the EPR spectrum for 1-3 ms, followed by a variable delay, and then a Hahn echo for detection. The delay is varied, and the results are fit to a monoexponential curve to obtain the relaxation time. T_{1S} for trityl was recorded at a field position of 4993 mT and T_{1S} for SA-BDPA were recorded at 4994.85 mT. For the 40 mM trityl sample, 100 time points are taken with a delay up to 8 ms, with 400 shots taken per point, and the Hahn echo timing is 41 ns–700 ns–82 ns. For the 40 mM SA-BDPA sample, 50 time points are taken with a delay up to 200 ms, with 200 shots taken per point, and a timing of 49 ns–350 ns–96 ns. For the trityl resonance in the mixture, 50 time points are taken with a delay up to 30 ms, with 400 shots taken per point, and a timing of 38 ns–800 ns –76 ns. Finally, for the SA-BDPA

resonance in the mixture, 50 time points are taken with a delay up to 30 ms, with 400 shots taken per point, and a timing of 38 ns–600 ns–76 ns.

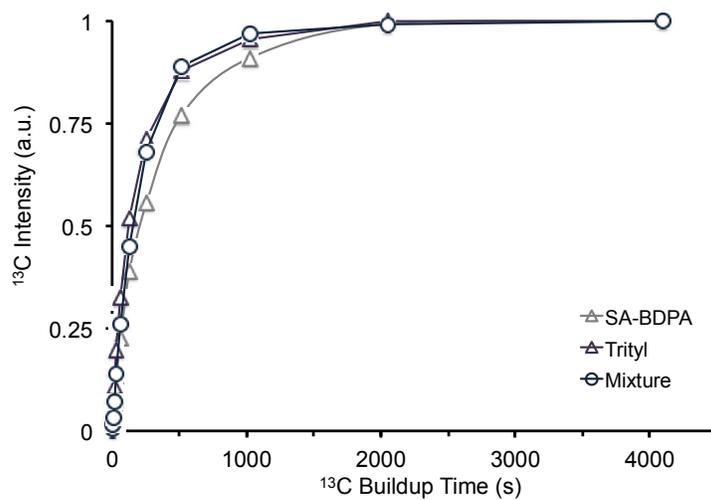


Figure S1: ^{13}C detected polarization buildup curves for SA-BDPA, trityl and the mixture.

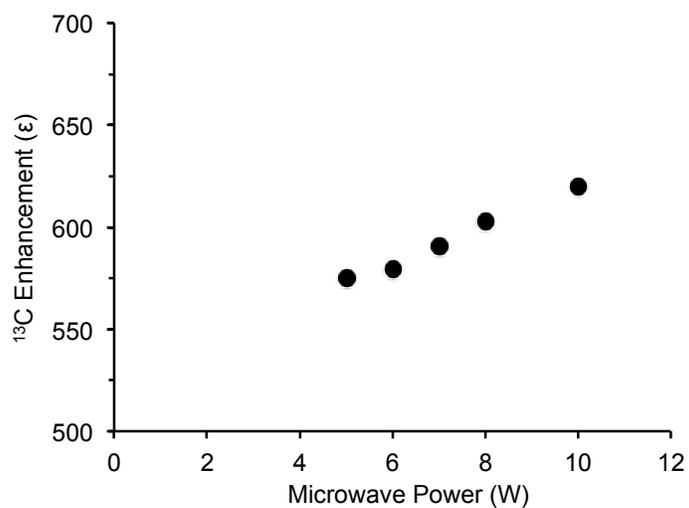


Figure S2: Dependence of the ^{13}C enhancement on microwave output power for the mixture sample.

References:

1- Bennett, A.E., Rienstra, C.M., Auger, M., Lakshmi, K.V. and Griffin, R.G. (1995), Journal of Chemical Physics, **103**(16), 6951-6958.