Supporting Information

High Field Dynamic Nuclear Polarization with High-Spin Transition Metal Ions

Björn Corzilius,[a] Albert A. Smith,[a] Alexander B. Barnes,[a] Claudio Luchinat,[b] Ivano Bertini,[b] and Robert G. Griffin[a,*]

For DNP experiments Na[GdDOTA], Na_2[GdDTPA], and Na_2[MnDOTA] were dissolved in d_8-glycerol/D_2O/H_2O (60:30:10 % v/v), respectively, containing 1 M ^{13}C-urea. Complex concentrations varied between 2 and 100 mM. For EPR experiments 1 mM solutions of the paramagnetic compounds were prepared in a protonated glycerol/water mixture with a volume ratio of 60:40. EPR spectra were recorded on a custom built pulsed EPR spectrometer operating at 139.49 GHz with a maximum microwave power of 30 mW.[16] DNP experiments were performed on a home-built NMR spectrometer operating at 212 MHz ^{1}H frequency (courtesy of David Ruben) using a custom designed quadruple channel (^{1}H, ^{13}C, ^{15}N, e^-) probe that employs a 4 mm o.d. Revolution NMR stator. Sapphire rotors with 0.7 mm walls (Inasco, Inc) were used because they are transparent to microwaves. The probe is equipped with a cryogenic sample eject system to quickly switch between different samples without the need to disassemble the system, therefore improving reproducibility and minimizing error when comparing different samples.[17] The magnet is equipped with a superconducting sweep-coil with ±0.1 T sweep width centered at 4.97 T. The sweep coil is essential for these types of experiments since the magnetic field has to be reset for each compound in order to fulfill the DNP matching condition. The sample was contained by Vespel spacers in a volume of about 4 mm height in the center of the rotor long axis. A custom designed gyrotron was used to generate microwaves at a frequency of 139.64 GHz, with a maximum power output of ~6 W.[18] Overmoded waveguides and miter bends were used to deliver the microwaves from the gyrotron output window to the stator. A gap of ~2 mm served as electrical break between the waveguide and the inner conductor of the probe rf transmission line, whose inner volume is used as microwave guide. Thus, the microwaves were launched through space into the inner conductor. The inner surfaces of the waveguides were corrugated in order to prevent the conversion of the HE_{11} mode into higher order modes and to reduce ohmic losses.