Supporting Information

Hyperpolarized ^{89}Y offers the potential of direct imaging of metal ions in biological systems by magnetic resonance

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Preparation of ^{89}Y complexes.

Equivalent amounts of freshly prepared $Y(OH)_3$ was added to DTPA (Aldrich), DOTA (Macrocyclics) or DOTP (Macrocyclics) in water and the pH of the reaction mixture was brought to 5 by the addition of NaOH solution (2M). The reaction mixtures were stirred at 40°C for 24 hours and the final pH was adjusted to 6 for $Y(DTPA)^{2-}$ and $Y(DOTA)^{-}$ and to 9 for $Y(DOTP)^{5-}$. The solutions were filtered and freeze-dried to give quantitative yields of the salt free complexes.

Hyperpolarization experiments.

16.6 mM (Tris{8-carboxyl-2,2,6,6-tetra[2-(1-hydroxyethyl)]-benzo(1,2-d:4,5-d')bis(1,3)dithiole-4-yl}methyl sodium salt) radical in equal parts water/glycerol was used as a glassing matrix for the samples. To each sample was added a volume of glassing agent equal to the initial sample volume. The sample was then placed in the hyperpolarizer. 20 μL of YCl_3 (3.0 M) and $Y(DTPA)^{2-}$ (1.52 M) or 40 μL of $Y(DOTA)^{-}$ (0.788 M), $Y(DOTP)^{5-}$ (1.0 M), and $Y(DOTP)^{5-}$ (0.5 M) were each polarized for 75±5 min with a microwave irradiation of 100 mW at 94.118 GHz. The temperature was held at 1.4K during the polarization process. The samples were each then removed by injection of 4 mL of a solution of 850 μM EDTA in H_2O. 1.5 mL of the solution was subsequently transferred to an 8

mm NMR tube. This volume filled the detection coil only, thereby removing effects of diffusion that artificially increase the apparent T_1 of the sample.

Spectrometer

^{86}Y NMR spectra were recorded using a Varian 600 MHz NMR system in a 10 mm broad band probe tuned to 29.4 MHz. A single scan with a flip angle of 10 degrees (5.5 μs) was taken every 11 seconds (interpulse delay =10 s, acquisition time =1 s) starting approximately 30±1 seconds after ejection from the HyperSense device. Data collection continued until the signal was no longer distinguishable from the noise. The total number of 1 scan acquisitions for each sample was: YCl_3 – 100 scans, $Y(DTPA)^{2-}$ – 90 scans, $Y(DOTA)^{-}$ – 117 scans, and both $Y(DOTP)^{5-}$ samples – 38 scans. The samples were each followed by collecting a thermal signal from 1.5 mL of YCl_3 (3 M) using a flip angle of 90 degrees (49.5 μs) and a single scan with the same receiver gain settings. Polarization enhancements were calculated by comparing the integrated areas of the signal from the first acquisition from the hyperpolarized samples and that from the YCl_3 standard in Matlab (MathWorks, USA), taking into account the final concentrations and the difference in flip angles.

Patyal, et al.,[1] had previously outlined a different method by which the polarization enhancement and the T_1's of hyperpolarized samples could be measured. Due to the low sensitivity for their thermally polarized gas samples, the pulse flip angle had to be calibrated on the fly with a hyperpolarized sample. In our case, the flip angle is calibrated with a standard. Therefore, the following expression can be fitted as a function of number of inspection pulses to estimate the T_1 of the hyperpolarized species.

$$M_y(n) = M_p \cos^{(n-1)}\theta \sin\theta \exp^{-(n-1)TR/T_1} \quad (1)$$

M_y is the transverse magnetization following a pulse of angle θ, M_p is the hyperpolarized Z-magnetization, TR is the experimental repetition time, and T_1 is the longitudinal relaxation time. The (n-1) term in the equation is derived from the magnetization retained from the previous scan.

References:

[1] B. R. Patyal, J. H. Gao, R. F. Williams, J. Roby, B. Saam, B. A. Rockwell, R. J. Thomas, D. J. Stolarski, *J. Magn. Reson.* **1997**, *126*, 58-65.