Supplementary Information

Microwave-Gated Dynamic Nuclear Polarization

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Relaxation rate constant

\[
R_{1p} = \frac{1}{r^6}\frac{16}{15}\frac{\mu_0^2}{(4\pi)^2}g_H^2(g_\mu_B^2)S(S + 1)\left\{\frac{4\tau_{s1}}{1 + \omega_1^2\tau_{s1}^2} + \frac{13\tau_{s2}}{1 + \omega_S^2\tau_{s2}^2} + \frac{3\tau_{s1}}{1 + \omega_I^2\tau_{s1}^2}\right\}
\]

(S1)

where \(\omega_1\), \(\omega_S\) and \(\omega_I\) are the nuclear angular nutation frequencies in the rotating frame (in our case \(\omega_1/(2\pi) \approx 20\) kHz), the electron angular frequency in the laboratory frame (in our case \(\omega_I/(2\pi) \approx 285\) MHz for \(^1\)H). In the case of isolated electron-nucleus spin pairs in the solid state at low temperature (no rotational or translational diffusion), \(\tau_{s1} = T_{1e}\) and \(\tau_{s2} = T_{2e}\). However, in our experiment the electron concentration is high (25 mM) which gives rise to electron-electron dipolar couplings on the order of several MHz. Therefore, the apparent transition rate of the electron spin seen by the nuclear spins is not \(T_{1e}\) but the flip-flop rate that is close to \(T_{2e}\).

As shown in Figure S1, for all values of \(\tau_{s1}\) and \(\tau_{s2}\) in the range of 0.1 \(\mu\)s to 0.1 s, it is the first term in Eq. (S1), i.e., \(\frac{4\tau_{s1}}{1 + \omega_1^2\tau_{s1}^2}\) (blue curve in Fig. S1) that dominates over the second and third terms in Eq. (S1) (green and yellow curves in Fig. S1) by at least two orders of magnitude.
We can therefore simplify equation S1 to:

\[ R_{1\rho} = \frac{C \tau_{s1}}{r^{\rho1} + \omega_1^2 \tau_{s1}^2} \]  
\[ (S2) \]

with

\[ C = \frac{4}{15} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 \left( g_e^2 g_B^2 \right)^2 S(S + 1) = 4.92 \times 10^{-8} \mu m^6 s^{-2} \].

**Fitting of cross-polarization curves**

A simple stretched exponential can describe the CP build-up as a function of \( \tau_{\text{CP}} \):

\[ I^{(13C)} = 1 - e^{-\left( t/\tau_{\text{CP}} \right)^\beta} \]  
\[ (S2) \]

Numerical fitting yields \( \tau_{\text{CP}} = 2.68 \) ms and \( \beta = 0.66 \).

A similar stretched exponential multiplied by a decaying stretched exponential can describe CP with continuous microwave irradiation,

\[ I^{(13C)} = \left( 1 - e^{-\left( t/\tau_{\text{CP}} \right)^\beta} \right) e^{-\left( t/T_{1\rho} \right)^\gamma} \]  
\[ (S3) \]

Numerical fitting yields \( \tau_{\text{CP}} = 2.68 \) ms, \( \beta = 0.66 \), \( T_{1\rho} = 7.4 \) ms and \( \gamma = 0.64 \).