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# Supplementary Materials for

## Time-optimized pulsed dynamic nuclear polarization

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# Supplementary Materials

## Section S1. Determining the effective field $\omega_{\text{eff}}$ with quaternions

We have defined that the effective field $\omega_{\text{eff}}$ as the net rotation angle $\beta_{\text{eff}}$ accumulated over a period of the cycle time $\tau_{\text{m}} = 2\pi/(\omega_{\text{m}})$ of a pulse sequence. We can determine $\beta_{\text{eff}}$ analytically using the quaternion description (35). The quaternion is comprised of 4 variables, which are the flip angle $\beta$ and the three unit-axis components of the rotation $S_{\text{xx}}$, $S_{\text{yy}}$ and $S_{\text{zz}}$. For TOP-DNP, which is a basic cyclic sequence comprised of two elements (a pulse and a delay), the effective nutation angle $\beta_{\text{eff}}$ can be determined by computing

$$Q_{\text{eff}} = Q_2 Q_1 \tag{1}$$

where the lower index represents the chronological order of the pulse, i.e. $Q_1$ represents the off-resonance pulse and $Q_2$ is the event when the microwave is turned off and the rotation is performed only by the offset $\Omega_{\text{S}}$. The matrix representations of the respective quaternions are given as

$$Q_1 = \begin{bmatrix} A_1 \\ B_1 \\ C_1 \\ D_1 \end{bmatrix} \text{ and } Q_2 = \begin{bmatrix} D_2 & -C_2 & B_2 & A_2 \\ C_2 & D_2 & -A_2 & B_2 \\ -B_2 & A_2 & D_2 & C_2 \\ -A_2 & -B_2 & -C_2 & D_2 \end{bmatrix} \tag{2}$$

where the symbols $A_{\text{i}}$, $B_{\text{i}}$, $C_{\text{i}}$ and $D_{\text{i}}$ of the respective quaternion $Q_{\text{i}}$ are

$$A_i = S_{\text{xx}}^i \sin\left(\frac{\beta_i}{2}\right), B_i = S_{\text{yy}}^i \sin\left(\frac{\beta_i}{2}\right), C_i = S_{\text{zz}}^i \sin\left(\frac{\beta_i}{2}\right), D_i = \cos\left(\frac{\beta_i}{2}\right) \tag{3}$$

Following that, we identify that the first rotation performed by the microwave pulse at an offset $\Omega_{\mathrm{S}}$ with a pulse length of $\tau_{\mathrm{p}}$ along *x*-axis in the rotating frame is given by

$$A_1 = \sin\theta \sin\left(\frac{\omega_{\mathrm{a}}\tau_{\mathrm{p}}}{2}\right), B_1 = 0, C_1 = \cos\theta \sin\left(\frac{\omega_{\mathrm{a}}\tau_{\mathrm{p}}}{2}\right), D_1 = \cos\left(\frac{\omega_{\mathrm{a}}\tau_{\mathrm{p}}}{2}\right) \tag{4}$$

where $\omega_{\mathrm{a}} = \sqrt{{\omega_{1\mathrm{S}}}^2 + {\Omega_{\mathrm{S}}}^2}$ and $\theta = \tan^{-1} \omega_{1\mathrm{S}}/\Omega_{\mathrm{S}}$. While the second rotation is only performed by the offset $\Omega_{\mathrm{S}}$ along the *z*-axis with a delay of $d$

$$A_2 = B_2 = 0, C_2 = \sin\left(\frac{\Omega_{\mathrm{S}} d}{2}\right), D_2 = \cos\left(\frac{\Omega_{\mathrm{S}} d}{2}\right) \tag{5}$$

According to the definition given in the formulation of the quaternion description, the overall net rotation $\beta_{\mathrm{eff}}$ of the TOP-DNP sequence is encoded in $Q_{\mathrm{eff}}$

$$Q_{\mathrm{eff}} = \begin{bmatrix} S_{\mathrm{xx}}^{\mathrm{eff}} \sin\left(\frac{\beta_{\mathrm{eff}}}{2}\right) \\ S_{\mathrm{yy}}^{\mathrm{eff}} \sin\left(\frac{\beta_{\mathrm{eff}}}{2}\right) \\ S_{\mathrm{zz}}^{\mathrm{eff}} \sin\left(\frac{\beta_{\mathrm{eff}}}{2}\right) \\ \cos\left(\frac{\beta_{\mathrm{eff}}}{2}\right) \end{bmatrix} = Q_2 Q_1 \tag{6}$$

Since we are only interested in the last matrix element, $\cos\left(\frac{\beta_{\mathrm{eff}}}{2}\right)$, we can write down the expression directly

$$\cos\left(\frac{\beta_{\mathrm{eff}}}{2}\right) = D_1 D_2 - (A_1 A_2 + B_1 B_2 + C_1 C_2) \tag{7}$$

$$\beta_{\mathrm{eff}} = 2\cos^{-1}\big(\cos(\Omega_{\mathrm{S}} d/2)\cos(\omega_{\mathrm{a}}\tau_{\mathrm{p}}/2) - \cos\theta\sin(\Omega_{\mathrm{S}} d/2)\sin(\omega_{\mathrm{a}}\tau_{\mathrm{p}}/2)\big)$$

as given in the main article after substituting into the equation $\omega_{\mathrm{eff}} = \beta_{\mathrm{eff}}/\tau_{\mathrm{m}}$.

**Section S2. Experimental details of NOVEL**

We have performed the NOVEL experiment on the same sample to compare the results with that measured with TOP-DNP. We have optimized several parameters and obtained a maximum enhancement of ε ~ 172, which is in good agreement with the value of ~175 reported by Can et al.(37) despite a higher concentration of radical (~ 40 mM) was used in latter experiment. Besides that, Mathies et al.(19) had also reported an enhancement of ε ~ 159 on a similar setup except that the sample contains 1 M urea. Note that the value of 159 was obtained by normalizing the reported value of 380 with respect to the definition of enhancement factor ε adopted in this publication for fair comparison, i.e. normalization with respect to equilibrated DNP enhancement and fully relaxed $^{1}$H signal, $\frac{(1-\exp(-8/8))}{(1-\exp(-8/26))} \times 380 = 159$. This is a fairly consistent result considering the fact that the experiments were performed by three different individuals and three different sample were prepared.

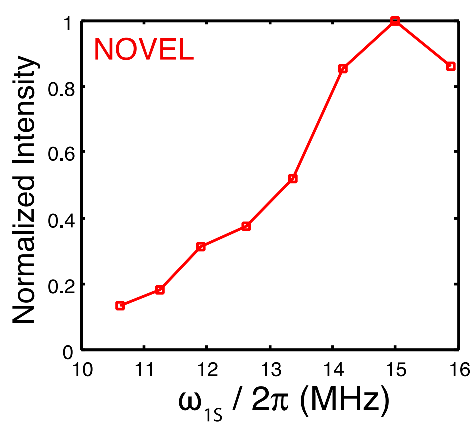


**Fig. S1. Experimentally measured enhancements of the NOVEL sequence as a function of the Rabi frequency at 0.35 T.** A maximum enhancement of ε ~ 172 was recorded using $\omega_{1S}/2\pi$ =15 MHz, repetition time $\tau_{Rep}$ = 2 ms, spin lock time of $\tau_{SL}$ = 2 μs, 16384 repetitions (~ 33 s), and a flip-back pulse was applied after the spinlock to conserve magnetization (19).