

Supporting information for: Role of Electron Spin Dynamics on Solid-State Dynamic Nuclear Polarization Performance

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EPR spectra at 8.5 T

The EPR lineshape for TOTAPOL and 4-Amino TEMPO are shown in Figure S1. It can be seen that the width of the EPR spectra for both mono- and bi-radicals between $C_{\text{mol}} = 5 - 40$ mM does not vary significantly (base-to-base width ~ 1.1 GHz), except that the TOTAPOL samples display slightly broader EPR spectra (by ~ 50 MHz) than 4-AT samples.

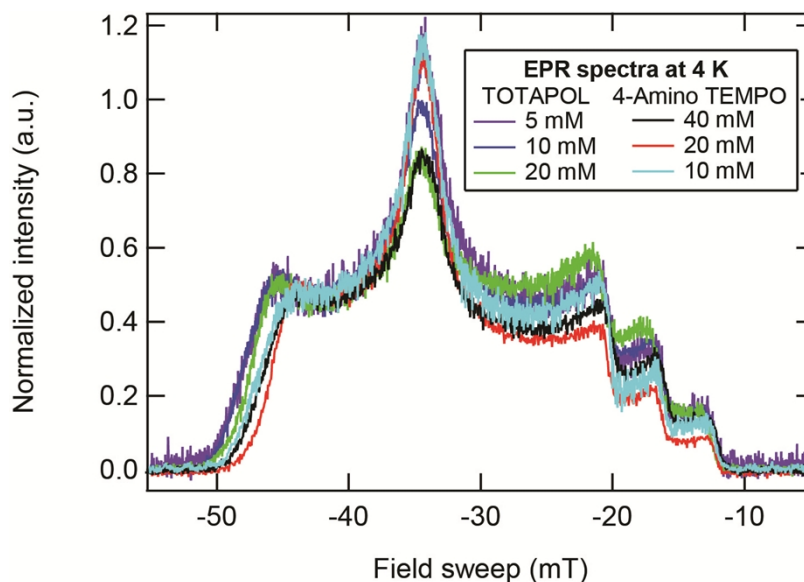


Figure S1 Field swept echo EPR spectra of 4-AT and TOTAPOL at 4 K and 8.5 T. Each spectrum is manually normalized to the maximum intensity of the left shoulder. This is done to help determine any broadening in EPR lineshape.

Determination of electron flip-flop rate of the majority unexcited EPR spins (W')

Given the typically > 500 ns long pulse durations available with current state of the art high field pulsed EPR spectrometers, which implies an exceptionally narrow frequency bandwidth for such pulse lengths, T_M is the timescale of the decoherence of the minority population of the excited electron spins (A spins) by the flip-flop process of the unexcited electron spins (B spins). Here, the flip-flop rate scales with the electron spin dipolar coupling of the B spins that comprise the majority electron spins. Only in the limit of complete saturation of the EPR line, and in the absence of nuclear decoherence, does T_M equal T_{2e} . The systematic dependence of T_M on the $e-e$

dipolar couplings modulated by the radical concentration has been previously quantified in frozen water-glass solutions of 4-AT⁶. The same concept is utilized here to extract the characteristic dipole-dipole flip-flop rate, W' , of the majority B spins from the measurements of T_M across a series of temperatures using a fit to the following equation^{1,2}:

$$\frac{1}{T_M} = \frac{W'}{(1 + \exp(-\frac{T_Z}{T}))(1 + \exp(\frac{T_Z}{T}))} + \Lambda \quad (\text{S1})$$

The first term represents the flip-flop rate of the majority B spins, where W' is its characteristic flip-flop rate and the denominator a temperature-dependent component that represents the probability of these flip-flops to occur, with T_Z being the electron Zeeman temperature, which is 11.5 K at 8.5 T. Importantly, the temperature series needs to encompass a range of temperatures above and below, or close to this Zeeman temperature, to ensure an accurate fit to this equation. The second term in Equation S1, Λ , represents the residual decoherence rate that is largely determined by the decoherence of the electron spins as induced by the nuclear spins, typically of the solvent. The measured temperature dependence of T_M is presented in Figure S2, together with the fitted curves to Equation S1. It can be seen that high quality fits can be obtained for all concentrations of the mono- and bi-radical, and that T_M increases with decreasing temperature around the Zeeman temperature, due to the quenching of the flip-flop process of the B spins, as more and more electron spins are aligned in the same direction with respect to the main magnetic field due to the increase in electron spin polarization. This observation is consistent with a previous study of 4-AT dissolved in a glycerol:water mixture².

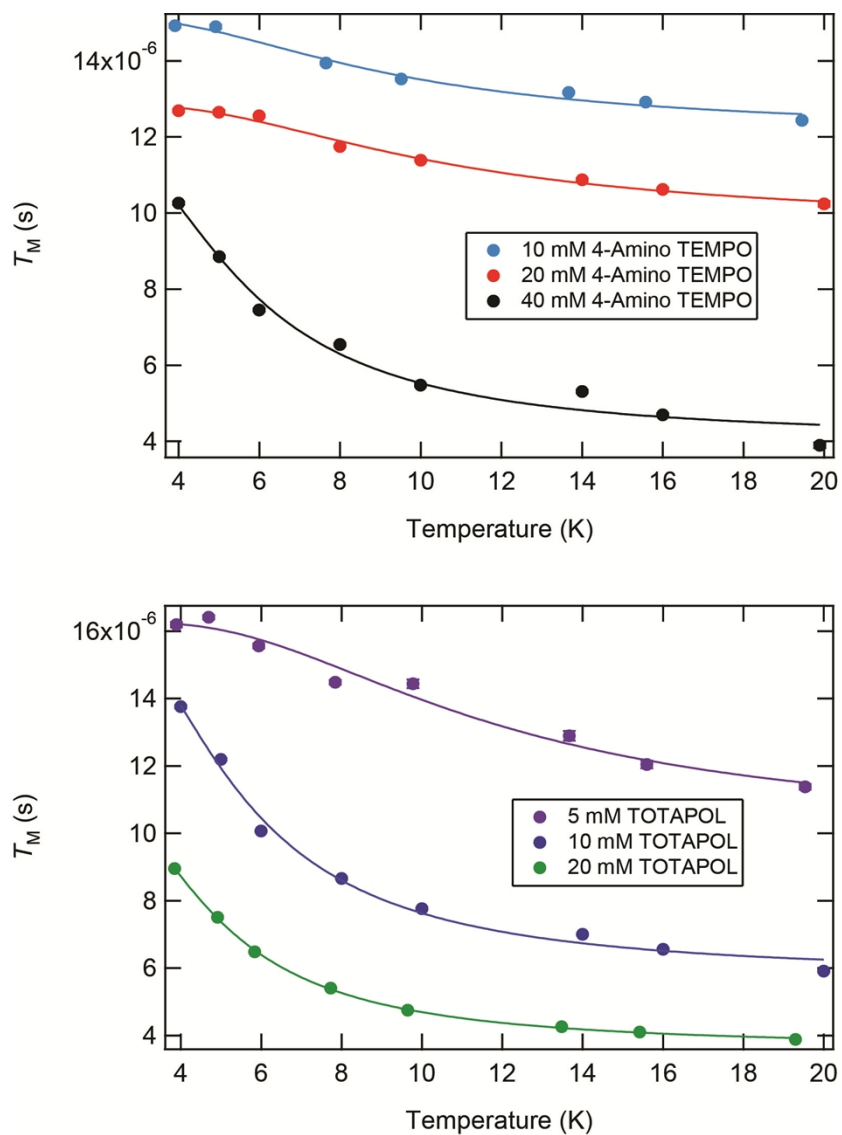


Figure S2 Temperature dependence of T_M for 4-AT (top) and TOTAPOL (bottom). The lines are fits to equation S1.

References

- (1) Takahashi, S.; Brunel, L.-C.; Edwards, D. T.; van Tol, J.; Ramian, G.; Han, S.; Sherwin, M. S. *Nature* **2012**, *489*, 409–413.
- (2) Edwards, D. T.; Takahashi, S.; Sherwin, M. S.; Han, S. *J. Magn. Reson.* **2012**, *223*, 198–206.