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1 Supplementary Material

1.1 Curve fitting results

The analysis of the DNP spectra shown in Fig. 6b-d is described in the main text. The experimental DNP spectra (circles) overlaid with the best fit spectra (solid line) for the non-degassed 40 mM the 10 mM samples at different temperatures are shown in Figs. S1-S2. The DNP spectra overlaid with the best fit spectra for the degassed 40 mM sample at 10 K and different MW intensities are shown in Fig. S3.

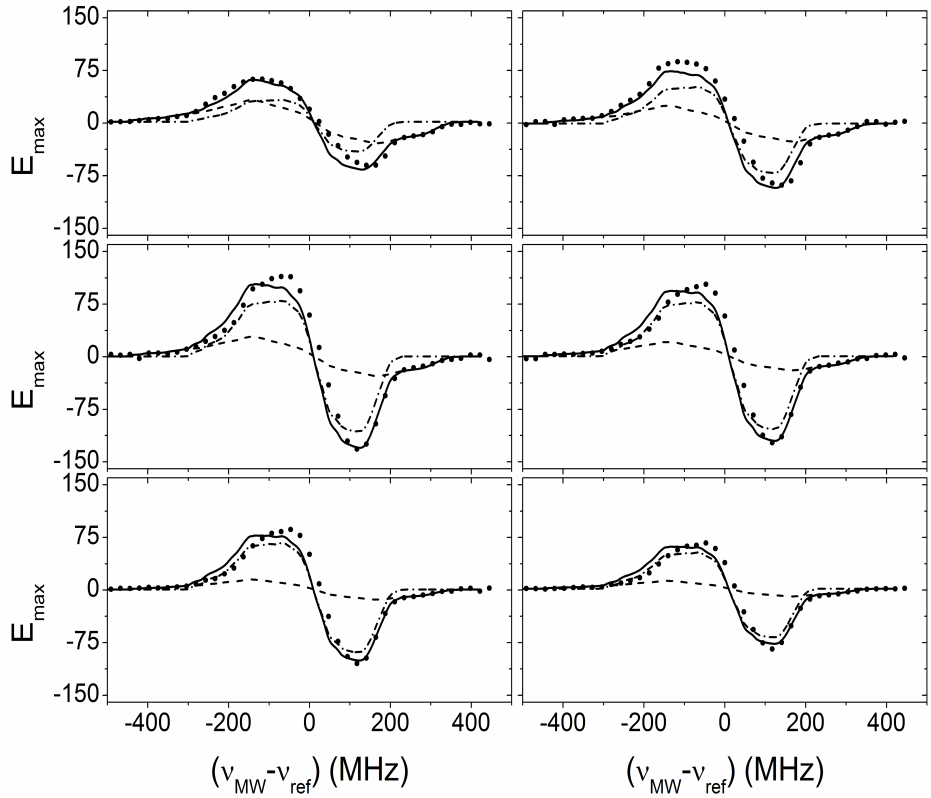

Figure S1: Experimental DNP spectra (circles) of the non-degassed 40 mM sample in the temperature range of 6 K− 50 K overlaid with the simulated DNP spectra (solid lines) constructed using the two spectra shown in Fig. 8. The SE (dashed line) and the CE (dash-dotted line) spectra used to construct the simulated DNP spectra are also shown. The MW frequency scale in MHz units $\nu_{MW} = \omega_{MW}/2\pi - \nu_{ref}$ is calibrated with respect to $\nu_{ref} = 95 \cdot 10^3\ MHz$.

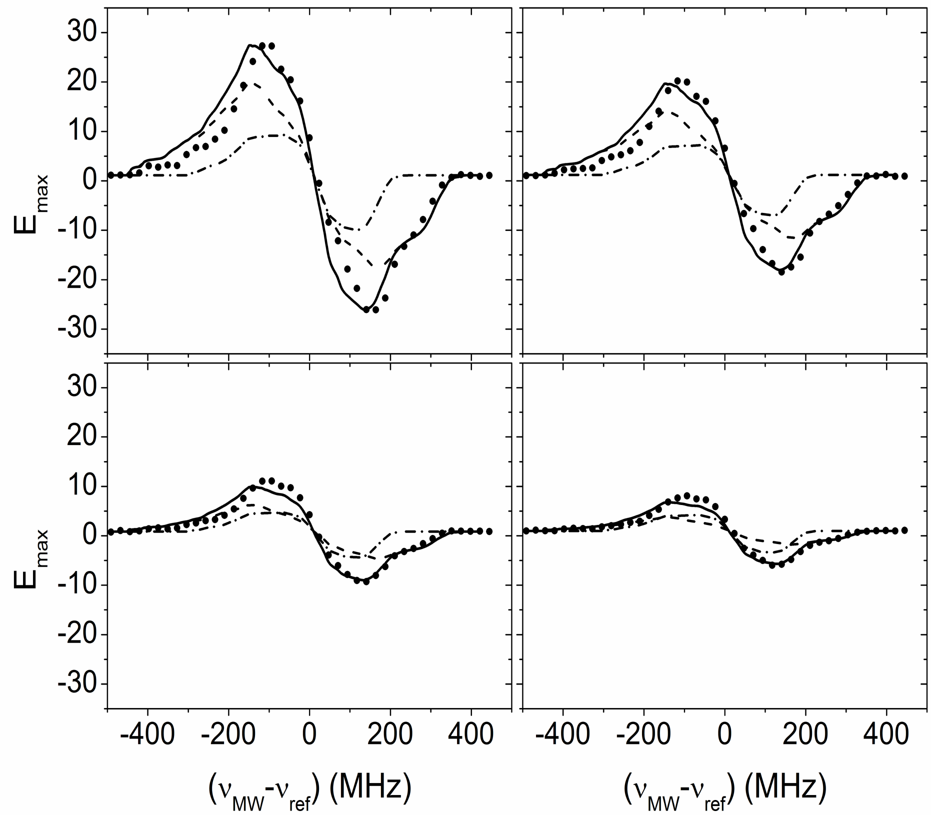

Figure S2: Experimental DNP spectra (circles) of the degassed 10 mM sample in the temperature range of 50 K−80 K overlaid with the simulated DNP spectra (solid lines) constructed using the two spectra shown in Fig. 8. The SE (dashed line) and the CE (dash-dotted line) spectra used to construct the simulated DNP spectra are also shown. The MW frequency scale in MHz units $\nu_{MW} = \omega_{MW}/2\pi - \nu_{ref}$ is calibrated with respect to $\nu_{ref} = 95 \cdot 10^3\ MHz$.

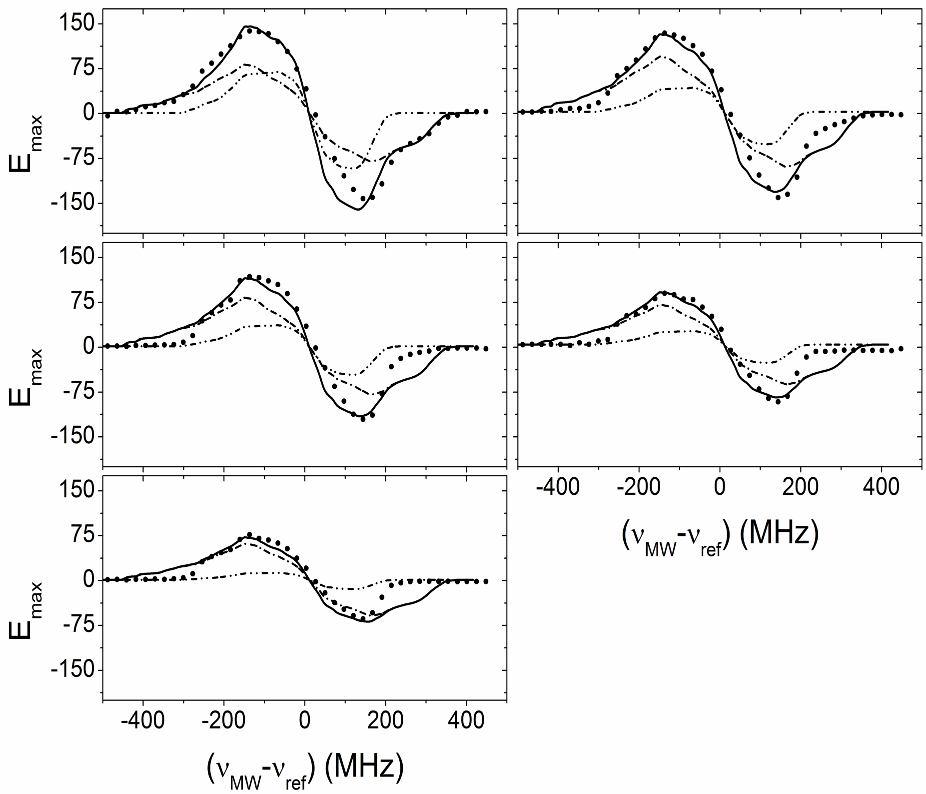

Figure S3: Experimental DNP spectra (circles) of the degassed 40 mM sample in the temperature range of 6 K−50 K overlaid with the simulated DNP spectra (solid lines) constructed using the two spectra shown in Fig. 8. The SE (dashed line) and the CE (dash-dotted line) spectra used to construct the simulated DNP spectra are also shown. The MW frequency scale in MHz units $\nu_{MW} = \omega_{MW}/2\pi - \nu_{ref}$ is calibrated with respect to $\nu_{ref} = 95 \cdot 10^3\ MHz$.

1.2 $\{e_b - e_a - n\}$ and $\{e_b - e_a - n_1 - n_2 - n_3\}$; a comparison

To demonstrate the changes in the contour plot of $P_n(\omega_a, \omega_b, \omega_{MW})$,shown in Fig. 5 for a three-spin system $\{e_b - e_a - n\}$, by adding removed nuclei we also calculated $P_{n_3}(\omega_a, \omega_b, \omega_{MW})$ for n_3 in a five-spin system $\{e_b - e_a - n_1 - n_2 - n_3\}$. Here only n_1 is hyperfine-coupled to electron e_a, while all nuclei are dipolar-coupled to each other. Only small areas of the $P_{n_3}(\omega_a, \omega_b, \omega_{MW})$ contour are shown in Fig. S4(c-d). Comparing these contours with the nuclear polarization of n, shown in Figs. S4(a-b), we notice that the results look very similar. The SE and CE regions are narrower in $P_{n_3}(\omega_a, \omega_b, \omega_{MW})$ than in $P_n(\omega_a, \omega_b, \omega_{MW})$ due to lower effective MW irradiation on n_3 than on n.

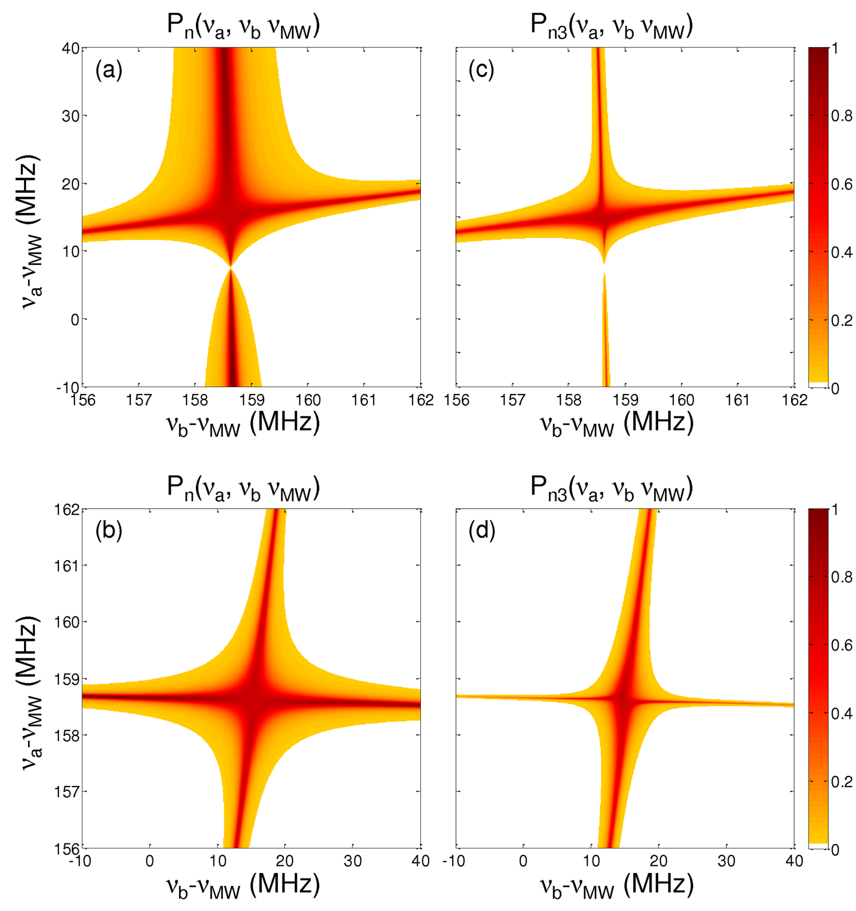

Figure S4: A comparison between two small areas of $P_n(\nu_a, \nu_b, \nu_{MW})$ calculated for a three-spin system $\{e_b - e_a - n\}$ (a-b) and $P_{n_3}(\nu_{ea}, \nu_{eb}, \nu_{MW})$ (c-d) calculated for n_3 in a five-spin system

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$\{e_b - e_a - n_1 - n_2 - n_3\}$. The parameters used in the simulations are as in the figure caption of Fig. 7 with the addition of the nuclear-nuclear dipolar interactions $d_{12} = 6\ Hz$, $d_{23} = 7\ Hz$, $d_{13} = 0\ Hz$ and the relaxation time $T_{1n} = 100\ s$.