Supporting Information

Nanometric distance measurements between Mn(II)DOTA centers

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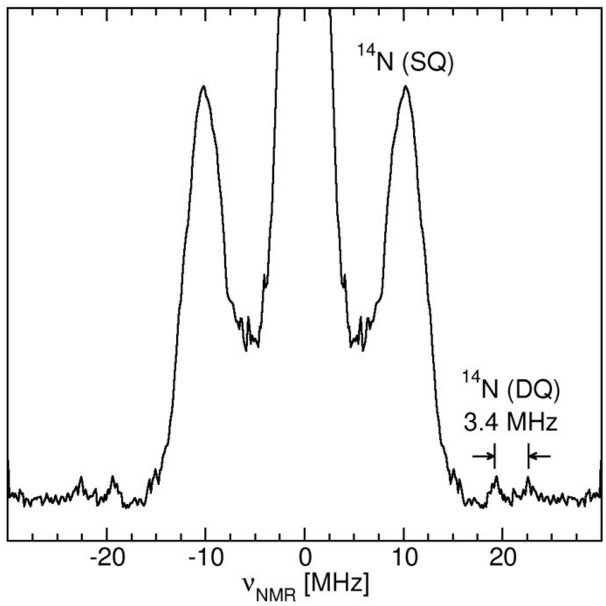

Fig. S1. ^{14}N ELDOR-NMR spectrum of $MnDOTA_2P6$ showing the single (SQ) and double (DQ) quantum associated with ^{14}N nuclei, centered at ν_{14N} and $2\nu_{14N}$. The latter was a doublet with a splitting of 3.4 MHz corresponding to twice the manganese ^{14}N hyperfine interaction coupling.

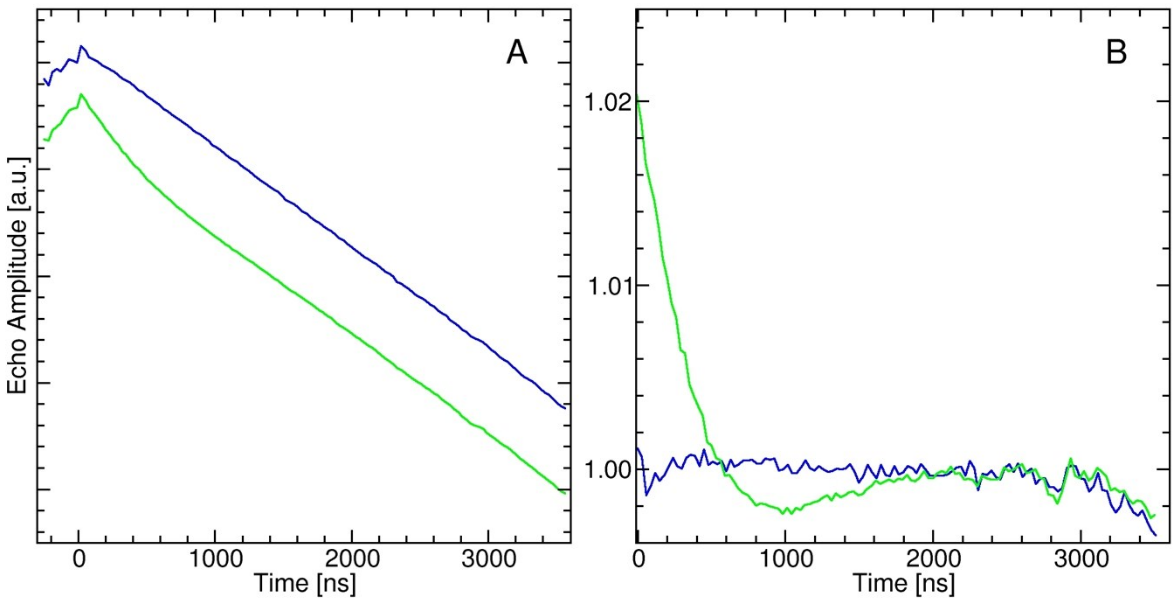

Fig. S2. Full PELDOR time traces for $MnDOTA_2P12$ (green) and MnDOTA (blue): **A.** the raw PELDOR time traces (arbitrarily offsetted) and **B**. The background divided PELDOR time traces. $MnDOTA_2P12$ had no discernible modulations beyond 2800 ns except for spectrometer related artifacts that also appeared in MnDOTA.

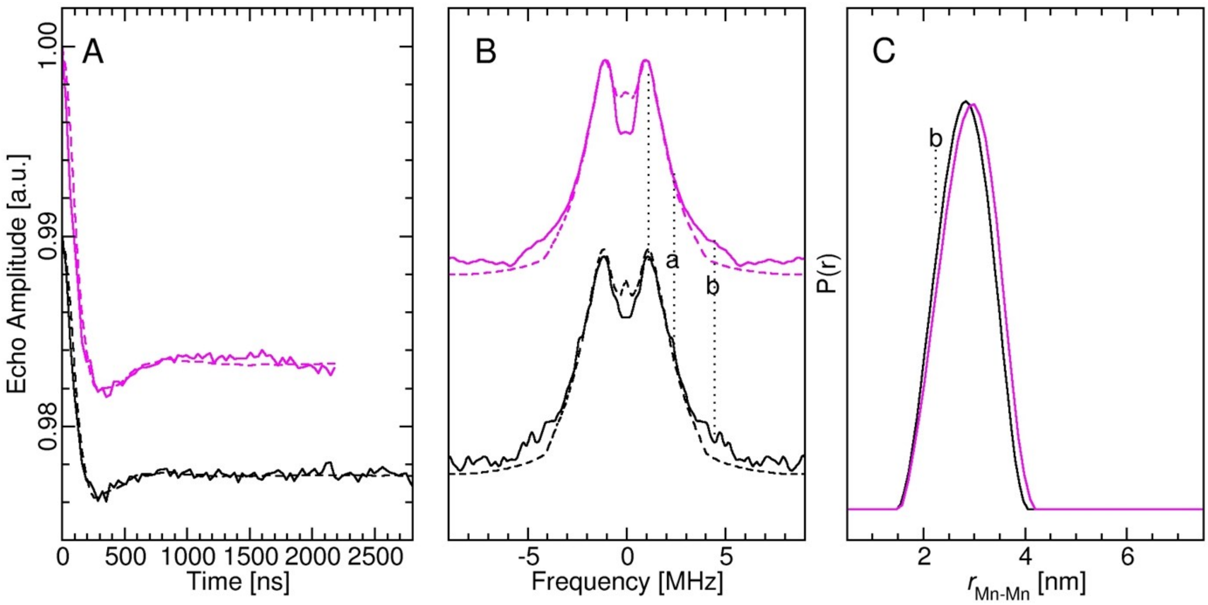

Fig. S3. PELDOR measurements of $MnDOTA_2P6$ with pump/detect frequency offset of 50 MHz (black), and 150 MHz (magenta): **A**) The background removed PELDOR time traces (solid line) with the inset showing raw data, the traces were arbitrarily offsetted; and **B**) the corresponding frequency-domain spectra (solid line); and **C**) the distance distributions obtained by Tikhonov analysis (solid line). The fits of the PELDOR time traces and frequency-domain spectra based on the Tikhonov analysis are also shown as blue dashed lines in panels A and B respectively. The discrepancy in the most probable distance between the two frequency offset experiment was 0.1 nm. The description of the dotted markers is discussed in the text. For the 150 MHz pump/detect frequency offset experiment, a 30 ns pump pulse, and 22 and 40 ns π/2 and π detection pulses were used.

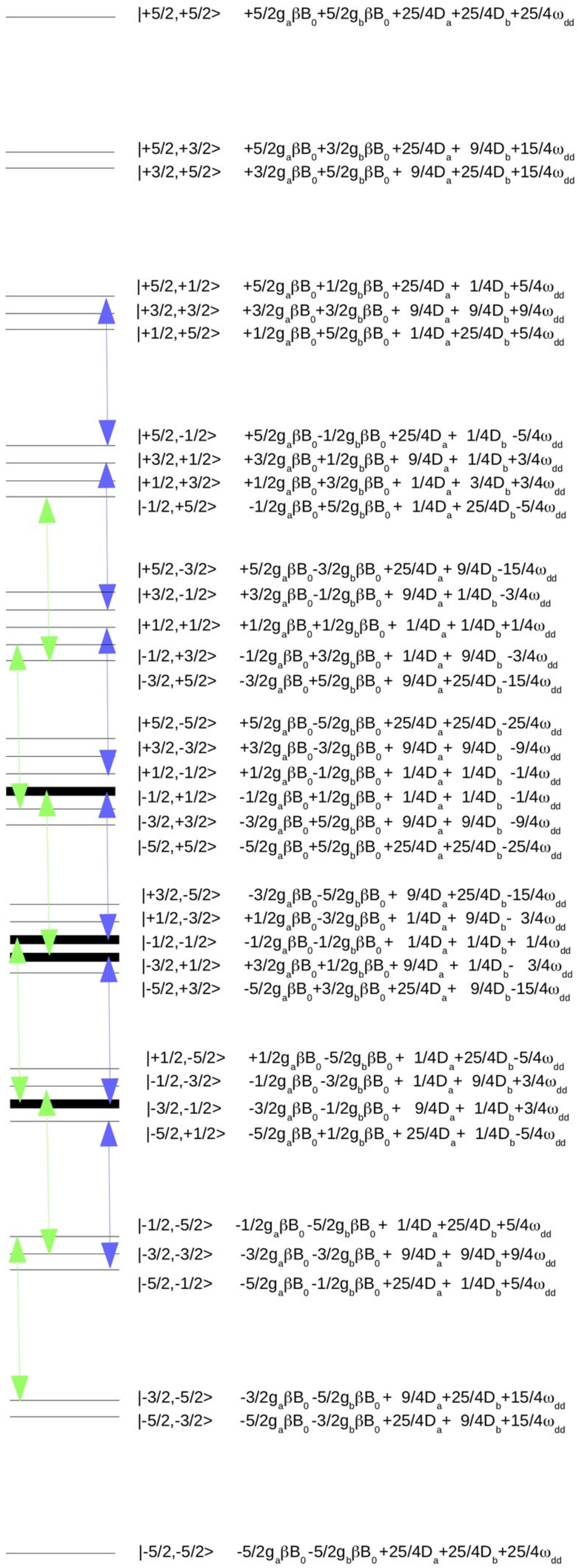

Fig. S4. The energy levels of a pair of S=5/2 spins, *a* and *b*, with g_a and g_b g-values, D_a and D_b zero-field interactions and a mutual dipolar coupling ω_{dd}. The pseudo–secular contribution to dipolar coupling and hyperfine coupling have been ignored. The blue transitions between $|m_{Sa},-1/2\rangle \leftrightarrow |m_{Sa},+1/2\rangle_0$ are the detected spins in Figure 6 and the red transitions between $|-3/2,m_{Sb}\rangle \leftrightarrow |-1/2,m_{Sb}\rangle$, the pumped spins. The energy levels marked by heavy lines indicate those that are common to both detected and pumped transitions.

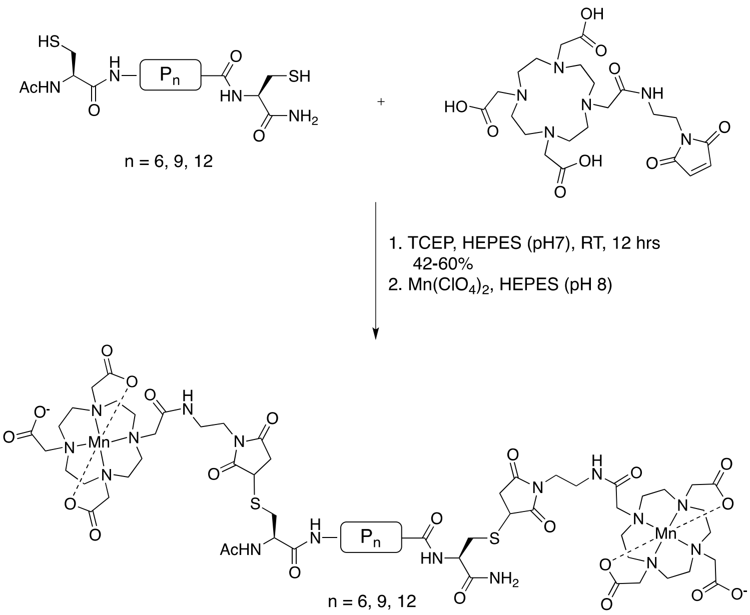

Fig. S5. Synthesis of $MnDOTA_2P_n$ by labelling of cysteines with DOTA-maleimide and *in-situ* metalation.

Circular dichroism measurements:

CD spectra were recorded on a Jasco J-815 spectropolarimeter using a 0.1 mm pathlength quartz cuvette. 200 μM solutions of each peptide were prepared in H_2O with 5% v/v glycerol, 100 mM phosphate buffer (pH 7.5) and 200 mM NaCl, and with or without 1.8 equivalents of $Mn(ClO_4)_2$•$6H_2O$. Measurements were conducted at 20 °C with a scanning speed of 20 nm/min. Reported spectra were averaged on 5 scans, smoothed, and corrected for buffer contributions.

The spectra show typical features of a PPII helix signature, with a small positive band around 228 nm and a large negative band around 206 nm. PPII helix contents were determined to be 92%, 87% and 85% for $DOTA_2P6$, $DOTA_2P9$ and $DOTA_2P12$. Analogous experiments on the Mn-metallated peptides gave similar spectra.

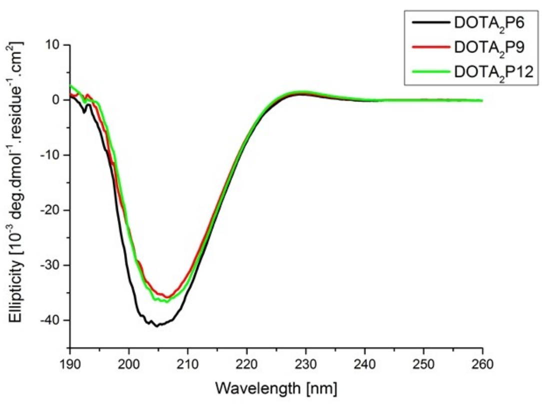

Fig. S6. CD spectra of $DOTA_2P\textit{n}$