Supplementary information

# The $^{13}$C Solid DNP Mechanisms with Perchlorotriphenylmethyl Radicals – the Role of $^{35,37}$Cl

F. Mentink Vigier[a], D. Shimon[a], V. Mugnaini[b,c], J. Veciana[b,c] A. Feintuch[a], M. Pons[d], S. Vega[a], D. Goldfarb[a].

[a]Chemical Physics Department Weizmann Institute of Science 76100 Rehovot, Israel, [b]Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Bellaterra, Spain, [c]Networking Research Center on Bioengineering, Biomaterials, and NanoMedicine (CIBER-BBN), Bellaterra, Spain, [d]Biomolecular NMR laboratory. Department of Organic Chemistry. University of Barcelona. Baldiri Reixac, 10-12 08028 Barcelona, Spain.

*corresponding author: daniella.goldfarb@weizmann.ac.il

## EPR spectrum fitting

The pulses used to collect the spectrum were π/2 and π of respective length of 100 and 200 ns and an interpulse delay τ = 550 ns. The experimental spectrum was simulated using Easyspin[1]

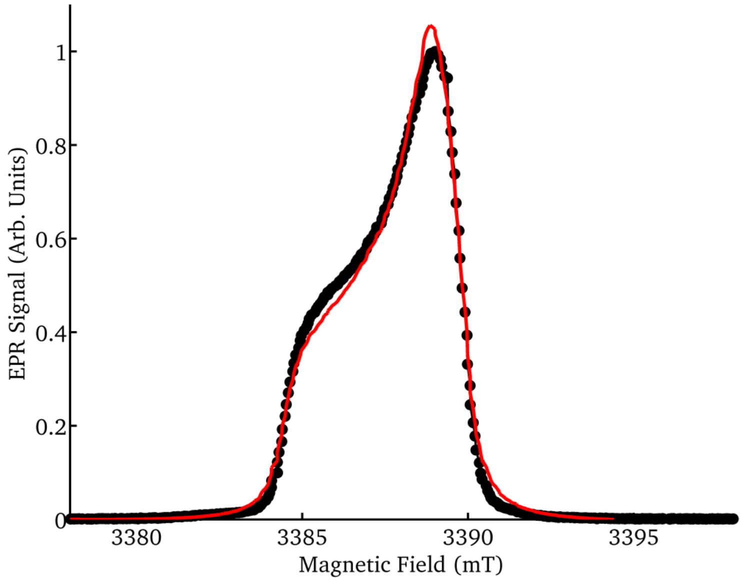

**Figure S1** : Experimental EDEPR spectrum (black) of 11 mM radical 1 recorded at 10 K, with a microwave frequency of 94.9 GHz and with π/2 and π pulses of of 100 and 200 ns respectively and an interpulse delay τ = 550 ns. Simulations (red) obtained with Easyspin Toolbox [1] and g = [2.00338, 2.00074, 2.0002], with an EPR linewidth as a combination of Gaussian and Lorentzian broadening {0.43 0.34} mT.

## Spin counting experiment

The concentrations of the radicals were determined by room temperature measurements using a dual cavity on a modified X-band Varian E12 spectrometer. This allowed recording the EPR spectrum of two samples under the same condition (Q factor, modulation amplitude, frequency, temperature...). In each sample tube we put the same volume of sample of the radical 1 DNP solution or the radical 2 DNP solution and a 1 mM OX63 solution in Glycerol/Water (50 % v/v). For each radical the EPR spectrum was recorded twice, first with the radical in the first cavity and the OX63 in the second, and a second time with the radical in the second cavity and the OX63 sample in the first. This was done in order to minimize the errors; for instance if the two cavity have slightly different field modulation amplitude, or if the sample is not exactly in the same position.

The EPR spectra were recorded with a microwave frequency of 9.537 GHz, 0.01 mT field modulation, 100 kHz frequency modulation, field range of 332.5 to 342.5 mT, 1024 points, and 50 s sweep duration. The EPR spectra were then doubly integrated, with a baseline correction before each integration procedure. The corresponding integral values are reported in Table S1.

**Table S1: Result of integration of the EPR spectra.**

| Experiment | Sample | Setup 1 | Setup 2 | Average | Concentration (mM) |
|---|---|---|---|---|---|
| Radical 1 | Radical 1 | 10.1 | 14.1 | 12.35 | 11.6 |
| | OX63 | 0.64 | 1.48 | 1.06 | |
| Radical 2 | radical 2 | 17.9 | 21.5 | 19.69 | 10.23 |
| | OX63 | 1.68 | 2.01 | 1.84 | |

Considering the uncertainty associated with the baseline subtraction (evaluated at about 10 %), the concentration of Radical 1 is 11 ± 1 mM and the concentration of Radical 2 is 10 ± 1 mM

## Temperature dependence of the DNP spectra

In this section we present the DNP spectra recorded at the various temperatures as well as their simulations using the method I.

## Radical 1 at 20 K, 30 K and 50 K:

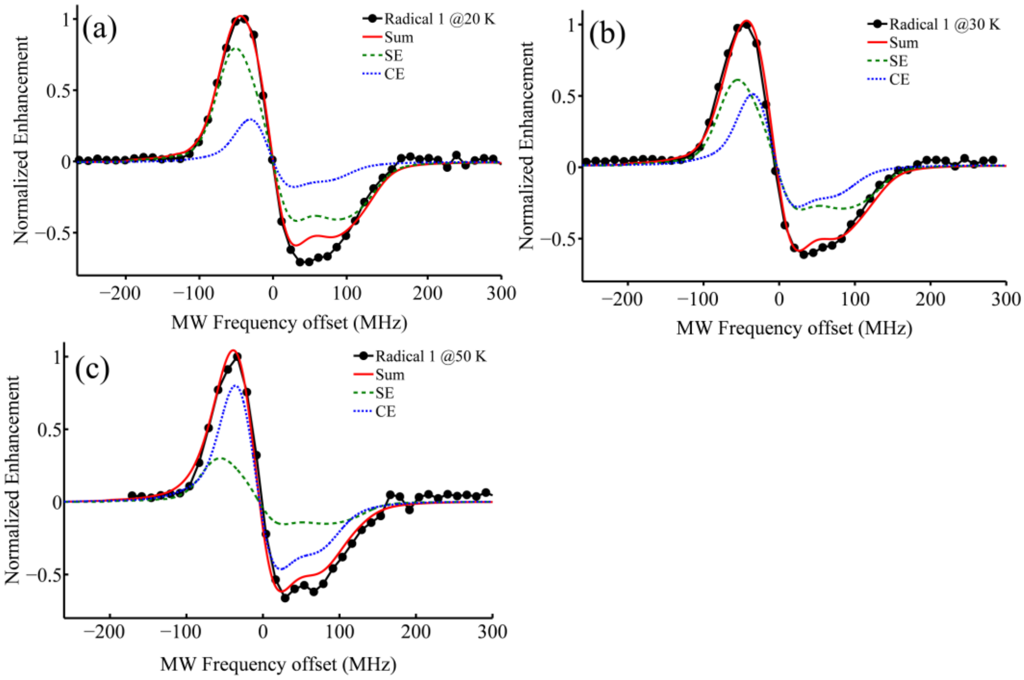

**Figure S2.** Temperature dependence of the DNP spectrum of Radical 1 obtained at 20 K (a), 30 K (b), 50 K (c) , as noted on the Figure. Black line with symbols corresponds to the experimental data, while the full red line corresponds to the simulations obtained with Method I. CE corresponds to the dotted blue line, SE is in dotted green and the combination is in red.

## Radical 2 at 10 K, 30 K and 50 K:

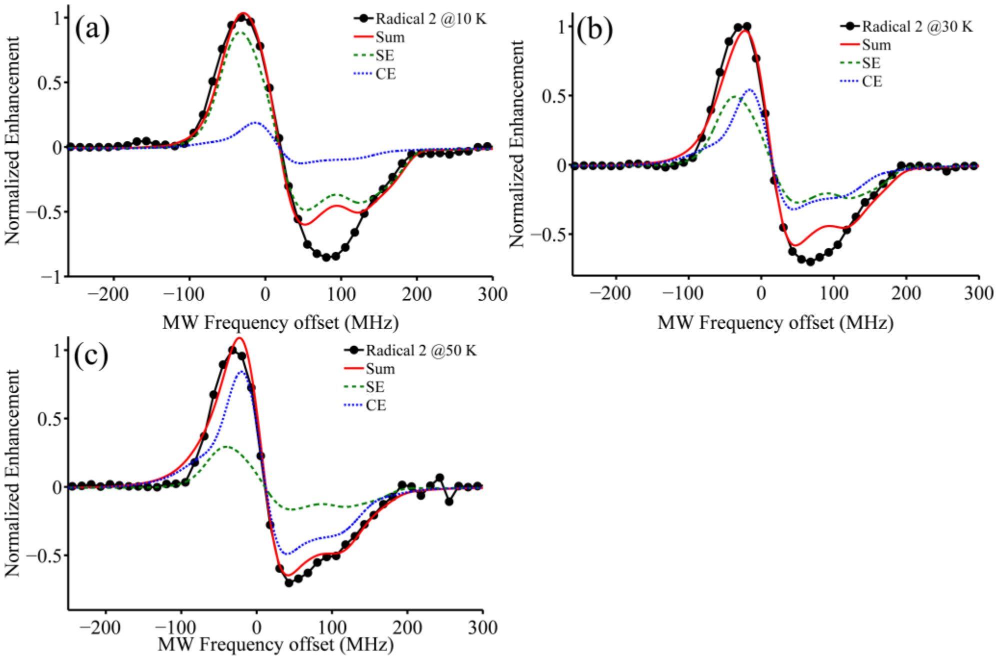

**Figure S3.** Temperature dependence of the DNP spectrum of Radical 2 obtained at 10 K (a), 30 K (b), 50 K (c), as noted on the Figure. Black line with symbols corresponds to the experimental data, while the full red line corresponds to the simulations obtained with Method I. CE corresponds to the dotted blue line, SE is in dotted green and the combination is in red.

**Additional simulations using method II:**

In this paragraph we detail the results of the simulations obtained with the simulation method II. In each plot the contribution of chlorine in *ortho* and *meta* positions are presented, as well as the effect of the isotope. Several simulations have been performed with different quadrupolar values. A scaling factor has been applied to the theoretical quadrupolar value published in [2] in order to address the effect of the quadrupolar coupling on the shape of the DNP spectrum. The Euler angles were not changed.

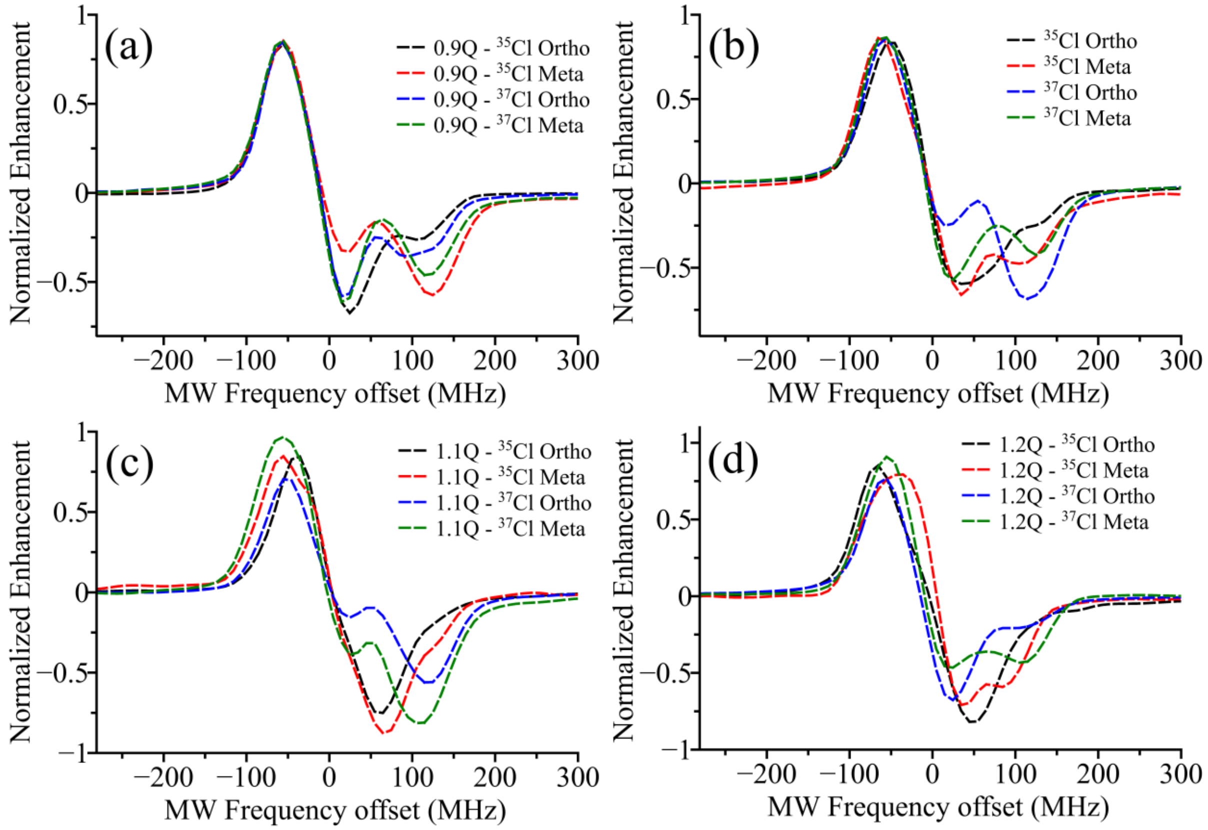

**Figure S4:** Calculated DNP spectra of Radical 1 obtained by Method II. In each plot is represented separately the contribution of $^{35}$Cl *ortho* (black line), $^{35}$Cl *meta* (red line), $^{37}$Cl *ortho* (blue line) and $^{37}$Cl *meta* (green line). Figure (a) (b), (c) and (d) correspond to different scaling value of the quadrupolar coupling with respect to the DFT calculated value[2] (a → factor 0.9, b → factor 1, c → factor 1.1, d → factor 1.2).

## References

[1] S. Stoll and A. Schweiger, "EasySpin, a comprehensive software package for spectral simulation and analysis in EPR.," *J. Magn. Reson.*, vol. 178, no. 1, pp. 42–55, 2006.

[2] D. Banerjee, J. C. Paniagua, V. Mugnaini, J. Veciana, A. Feintuch, M. Pons, and D. Goldfarb, "Correlation of the EPR properties of perchlorotriphenylmethyl radicals and their efficiency as DNP polarizers.," *Phys. Chem. Chem. Phys.*, vol. 13, no. 41, pp. 18626–37, 2011.