Supplemental Information for:

Oxygen-17 Dynamic Nuclear Polarisation Enhanced

Solid-State NMR Spectroscopy at 18.8 T

Nick J. Brownbill,¹ David Gajan,² Anne Lesage,² Lyndon Emsley³ and

Frédéric Blanc^{*1,4}

¹ Department of Chemistry, University of Liverpool,

Crown Street, Liverpool, L69 7ZD, United Kingdom;

² Centre de RMN à Très Hauts Champs, Institut de Sciences Analytiques,

Université de Lyon (CNRS/ENS Lyon/UCB Lyon 1), 69100 Villeurbanne, France;

³ Institut des Sciences et Ingénierie Chimiques,

Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland;

⁴ Stephenson Institute for Renewable Energy, University of Liverpool,

Crown Street, Liverpool, L69 7ZD, United Kingdom.

* To whom correspondence should be addressed (F.B.).

E-mail: frederic.blanc@liverpool.ac.uk.

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S1. Materials and Methods

Materials

 $Mg(OH)_2$ and ¹⁷O enriched $Mg(OH)_2$ ($Mg(^{17}OH)_2$) were prepared by reaction of MgO with H₂O and ¹⁷O-enriched H₂O, respectively, as described previously.¹

For DNP samples with a 1,1,2,2-tetrachloroethane (TCE) matrix, 40 μ l stock solution of 16 mM TEKPol² or 32 mM BPDA (Sigma Aldrich, complexed 1:1 with benzene) radicals in TCE (Sigma Aldrich, \geq 98 %) was added to a pre-weighed amount of powdered sample (typically 35 mg) until the powder appeared slightly saturated with TCE solution and was then mixed homogeneously. The samples were then packed directly in to the 3.2 mm sapphire rotor, along with some KBr (Sigma Aldrich) (~1 mg) at the bottom and closed with a poly-tetrafluoroethane (PTFE) plug and Vespel cap. When stated, samples were "freeze/thaw cycled"; this process involved the sample being inserted in to the probe at 115 K to freeze the matrix, and then ejected to thaw the solvent and was repeated 5 times.³

For DNP samples with an *o*-terphenyl matrix, OTP (Sigma Aldrich, 99 %) and OTP- d_{14} (Cambridge Isotope Laboratories, 98 %, 98 %D) were mixed in predefined ratios (100:0, 50:50, 90:10 and 95:5, respectively) and radical added to comprise 1.3 wt% of the mixture for TEKPol (corresponding to 17 mM) or 1.4 wt% for BDPA (corresponding to 34 mM). A typical OTP matrix contains a mixture of OTP/ OTP- d_{14} (520 mg) with BDPA (7.2 mg), or OTP/OTP- d_{14} (156 mg) with TEKPol (2mg). The radical/OTP mixtures were then dissolved in a minimum volume of CDCl₃ (Sigma Aldrich, 100 %, ≥99.96 %D) (typically 300 µl) to give stock radical solutions. The samples for the DNP experiments were prepared by typically adding 120 µl of stock radical solution a pre-weighed amount of Mg(OH)₂ or Mg(¹⁷OH)₂ sample (typically 35 mg) followed by an additional 120 µl of CDCl₃; the slurry was then thoroughly mixed before leaving the CDCl₃ to evaporate. The residual solid mixture was then finely ground and packed into a sapphire rotor with some KBr at the bottom (around 1 mg), sealed with a PTFE plug and Vespel cap. When stated, samples underwent a "freeze/melt process" modified from the literature;⁴ the packed sample was melted at 343 K in a water bath for 2 minutes, followed by flash freezing in liquid nitrogen for ten seconds. This process was repeated five times before the melt was rapidly inserted into the NMR probe precooled at 115 K. For non-DNP experiments, a pre-weighed amount of finely ground sample was packed in to a 3.2mm zirconia rotor (18.8 T) or a 4 mm zirconia rotor (9.4 T) and sealed with a Vespel cap.

NMR methods

All high field DNP solid-state NMR experiments were performed on a commercial 18.8 T Bruker Avance III DNP solid-state NMR spectrometer equipped with a 527 GHz gyrotron microwave system. NMR experiments were recorded with a 3.2 mm HXY triple-resonance MAS probe, with all cross effect experiments being recorded at $v_0(^1H) = 800.130$ MHz corresponding to the maximum enhancement ¹H position ε_H for TOTAPOL at $v_0(e^-) = 527$ GHz, with the X channel tuned to ¹³C at $v_0(^{13}C) = 201.193$ MHz and the Y channel tuned to ¹⁷O at $v_0(^{17}O) = 108.469$ MHz. All Overhauser effect experiments were recorded at $v_0(^1H) = 800.215$ MHz, corresponding to the maximum enhancement ¹H position ε_H for BDPA at $v_0(e^-)$ = 527 GHz, with the X channel tuned to ¹³C at $v_0(^{13}C) = 201.214$ MHz and the Y channel tuned to ¹⁷O at $v_0(^{17}O) = 108.481$ MHz. All experiments were performed under magic angle spinning (MAS) at $v_r = 12.5$ kHz. All DNP experiments were conducted at ~ 131 and 115 K with (μ w on) and without (μ w off) microwave, respectively.

All ¹H pulses and SPINAL-64 heteronuclear decoupling were performed at a radio-frequency (rf) field amplitude of 100 kHz.⁵ All ¹H-¹³C cross polarisation (CP) MAS experiments (Figure S1(b)) were obtained with a ¹³C rf field of 51 kHz, while the ¹H rf field amplitude was ramped to obtain maximum signal at a ¹H rf field of approximately 76 kHz. All ¹⁷O selective pulses were obtained with an rf field of 14 kHz for Hartmann – Hahn contact, while the ¹H rf field amplitude was ramped to obtain maximum signal at a ¹H rf field of approximately 76 kHz. All ¹⁷O selective pulses were obtained with a ¹⁷O rf field of 14 kHz for Hartmann – Hahn contact, while the ¹H rf field amplitude was ramped to obtain maximum signal at a ¹H rf field of approximately 76 kHz, at a contact time of 1 ms. All ¹H-¹⁷O PRESTO⁶ MAS experiments were obtained with symmetry-based R18₁⁷ ¹H recoupling⁷ optimised to a recoupling duration of 80 µs, corresponding to 1 rotor period. The PRESTO-II pulse program, consisting of two R18₁⁷ recoupling blocks on ¹H channel, with a $\pi/2$ pulse during these two blocks and a π pulse directly after on the ¹⁷O channel was used for all experiments (Figure S1(d)).

Standard 298 K solid state NMR measurements at 18.8 T data were conducted on the same spectrometer as stated above with a 3.2 mm HXY triple-resonance MAS probe, with all experiments being recorded at $v_0(^{1}H) = 800.130$ MHz, with the X channel tuned to ^{13}C at $v_0(^{13}C) = 201.193$ MHz and the Y channel tuned to ^{17}O at $v_0(^{17}O) = 108.469$ MHz. All other experimental parameters remained unchanged.

Standard solid state NMR measurements at 9.4 T were performed on a commercial 9.4 T Bruker Avance III HD solid-state NMR spectrometer fitted with a 4 mm HXY triple-resonance MAS probe (in double-resonance mode), tuned to $v_0(^1H) = 400.13$ MHz and X to $v_0(^{13}C) = 100.03$ MHz. Experiments were performed at 298 K under MAS at $v_r = 12.5$ kHz. All ¹H pulses and SPINAL-64 heteronuclear decoupling were performed at a radio-frequency (rf) field amplitude of 83 kHz.⁵ All ¹H-¹⁷O CP-Hahn echo MAS experiments were obtained with a ¹⁷O rf field of 17 kHz, while the ¹H rf field amplitude was ramped to obtain maximum signal at a ¹H rf field of approximately 70 kHz at a contact time of 2 ms. ¹⁷O selective pulses were obtained with an rf field of 10 kHz.

Recycle delays that produce optimal signal-to-noise per unit time were used (1.3 x build up).⁸ Chemical shifts were externally referenced at room temperature to water at 0.0 (for ¹⁷O) and 4.8 ppm (for ¹H), and to 29.45 ppm for the CH of adamantane (for ¹³C)⁹.

NMR data were processed with TopSpin 3.2 and MatLab. The signal enhancement factor was determined by comparing the intensity of the spectra with microwave irradiation turned on and turned off (unless explicitly stated to have been a comparison of total signal integrals).

Pulse Program Schemes



Figure S1: DNP pulse program depictions of (a) ¹H saturation recovery experiment, where τ_{vd} is a variable delay, to calculate $T_{1, RT}$ with μw off, or τ_{DNP} with μw on where τ_{DNP} is the DNP build up time and $T_{1, RT}$ is the ¹H relaxation time at room temperature. (b) Pre-saturated CP pulse program used, where $\tau = 1.3 \times T_{1, RT}$ with μw off, or 1.3 x τ_{DNP} with μw on. (c) Pre-saturated CP Hahn Echo pulse program used, where $\tau = 1.3 \times T_{1, RT}$ with μw off, or 1.3 x τ_{DNP} with μw on, and $\tau_r =$ one rotor period. (d) PRESTO-II using R18₁⁷ recoupling sequences, where τ_{R1} , τ_{R2} and T are all equal to an integer of rotor periods. In all experiments N = 100, with a 1 μ s delay between pulses.

S2. Overall DNP sensitivity enhancement factor $\Sigma^{^{\dagger}}$

The overall DNP sensitivity enhancement factor $\Sigma^{\pm 10-14}$ is a measure of the enhancement of DNP, taking in to consideration the differing conditions from standard solid state NMR at room temperature, and time differences between the two experiments. Σ^{\pm} was determined using the following experiments:

- (a) DNP NMR at 131 K, at 18.8 T with μ w at $v_0(e^-)$ = 527 GHz,
- (b) DNP NMR at 131 K, at 18.8 T without $\mu w,$
- (c) Room temperature NMR data, at either 18.8 T or 9.4 T,
- (d) NMR data at 131K, at 18.8T in the same matrix as (a) without radical added,

and calculated using the following equation:

$$\Sigma^{\dagger} = \left(\frac{\Lambda_{RT}}{\Lambda_{DNP}}\right) \left(\frac{T_{RT}}{T_{DNP}}\right) \left(\frac{S_{DNP} \ m_{RT}}{S_{RT} \ m_{DNP}}\right) \sqrt{\frac{NS_{RT} \ T_{1,RT}}{NS_{DNP} \ \tau_{DNP}}} \ \theta$$
Eq. S1

where Λ , S, m and NS are the full width of the line shape at half maximum (FWHM), the signal to noise ratios, the mass of sample used and the number of scans recorded, respectively. Subscript DNP and RT indicate data taken from experiments (a) and (c), respectively. $T_{1, RT}$ is the ¹H relaxation time at room temperature (spectrum (c)) and τ_{DNP} is the DNP build up time (spectrum (a)) and are determined through a saturation recovery experiment (Figure S1a). At low temperature, both values are often similar but not always as the signal build up during μ w irradiation is driven predominantly by DNP polarisation transfer rather than ¹H longitudinal relaxation. θ is the bleaching factor determined as:

$$\theta = \frac{1}{\epsilon} \left(\frac{S_{DNP} m_{LT}}{S_{LT} m_{DNP}} \right) \sqrt{\frac{NS_{LT}}{NS_{DNP}}}$$
Eq. S2

where ε is the DNP signal enhancement between (a) and (b), respectively, and S_{LT} , m_{LT} and NS_{LT} are the signal to noise ratio, the mass and the number of scans recorded in (d), respectively.

In this paper, two Σ^{\dagger} values were calculated: 18.8 T DNP vs 18.8 T room temperature data using 3.2 mm rotors, and 18.8 T DNP vs 9.4 T room temperature data using 4 mm rotors (the latter being perhaps the most commonly used solid state NMR hardware).

Effect	Cross Effect					Overhauser Effect			
Radical	1.3 wt% TEKPol				1.4 wt% BDPA				
Matrix	TCE	ОТР	OTP / OTP-d ₁₄ (50:50)	OTP / OTP-d ₁₄ (90:10)	OTP / OTP-d ₁₄ (95:5)	TCE	ΟΤΡ	OTP / OTP-d ₁₄ (90:10)	OTP / OTP-d ₁₄ (95:5)
3	14	6	12	11	12	5	2	17	3
Λ _{DNP} (Hz)	3700	3600	3600	3600	3600	3700	3600	3550	3700
S _{DNP} (a.u.)	860	182	120	337	534	291	48	173	30
m _{DNP} (mg)	0.016	0.019	0.011	0.019	0.021	0.018	0.003	0.006	0.004
NS_{DNP}	16	8	8	8	8	16	8	8	8
θ	0.8	0.8 ^c	0.8 ^c	0.8 ^c	0.8 ^c	0.8	0.8 ^c	0.8	0.8 ^c
$ au_{DNP}(s)$	11.2	2.6	7.9	8.3	9.8	30	19.2	31.2	27
Σ [†] 。 (18.8 T)	72	38	54	71	53	13	24	34	9
Σ [†] 。 (9.4 T)	400	211	300	399	294	74	132	189	51

Table S1. $\Sigma^{\dagger}_{O CP}$ Calculation Parameters Compared to 18.8 T^a and 9.4 T^b Room Temperature Spectra For Mg(¹⁷OH)₂

^a Λ_{RT} = 3500 Hz, S_{RT} = 34 a.u., m_{RT} = 20 mg, NS_{RT} = 128, τ_2 = 3 s, $T_{1,RT}$ = 0.7 s, T_{DNP} = 131 K (calculated through T_1 of ⁷⁹Br in KBr added to rotor¹⁵), T_{RT} = 298 K. ^b Λ_{RT} = 7100 Hz, S_{RT} = 56 a.u., m_{RT} = 70 mg, NS_{RT} = 80, τ_2 = 8.5 s, $T_{1,RT}$ = 6.5 s, T_{DNP} = 131 K. T_{RT} = 298 K.^c Value assumed from the other calculated data that are constant at θ = 0.8.

S3. Additional Figures



Figure S2. Σ_{OCP}^{\dagger} measured on the Mg(¹⁷OH)₂ sample and OTP matrix at the CE position (square) with 1.3 wt% TEKPol as the polarising agent and the OE position (triangle) with 1.4 wt% BDPA as the polarising agent with positions as a function of the OTP- d_{14} component of the OTP matrix compared with room temperature NMR spectra at (a) 18.8 T and (b) 9.4 T.



Figure S3. Comparison of ¹⁷O NMR line shapes of Mg(¹⁷OH)₂ impregnated with 16 mM TEKPol in TCE and obtained with (a) a CP Hahn echo and (b) a PRESTO⁶ Hahn echo sequence, plotted in absolute intensity, showing difference in line shape and intensity between CP and PRESTO polarisation transfer steps. Asterisks (*) denote spinning sidebands. See Figure 1 for all other information.



Figure S4. Comparison of ¹⁷O CP Hahn Echo (a, b) and ¹H one pulse (c, d) NMR spectra of $Mg(^{17}OH)_2$ with 16 mM TEKPol in TCE and recorded at $v_0(^{1}H) = 800.130$ MHz with μw at $v_0(e^{-}) = 527$ GHz (green) at T = 131 K and without μw (red) at T = 115 K. (b, d) are freshly prepared material after 5 freeze-thaw cycles and (a, c) are the same sample after 20 h at 253 K and 5 freeze-thaw cycles. Asterisks (*) denote spinning sidebands.



Figure S5. Comparison of ¹⁷O CP Hahn Echo (a) and ¹H one pulse (b) NMR spectra of Mg(¹⁷OH)₂ with 32 mM BDPA in TCE recorded at $v_0(^{1}H) = 800.215$ MHz with μ w at $v_0(e^{-}) = 527$ GHz (green) at T = 131 K and without μ w (red) at T = 115 K after 5 freeze-thaw cycles. Asterisks (*) denote spinning sidebands.



Figure S6. Comparison of ¹³C CP (a, b) and ¹H one pulse (c, d) NMR spectra of Mg(¹⁷OH)₂ with 1.4 wt%. BDPA in OTP/OTP- d_{14} (90:10) and recorded at $v_0(^{1}H) = 800.215$ MHz with μ w at $v_0(e^{-}) = 527$ GHz (green) at T = 131 K and without μ w (red) at T = 115 K. (b, d) are materials packed and run with no freeze/melt cycling (a, c) are the same sample after 5 freeze-melt cycles. Asterisks (*) denote spinning sidebands.

5. References for supplementary information

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