Surface-Selective Direct ¹⁷O DNP NMR of CeO₂ Nanoparticles: Supplementary Information

1 Experimental

All DNP NMR experiments were performed at the UK DNP MAS NMR Facility at the University of Nottingham on a 14.09 T AVANCE III HD spectrometer, corresponding to a ¹H Larmor frequency of 600 MHz, with a 395 GHz gyrotron microwave source and using a 3.2 mm double resonance widebore probe. A microwave source power of 7 W was used for direct DNP experiments on ¹⁷O while 12 W was used for indirect ¹H-¹⁷O DNP experiments because these were found to give the optimal balance between saturating the radical electron spin resonance (ESR) transitions and minimising sample heating. A radio-frequency strength of 55.6 kHz was used for the ¹⁷O direct DNP experiments and a radio-frequency strength of 96.2 kHz was used for the ${}^{1}\text{H} \pi/2$ in the indirect DNP experiments. Cross polarisation in the indirect DNP experiments was established with a lower power for ¹⁷O of 1 kHz and a ¹H power of 73 kHz; a Hahn-echo was appended to the sequence to suppress background distortions and the ¹⁷O NMR spectrum was recorded with ¹H decoupling using a sweptfrequency two-pulse phase modulation (SW-TPPM) sequence.^{1,2} Conventional ¹⁷O ssNMR spectra of CeO₂ nanoparticles were recorded on a 11.7 T AVANCE III spectrometer, corresponding to a ¹H Larmor frequency of 500 MHz, using either a 2.5 mm double resonance probe and a radio-frequency strength of 90.9 kHz or a 1.3 mm double resonance probe and a radio-frequency strength of 125 kHz. Conventional ¹⁷O ssNMR spectra of CeO₂ nanorods were recorded on a 7.05 T AVANCE III spectrometer, corresponding to a ¹H Larmor frequency of 300 MHz, using a 2.5 mm double resonance probe and a radio-frequency strength of 153 kHz. DNP and 1.3 mm ssNMR ¹⁷O spectra were referenced to room temperature bulk CeO₂ at 877 ppm and 2.5 mm ssNMR ¹⁷O spectra were referenced to H₂O at 0 ppm.

TEM images were attained using a JEOL JEM-3010 electron microscope fitted with a LaB6 filament operating at an accelerating voltage of 250 kV. TEM images were recorded using a Gatan Multiscan 794 1k \times 1k CCD camera. Image analysis was performed using the free ImageJ software.

2 NMR of CeO₂ nanoparticles without radicals

To determine the effect of the radicals on the spectrum, a ¹⁷O spectrum of the CeO₂ nanoparticles enriched at 350 °C and stored under inert atmosphere was recorded with conventional ssNMR, without the addition of radicals (Figure S1) and fitted (Figure S2). Firstly, the (sub-)surface resonances are much sharper without the addition of radicals, presumably due to BMS effects and the electron-nuclear dipolar coupling. Table S1 shows a comparison between the chemical shifts of the signals observed in the ¹⁷O NMR spectra of CeO₂ nanoparticles nanoparticles recorded with DNP at low temperature, at room temperature with conventional ssNMR, and the previous results of Wang *et al.*.³ There is little difference between the DNP and conventional ssNMR chemical shifts, showing the effect of temperature and radicals are minimal. The difference between the current results and the previous work of Wang *et al.* is therefore ascribed to minor differences between the syntheses of the nanoparticles.

To ascertain the degree of quenching by the radicals, the ratio of the intensities of the (sub-)surface sites was recorded with and without the addition of the radicals by fitting the spectra (Table S2). This shows that the enrichment of the three layers is approximately equal, giving an approximately equal

signal intensity in the conventional spectrum. Furthermore, as there is more signal relatively from the third layer under DNP, and we know from measurements of the DNP enhancement factor that the third layer enhances less than the second layer, the first two layers must be quenched more by the radicals.



Figure S1: Conventional ssNMR ¹⁷O spectrum (11.7 T) of ¹⁷O enriched CeO₂ nanoparticles recorded overnight at room temperature with a recycle delay of 5 s under 30 kHz MAS with 13904 scans. The signal due to the ZrO_2 can also be observed at 377 ppm. The sidebands are labelled with the numeral of the layer from which they arise, or with 'z' for the ZrO_2 signal.

Table S1: Comparison of the chemical shifts in ppm of the signals observed in the ¹⁷O NMR spectra of CeO_2 nanoparticles recorded with DNP at low temperature, the same sample recorded at room temperature with conventional ssNMR and without radicals, the previous results of Wang *et al.*, and a second sample of CeO_2 nanoparticles prepared in air (see Section 4).

	Bulk	1^{st}	2 nd	3 rd
95 K (DNP)	875	1055	893	843
298 K (this work)	876	1056	896	846
298 K (Ref 3)	877	1040	920	825
95 K (DNP –	875	a	893	847
prepared in air)				

^a Not observed for this sample.

Table S2: Fitted intensity ratios relative to the first layer for the ¹⁷O (sub-)surface signals in CeO₂ nanoparticles recorded with conventional ssNMR and DNP, as determined by spectra which are quantitative with respect to the (sub-)surface sites with recycle delays of 5 s and 375 s respectively. N.B. the ratios are not comparable between the experiments, but are normalised with respect to the first layer.

	1 st Layer		2 nd Layer		3 rd Layer
Conventional ssNMR	1	:	1.08	:	1.12
DNP	1	:	2.41	:	3.31



Figure S2: Exploded fit of the conventional ssNMR ¹⁷O spectrum (11.7 T) of ¹⁷O enriched CeO₂ nanoparticles. The two broad peaks observed could be either due to near-bulk sites, paramagnetic Ce^{3+} centres or artefacts of the fit.

3 Origin of spinning sidebands

To determine the origin of the spinning sidebands of the (sub-)surface sites in the ¹⁷O DNP NMR spectra of CeO₂ nanoparticles, spectra were simulated with different NMR parameters. First, the spectrum was calculated using the DFT calculated parameters from Wang *et al.*, for which the sidebands are dominated by the quadrupolar satellite transitions (Figure S3a, parameters in Table S3); although the simulated spectra to exhibit sidebands, the intensity is clearly insufficient, especially for sidebands further from the isotropic resonance. To determine whether the sideband intensity could be explained by dipolar interaction with the paramagnetic radicals, the quadrupolar parameters were fixed and the chemical shift anisotropy (CSA) parameters varied (Figure S3b, parameters in Table S3), because the dipolar interaction gives rise to an anisotropy which is equivalent to a CSA. The Euler angles relating the quadrupolar coupling and CSA tensors were also fitted, but α and γ did not have any effect on the simulated spectrum so were fixed at 0°. Fitting the CSA also could not correctly reproduce the sideband manifold, supporting the assertion that bulk magnetic susceptibility (BMS) effects are distorting the spectrum.



Figure S3: Simulated ¹⁷O NMR spectra for CeO₂ nanoparticles using a) the DFT calculated parameters and b) fitting the CSA.

Table S3: The quadrupolar parameters determined from DFT calculations³ and the fitted CSA parameters and β Euler angle for the (sub-)surface oxygen sites of the ¹⁷O spectrum of CeO₂ nanoparticles recorded with DNP.

	DFT Calculated		Fitted		
	C _Q /kHz	$\eta_{\rm Q}$	$\Delta_{\rm CSA}$ /ppm	η_{CSA}	β /°
1 st	135	0.004	504	0.00	15
2^{nd}	107	0.002	-385	0.69	90
3 rd	117	0.009	-411	0.51	0

Furthermore, it is possible to estimate how close the radicals would have to be to induce an anisotropy of the fitted magnitude. The energy of the dipolar interaction is given by:⁴

$$E = \frac{\mu_0}{4\pi} \overline{\mu_e} \, \mathbf{D} \, \mu_N$$

where μ_0 is the permeability of free space, $\overline{\mu_e}$ is the time average magnetic moment of the radical, **D** is the dipolar interaction matrix and μ_N is the magnetic moment of the nucleus. Substituting in for $\overline{\mu_e}$ and μ_N , assuming the g-tensor is isotropic

$$E = \frac{\mu_0}{4\pi} \ \mu_B^2 g^2 \frac{S(S+1)}{3kT} B_0 \ \mathbf{D} \ \gamma_N I_z \hbar$$

where μ_B is Bohr magneton, g the g-factor the electron, S the spin of the electron, k the Boltzmann constant, T the temperature, B_0 the applied field, γ_N the gyromagnetic ratio for the nucleus and I_z the

nuclear spin. The assumption that the g-tensor is isotropic is not valid for biradicals due to the electron-electron interactions, but will suffice for this approximation. The chemical shift introduced by this interaction for $\Delta I_z = 1$ is then, in ppm,

$$\delta = \frac{\Delta E}{E} \times 10^{6} = \frac{\frac{\mu_{0}}{4\pi} \ \mu_{B}^{2} g^{2} \frac{S(S+1)}{3kT} \ B_{0} \ \mathbf{D} \ \gamma_{N} \Delta I_{z} \hbar}{\hbar \gamma_{N} B_{0}} \times 10^{6}$$
$$= \frac{\mu_{0}}{4\pi} \ \mu_{B}^{2} g^{2} \frac{S(S+1)}{3kT} \ \mathbf{D} \times 10^{6}$$

The anisotropy of the dipolar tensor is given by $2/r^3$, where r is the separation of the nucleus and electron.⁵ Assuming the interaction is dominated by one of the electrons of the biradical then S = 1/2, and for the DNP experiments T = 100 K, an anisotropy of 500 ppm as predicted by the fitting would require a separation of r = 3.0 Å. This is significantly closer than would be expected, again supporting the assertion that BMS effects are significant.

4 DNP of CeO₂ nanoparticles handled under air

In a separate experiment the same batch of CeO₂ nanoparticles (Sigma Aldrich) was enriched in a higher pressure of ${}^{17}O_2$ at 300 °C for 24 hours but wetted with TEKPol/TCE and packed under ambient conditions. Figure S4 shows the ${}^{17}O$ NMR spectra recorded at 12.5 kHz MAS with and without microwave irradiation, with 8 scans and a recycle delay of 60 s, with the chemical shifts recorded in Table S1. Again the second and third (sub-)surface layers can be seen with a large enhancement, but in this case the first layer cannot be seen, even when the MAS frequency was varied to move the spinning sidebands; this is ascribed to loss of the enrichment of the first layer when exposed to air (see section 5). The bulk signal here is much greater than for the other sample (see main text), by a factor of ~15; this is ascribed to the higher pressure of ${}^{17}O_2$ for the enrichment.



Figure S4: ¹⁷O NMR (14.1 T) spectra of ¹⁷O enriched CeO₂ nanoparticles mixed with the TEKPol radical in tetrachloroethane (TCE) under ambient conditions, with and without microwave irradiation, performed at 12.5 kHz MAS using a presaturated Hahn echo experiment and a recycle delay of 60 s.

For this sample a long microwave off experiment was performed in order to determine the DNP signal enhancement (480 scans, Figure S5), although technical difficulties necessitated it to be recorded at room temperature. Nevertheless, accounting for the Boltzmann temperature factor, this allowed an estimate to be calculated of the DNP enhancement for each environment ($\varepsilon_{ON/OFF}$, Table S4). These confirm the surface selective enhancement, with the second layer having a greater enhancement than the third layer, as expected because the polarisation must transfer further. The bulk site exhibits only a very minor enhancement as it is dominated by atoms far from the surface which are not hyperpolarised. In comparison, the enhancement of the bulk signal for the other sample prepared under an inert atmosphere (see main text) could be calculated as $\varepsilon_{ON/OFF} \approx 7.7$; this may suggest that due to the lower pressure of ${}^{17}O_2$, the enrichment of this sample was not uniform so that the bulk signal actually corresponds to environments nearer the surface which therefore show a greater DNP enhancement. The signals due to the (sub-)surface sites also appear sharper than under DNP conditions; the radicals are still present and this suggests that it is the low temperature (~95 K) which freezes out motional narrowing that gives rise to broader signals under DNP conditions.



Figure S5: Overnight, microwave off, room temperature ¹⁷O NMR spectrum of enriched CeO₂ nanoparticles mixed with the TEKPol radical in tetrachloroethane under ambient conditions, performed at 12.5 kHz MAS using a presaturated Hahn echo experiment and a recycle delay of 60 s. The signal due to the bulk has been truncated to emphasise the signals which can now be distinguished from the second and third layers.

Table S4: Chemical shifts, DNP enhancements and fitted DNP build-up time constants for the three environments observed in 17 O enriched CeO₂ nanoparticles prepared under ambient conditions.

Assignment	Shift /ppm	ε _{on/off}	$T_{\rm DNP}$ /s
2 nd Layer	893	56	97.9
Bulk	875	1.3	586
3 rd Layer	846	29	134

Saturation recovery experiments were also performed on this sample (Figure S6) and the intensities fitted to a stretched exponential function to find the DNP build-up time constants (Table S4). Again the deeper third layer has a longer build-up time than the second layer, but the time constants are slightly longer in this case. This may be due to the greater enrichment, because each radical then has to hyperpolarise more nuclei; the polarisation of the electron is split between more nuclei and each therefore takes longer to hyperpolarise. In contrast, the build-up time of the bulk site is significantly shorter than for the other sample (for which $T_{DNP} > 1600$ s); this may also be explained by the greater level of enrichment of this sample, because the hyperpolarisation must travel into the bulk *via* spin

diffusion, which is highly dependent on the concentration of the spin active nucleus and will be considerably faster for a higher level of enrichment.



Figure S6: The ¹⁷O DNP build up curves for ¹⁷O enriched CeO₂ nanoparticles packed in air and the fitted stretched exponential functions. The intensity is calculated by deconvoluting the isotropic peaks.

5 Effect of exposure to air

To test whether the lack of signal due to the first layer in the sample prepared under ambient conditions was due to loss of enrichment *via* exchange with air, the ¹⁷O NMR spectrum of ¹⁷O enriched CeO₂ nanoparticles was recorded without any exposure to air and after exposure to air for 1 hr and overnight (Figure S7). There is a clear loss in signal from the first layer, confirming the need to prepare samples under inert atmosphere. A short recycle delay of 0.2 s was necessary to obtain sufficient signal from the (sub-)surface sites, which relax significantly faster than the bulk; this is why the bulk signal is not observed.



Figure S7: ¹⁷O NMR (11.7 T) spectra of ¹⁷O enriched CeO₂ nanoparticles without any exposure to air and after exposure to air for 1 hr and overnight, showing the loss of signal from the first layer, recorded at 60 kHz MAS with a recycle delay of 0.2 s.

6 Analysis of the DNP build-up curves

To elucidate the build-up curves of the different environments from the saturation recovery experiment, each spectrum was deconvoluted using dmfit.⁶ The exploded fit for the final spectrum with the longest build-up time (1581 s) is shown in Figure S8 with the parameters for the stretched exponential fits recorded in Table S4. As well as the signals due to the bulk and the first three layers, fitting revealed a broad component at 872 ppm; this may be a deeper sub-surface or near-bulk layer with an average shift similar to that of the bulk but still a broader signal due to the reduction of symmetry near the surface, or it could simply be an artefact of the fit. Furthermore, at very long build-up times, two sharp signals can be observed at 858 ppm and 901 ppm respectively, i.e. on the higher frequency shoulder of the second and third layer signals respectively. The direct DNP build-up time constants for these signals cannot be determined accurately as the saturation recovery experiment did not extend to long enough build-up times, however it is clear from the build-up curves (Figure S9) that the time constants are significantly longer than 1600 s. The nature of these peaks is the subject of future work but one possible explanation is ¹⁷O environments with nearby paramagnetic Ce³⁺ centres in different relative positions which introduce a hyperfine shift.^{3,7}

All the parameters which define the stretched exponentials used to fit all the different signals deconvoluted from the ¹⁷O direct DNP build-up curves are shown in Table S5. Fitting the signals with slow build-up does not give meaningful parameters as insufficient data is available.



Figure S8: The exploded fit for the ¹⁷O direct DNP NMR spectrum of ¹⁷O enriched CeO₂ nanoparticles particles packed under inert atmosphere recorded with a 1581 s recycle delay.



Figure S9: The ¹⁷O saturation recovery build-up curves for the two sharp signals observed for long build-up times in CeO₂ nanoparticles and the fitted stretched exponentials.

Table S5: All the fitting parameters for the stretched exponentials used to fit all the deconvoluted signals in the ¹⁷O saturation recovery experiments performed on CeO_2 nanoparticles. Errors reflect one standard deviation in fitted parameters as determined through total least squares fitting.

	Shift / ppm	$T_{\rm DNP}$ / s	I_0 / arb. units	β
Bulk	875	> 1600		
1 st layer	1055	67 ± 6	355 ± 7	0.72 ± 0.05
2 nd layer	893	62 ± 2	806 ± 7	0.82 ± 0.03
3 rd layer	843	85 ± 3	1130 ± 12	0.82 ± 0.03
Near-bulk	872	66 ± 4	1205 ± 15	0.87 ± 0.04
''Sharp #1''	858	> 1600	—	—
''Sharp #2''	901	> 1600		

7 Field sweep

The DNP enhancement in this case is due to the cross effect which depends on the matching of the microwave frequency, the electron spin resonance (ESR) spectrum of the radical and the NMR frequency of the nucleus in question.⁸ In practice the microwave frequency is fixed and as the latter two are dependent on the magnetic field of the NMR spectrometer, the magnetic field can be varied to some degree to optimise the DNP enhancement which yields a characteristic field profile of the enhancement (see e.g. figure 3 in reference ⁸).

A field sweep experiment was performed for the CeO₂ sample prepared under ambient conditions (Figure S10) and shows the positive lobe of the TEKPol field profile. All other experiments were performed at $v_0(^{17}O) = 81.44$ MHz and it can be seen that the observed enhancements were near optimal. The surface selectivity of direct DNP can also be seen in the field profiles in that the profile from the bulk signal is flatter than for the sub-surface signals; this is because there is less enhancement of the bulk signal under DNP conditions as the nuclei are far from the radicals, but there are more bulk sites so without DNP, i.e. when the field is incorrectly set, there is more bulk signal.



Figure S10: A field sweep experiment showing the fitted intensities of the three environments in the ¹⁷O enriched CeO₂ nanoparticle/TEKPol/TCE sample packed under ambient conditions as a function of the magnetic field, and hence the ¹⁷O Larmor frequency.

8 DNP of CeO₂ Nanorods

To assess whether the chemical shifts of the (sub-)surface sites are sensitive to sample preparation conditions and morphology, CeO₂ nanorods were investigated. The nanorods were synthesised as in reference 3 and enriched with ¹⁷O₂ at 350 °C; TEM characterisation (Figure S11) showed an average thickness of 9.1 ± 0.6 nm with lengths of 50 - 100 nm. The nanorods were stored, mixed with TEKPol/TCE and packed all under inert atmosphere. The ¹⁷O NMR spectra with and without microwave irradiation are shown in Figure S12 and although surface selectivity is again observed, there are clear differences between the nanorods and the CeO₂ nanoparticles (see Figure 2a, main text). The signal at 893 ppm for the nanoparticles, ascribed to the second layer, is not observed; however, studying the sideband manifold shows that there must be an additional signal under the bulk signal which gives rise to a series of spinning sidebands (to higher frequency from the sideband manifold of the 850 ppm resonance), because the bulk signal arises from cubic local environments and is too sharp to produce these sidebands. Deconvolution of the spectrum (Figure S13) reveals this signal at 893 ppm, the environment at 850 ppm ascribed to the third layer in the nanoparticles, and the first layer at 1049 ppm, although the intensity of this last peak is very small. The build-up curves were also recorded for this sample (Figure S9) and the fitted build-up constants are given in Table S6, as well as all the fitted chemical shifts, the enhancement factors ($\epsilon_{ON/OFF}$), and a comparison of these values with those of the nanoparticles.

The room temperature conventional ssNMR spectrum of the nanorods (Figure S15) is similar to that of the nanoparticles and can be deconvoluted to show signals from the first, second and third layers as well as a sharp bulk signal and the broad resonance. The latter is assigned, at least in part, to the nearbulk signal (*i.e.* oxygen atoms in the 4th, 5th and deeper layers). The intensity of the second layer signal is, however, approximately half that of the third layer. This result should be contrasted to the prior study of ceria nanorods where this signal was approximately the same intensity as the signal assigned to the third layer;³ this may be due to aging of the sample or differences in the enrichment procedure.



Figure S11: TEM images of CeO_2 nanorods at a) 100,000x and b) 500,000x magnification. Identification of the (111) fringes indicates that the rods are dominated by (111) facets along the long axis.



Figure S12: ¹⁷O NMR (14.1 T) spectra of ¹⁷O enriched CeO_2 nanorods mixed with the TEKPol radical in tetrachloroethane, with and without microwave irradiation, performed at 10 kHz MAS using a presaturated Hahn echo experiment and a recycle delay of 60 s.



Figure S13: The exploded fit for the ¹⁷O direct DNP NMR spectrum of ¹⁷O enriched CeO₂ nanorods recorded with a 60 s recycle delay.



Figure S14: The ¹⁷O DNP build up curves for ¹⁷O enriched CeO_2 nanorods and the fitted stretched exponential functions. The intensity is calculated by deconvoluting the isotropic peaks.

Table S6: Comparison of the chemical shifts, build-up time constants (T_{DNP}) and enhancement factors ($\epsilon_{\text{ON/OFF}}$) for the different environments in the ¹⁷O direct DNP NMR spectra of CeO₂ nanorods and nanoparticles, as well as the conventional ssNMR room temperature ¹⁷O chemical shifts.

		Bulk	1^{st}	2 nd	3 rd	Near-bulk
Nanorods	Shift /ppm (DNP)	874	1049	Ť	850	873
	Shift /ppm (298 K)	877	1043	893	847	878
	$T_{\rm DNP}$ /s	198	55	ţ	64	91
	ε _{on/off}	2.9	*	Ť	22	10
Nanoparticles	Shift /ppm (DNP)	875	1055	893	843	872
	Shift /ppm (298 K)	876	1056	896	846	878
	$T_{\rm DNP}$ /s	~2100	67	62	85	66
	ε _{on/off}	1.3	‡	56	29	§

* Insufficient signal in the off spectrum to calculate $\epsilon_{\text{ON/OFF}}$

† The second layer could not be observed in the direct DNP spectra of the nanorods

 \ddagger The sample used to calculate $\epsilon_{ON/OFF}$ was stored under air, so there is no signal from the 1st layer.

§ The near-bulk signal could not be observed in the microwave off spectrum

The cause of the loss of the 893 ppm signal in the DNP experiment is unclear. One possible explanation is the signal at 873 ppm is due to the second layer, the resonance shifting by approximately 20 ppm between room and low temperature. However, T_{DNP} for this signal is greater than for the signal at 850 ppm and $\varepsilon_{\text{ON/OFF}}$ is lower, both of these factors suggesting that the signal at 873 ppm arises from a layer deeper than that which causes the signal at 850 ppm. It is likely that the presence of other facets complicates the analysis. For example, the DFT calculations of Wang *et. al.* indicate that for other facets such as (110), the assignments are reversed with the signal at 873 ppm being due to the third layer and that at 850 ppm being due to the second layer; the signal due to the first layer remains at approximately the same chemical shift (see reference 3, supplementary information). The TEM analysis shows the nanorods to be dominated by (111) facets, but other facets are clearly present which we have not analysed in any detail. However, this does not explain why the 893 ppm resonance is only seen at room temperature.

Of note, spectra of CeO₂ nanoparticles that were studied following reduction under H₂ to create oxygen vacancies and Ce³⁺ were dominated by a ¹⁷O resonance at 870 ppm, shifted by 7 ppm from the signal due to bulk CeO₂.³ A weaker resonance was observed at 845 ppm. Thus the broad "near-bulk" and the 847 ppm resonances observed here may similarly indicate the presence of Ce³⁺ and oxygen vacancies. One possible explanation for the absence of the second layer (893 ppm) signal is that the oxygen vacancies are preferentially located in the second sub-surface layer, as suggested by DFT calculations;⁹ in addition, the presence of paramagnetic Ce³⁺ may result in additional relaxation phenomena at low temperatures and loss of signal of the 2nd (and albeit to a lesser extent, the 1st layer) oxygen atoms. This hypothesis requires further testing by studying samples prepared in more reducing conditions. It is clear that a wider range of sample morphologies needs to be investigated to obtain more detailed correlations between chemical shift and local environments; relaxation effects due to paramagnetic ions also require further investigation as a function of temperature.



Figure S15: The conventional ssNMR ¹⁷O spectrum (7.05 T) of ¹⁷O enriched CeO₂ nanorods recorded at room temperature with a recycle delay of 0.1 s under 30 kHz MAS and the fitted deconvolution.

References

- 1 R. S. Thakur, N. D. Kurur and P. K. Madhu, Chem. Phys. Lett., 2006, 426, 459–463.
- 2 S. Paul, N. D. Kurur and P. K. Madhu, J. Magn. Reson., 2010, 207, 140–148.
- M. Wang, X.-P. Wu, S. Zheng, L. Zhao, L. Li, L. Shen, Y. Gao, N. Xue, X. Guo, W. Huang, Z. Gan, F. Blanc, Z. Yu, X. Ke, W. Ding, X.-Q. Gong, C. P. Grey and L. Peng, *Sci. Adv.*, 2015, **1**.
- 4 C. P. Grey and N. Dupré, *Chem. Rev.*, 2004, **104**, 4493–4512.
- 5 M. J. Duer, Introduction to Solid-State NMR Spectroscopy, Blackwell Publishing Ltd, 2004.
- 6 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70–76.
- 7 S. Tsunekawa, R. Sivamohan, S. Ito, A. Kasuya and T. Fukuda, *Nanostructured Mater.*, 1999, **11**, 141–147.
- 8 Q. Z. Ni, E. Daviso, T. V Can, E. Markhasin, S. K. Jawla, T. M. Swager, R. J. Temkin, J. Herzfeld and R. G. Griffin, *Acc. Chem. Res.*, 2013, **46**, 1933–1941.
- 9 Z. Yang, T. K. Woo, M. Baudin and K. Hermansson, J. Chem. Phys., 2004, 120, 7741–7749.