Electronic Supplementary Material (ESI) for Chemical Communications

Dynamic Nuclear Polarization of Quadrupolar Nuclei Using Cross Polarization from Protons: Surface-Enhanced Aluminum-27 NMR.

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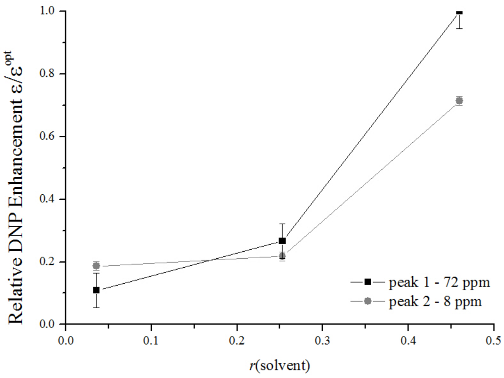
Electronic Supplementary Information

a)



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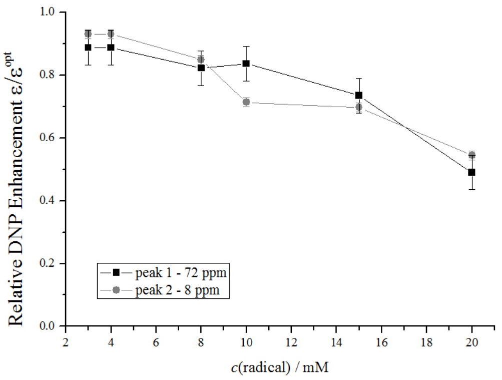

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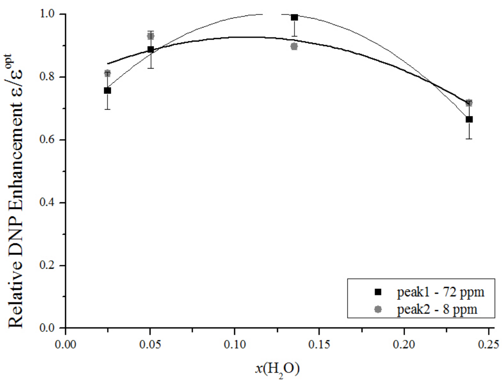

Fig. S1: Relative DNP enhancements $\varepsilon/\varepsilon^{opt}$ for ^{27}Al in γ-alumina after cross-polarization from protons to ^{27}Al as a function of (Top) the ratio r(solvent) between the mass of doped solvent and the total mass of the sample, (Middle) the TOTAPOL concentration c (mM) and (Bottom) the mole fraction x of H_2O in the H_2O/D_2O mixture. Best conditions are $r = 0.45$, $c = 4$ mM and $x = 0.10$.

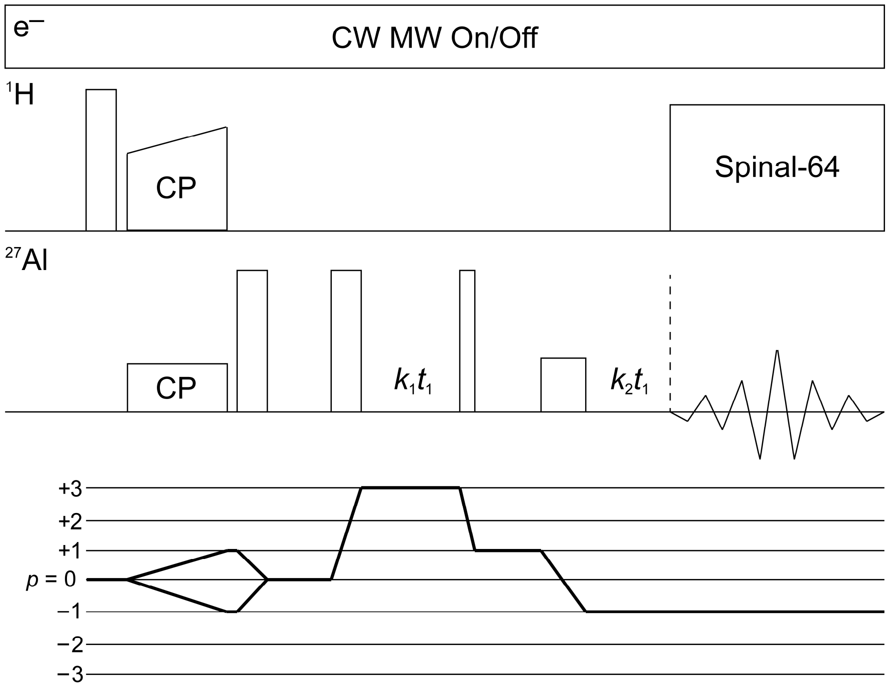

Figure S2. Pulse sequence used for DNP-enhanced cross-polarization shifted-echo triple-quantum magic-angle spinning experiments (CP-TQ-MQMAS) with coherence transfer pathways for ^{27}Al. A 192-step phase cycle allows one to select the desired $p = +3 \rightarrow +1 \rightarrow -1$ pathway and to eliminate signals which do not arise from CP. The evolution time t_1 is split between the +3 and −1 coherences according to the ratios $k_1 = 12/31$ and $k_2 = 19/31$, respectively. Continuous wave (CW) MW irradiation was 'on' or 'off' during the entire pulse sequence. Pulse programs and phase cycles are available upon request.

Experimental

The *rf* field amplitudes for cross-polarization were $\omega_1(^1\mathrm{H})/(2\pi) \approx 60$ kHz and $\omega_1(^{27}\mathrm{Al})/(2\pi) \approx 15$ kHz for ^{27}Al and ^{1}H, respectively, and the spinning frequency was $\nu_{rot} = 10$ kHz for all experiments. Thin-walled zirconia rotors of 3.2 mm outer diameter were utilized to avoid ^{27}Al background signals from sapphire rotors.

During all measurements the temperature was held stable and controlled with KBr using our recently developed method[1]. The enhancement ε was defined as the ratio of signals obtained in two identical experiments with and without microwave irradiation. In our hands, the optimum conditions gave $\varepsilon \approx 20$. Under MW irradiation (after saturation of the proton magnetization by a train of pulses) the characteristic build-up time was measured to be $T_{DNP} \approx 5$ s.

The sample preparation was carried out in an 80 g agate mortar on a Mettler Toledo analytical balance with a 200 g range and 0.1 mg resolution. For a generic sample, *ca.* 80 mg of γ-alumina was mixed with *ca.* 100 µl of a D_2O/H_2O mixture with a mole fraction $x = 0.2$ of H_2O and a TOTAPOL concentration $c = 5$ mM. After soaking for 1 minute, the mixture should be a smooth paste. Then the surface of this paste is covered with *ca.* 20 mg of dry γ-alumina to obtain a solid paste, which is then finely ground with an agate pestle. No solvent should be released while crushing.

[1] P. Miéville, V. Vitzthum, M. A. Caporini, S. Jannin, S. Gerber-Lemairea, G. Bodenhausena, *Magn. Reson. Chem.*, 2011, online, DOI 10.1002/mrc.2811