Supporting information

Multinuclear solid-state NMR study: a powerful tool for understanding structure of ZnO hybrid nanoparticles.

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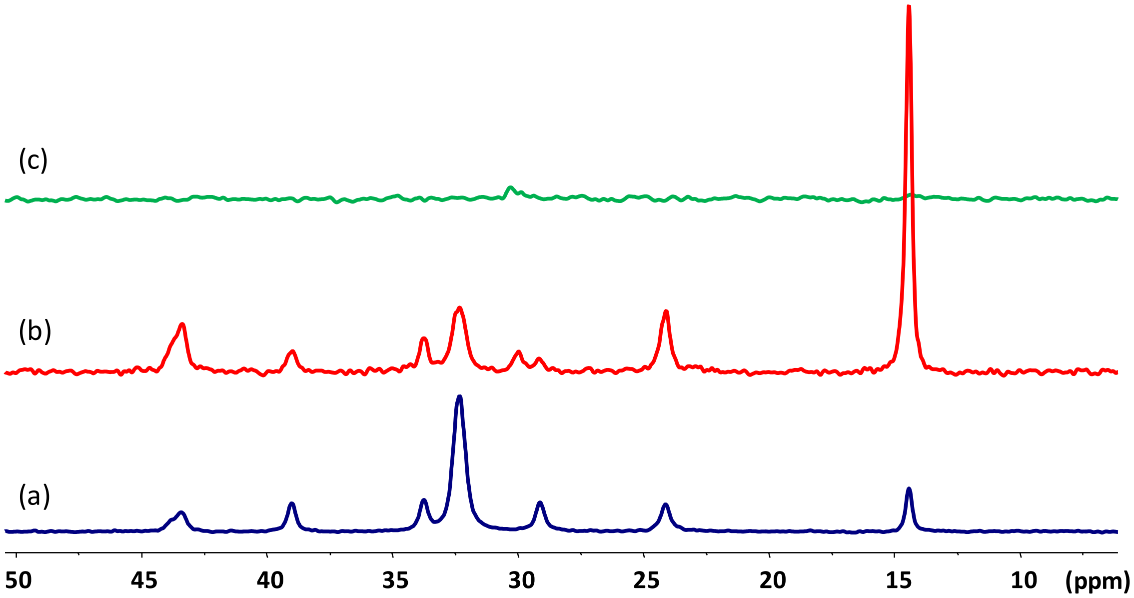
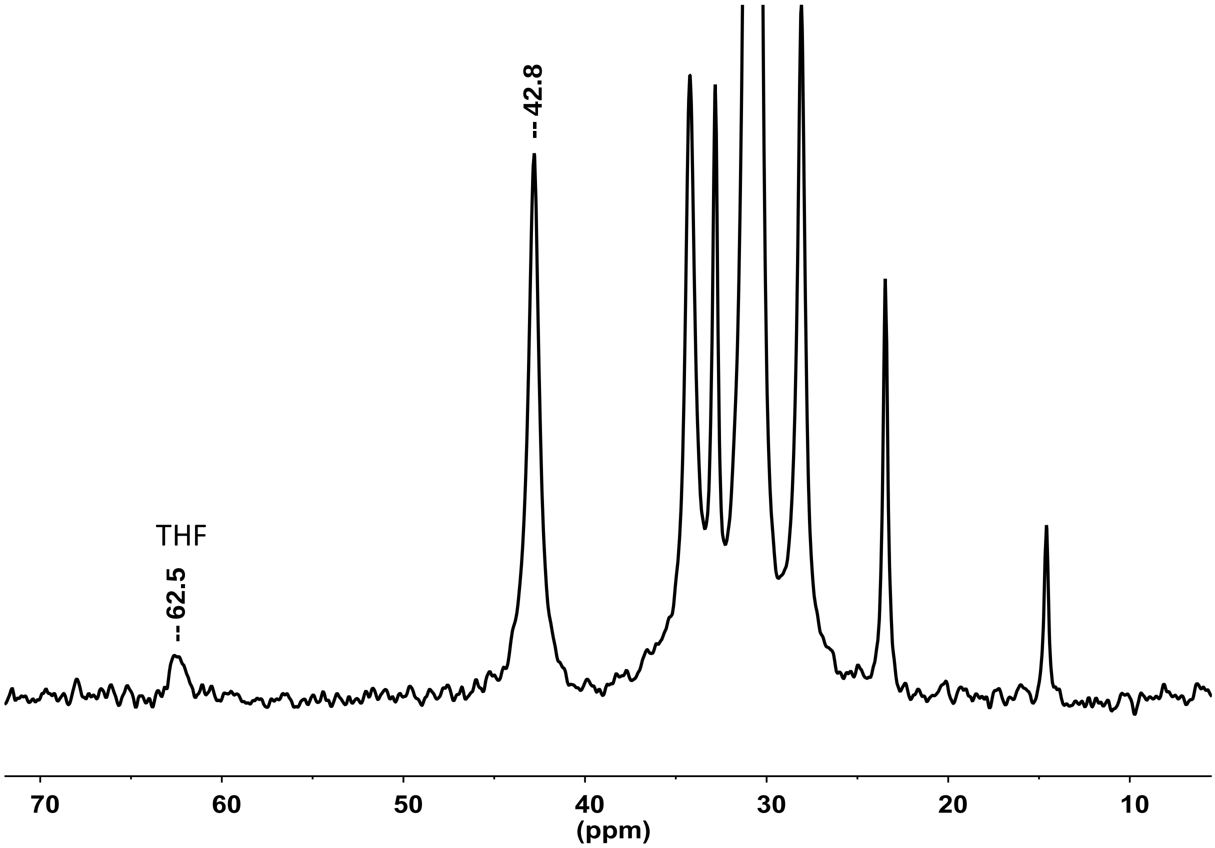
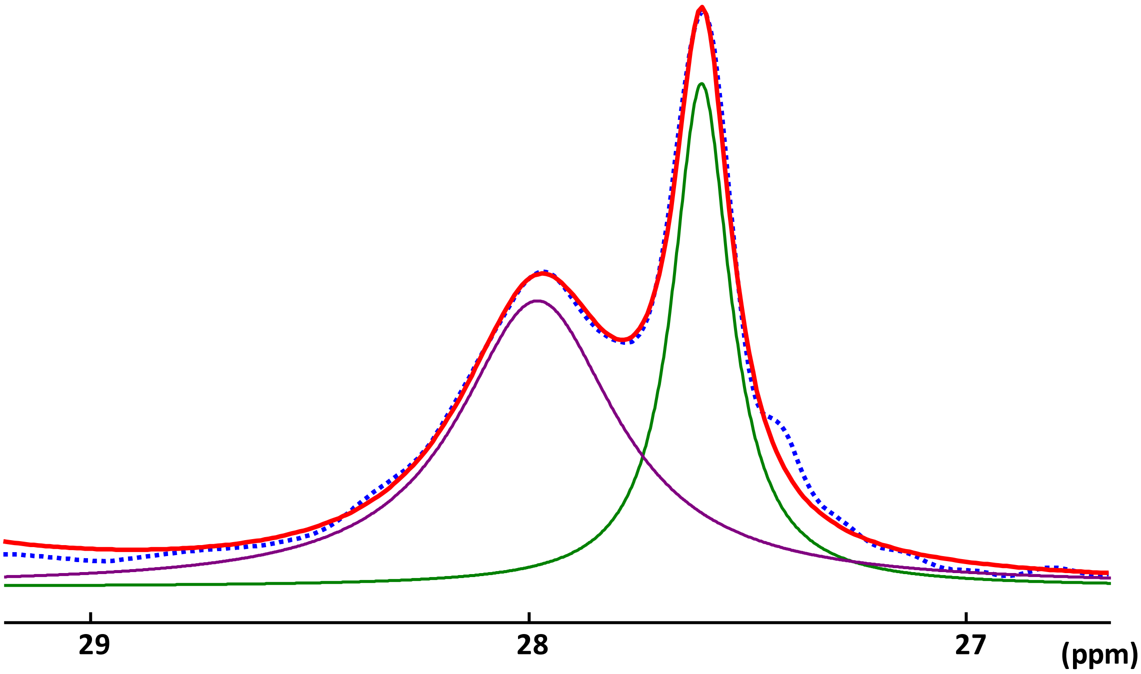


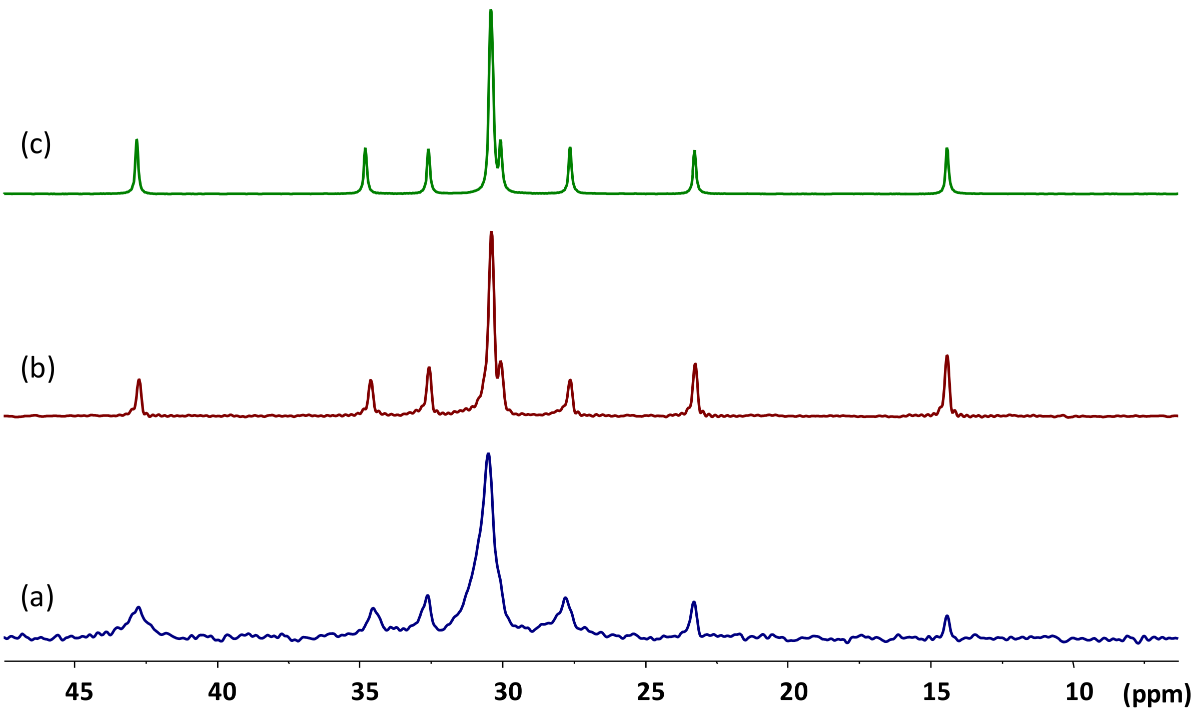
S1: ^{13}C MAS spectra of DDA alone with CP (a), DP (b) and INEPT (c) polarizations.



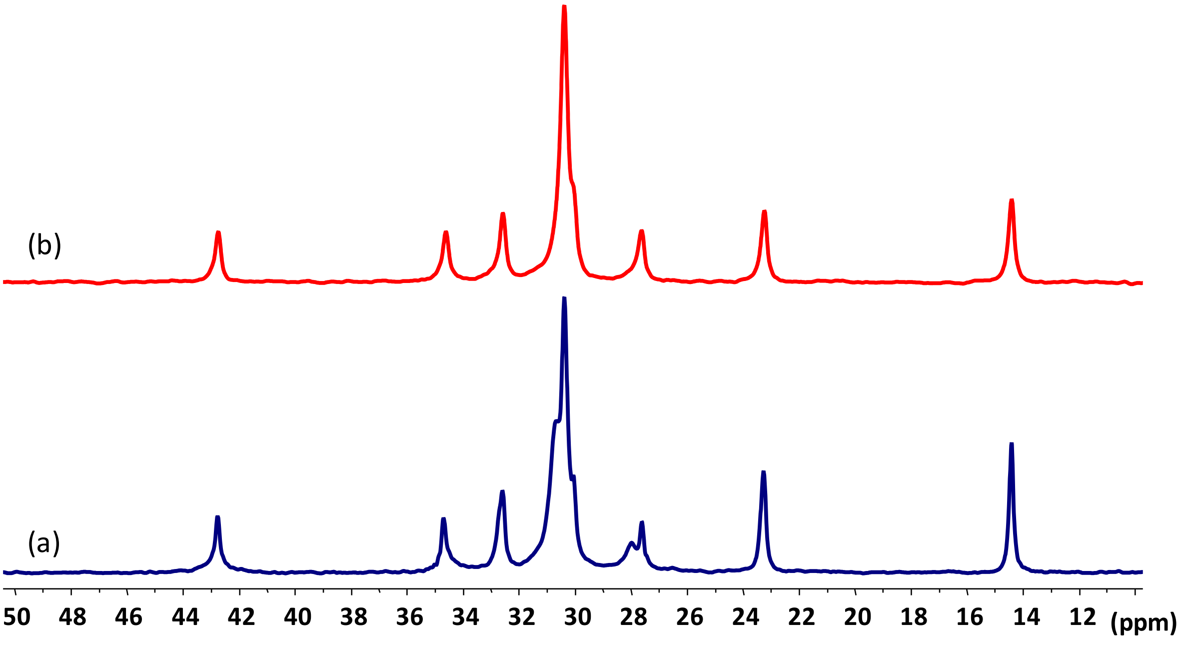
S2: ^{13}C CP MAS spectrum of ZnO@DDA (0.2 eq. DDA) with enlargement of the broad THF signal at 62.5 ppm.



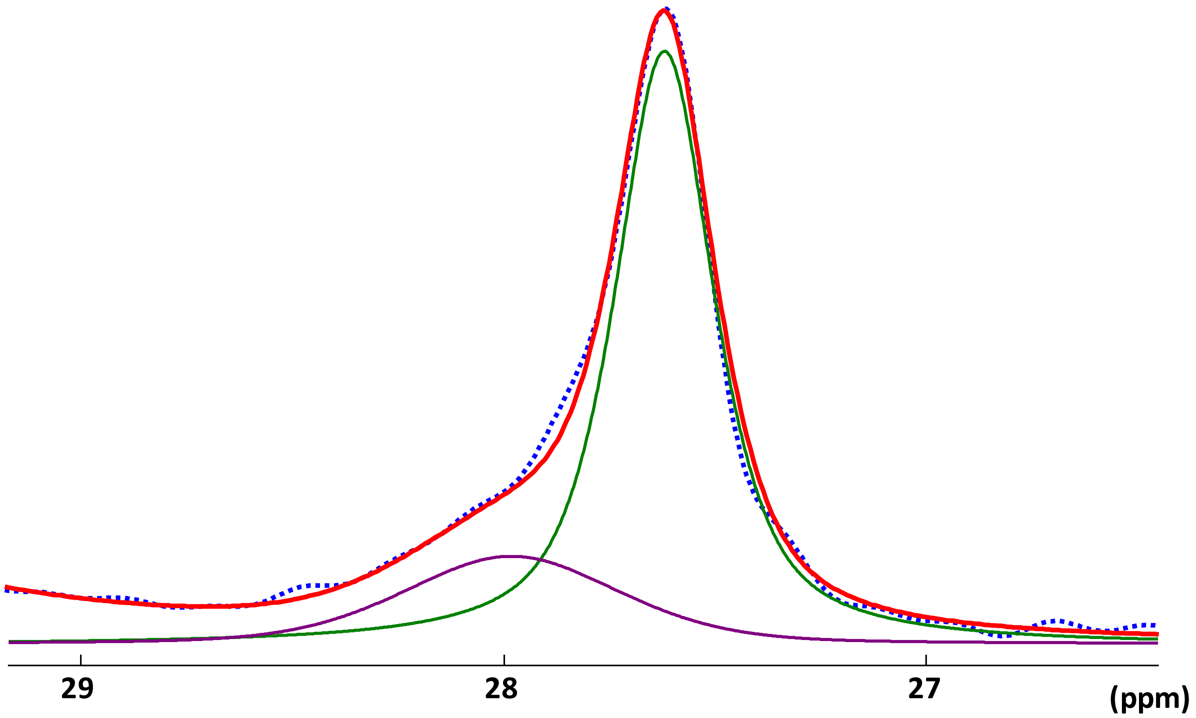
S3: Deconvolution of the γ-$CH_2(NH_2)$ signals in the ^{13}C DP MAS spectrum of ZnO@DDA (0.2 eq. DDA).



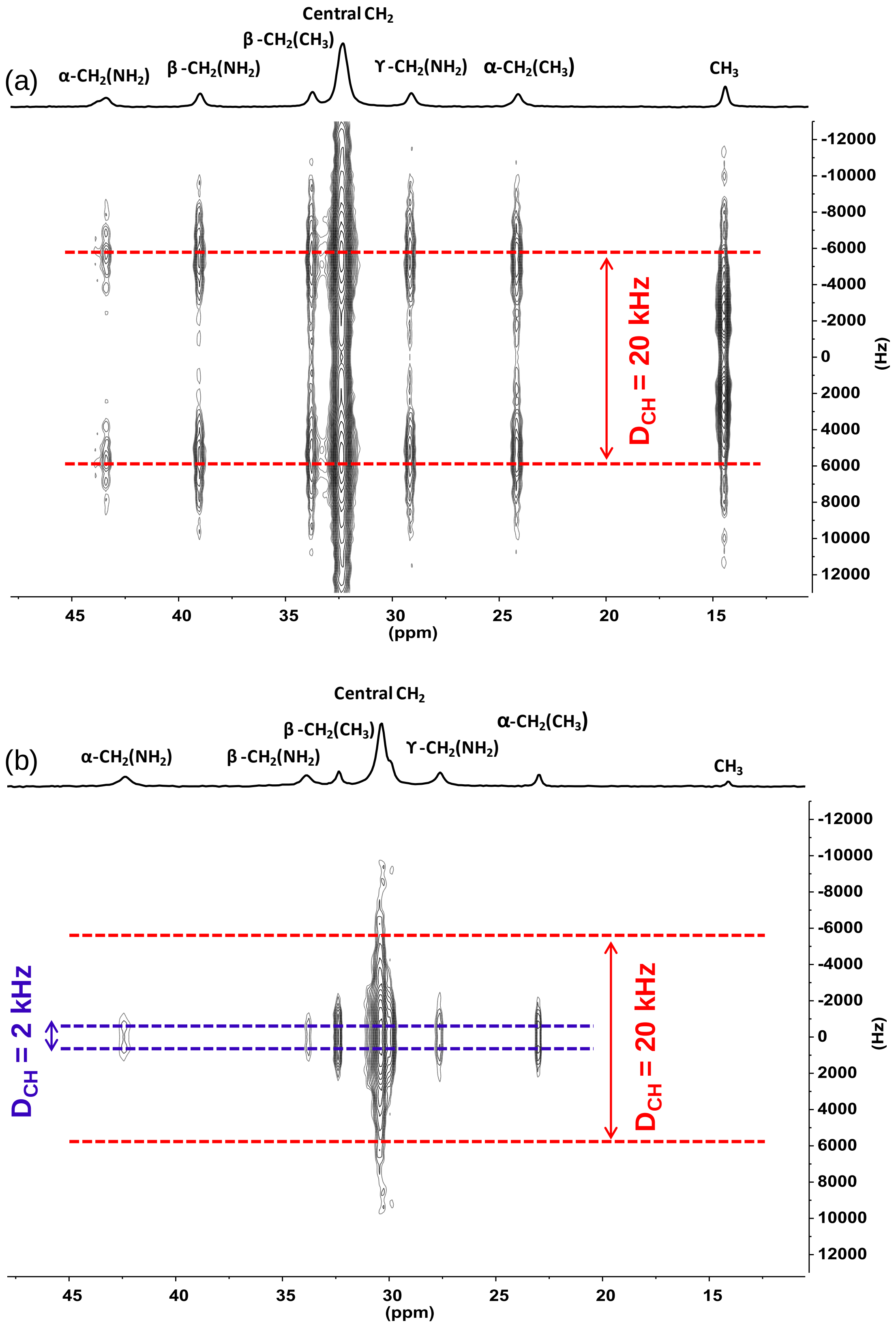
S4: ^{13}C MAS spectra of ZnO@DDA (1 eq. DDA) with CP (a), DP (b) and INEPT (c) polarizations.



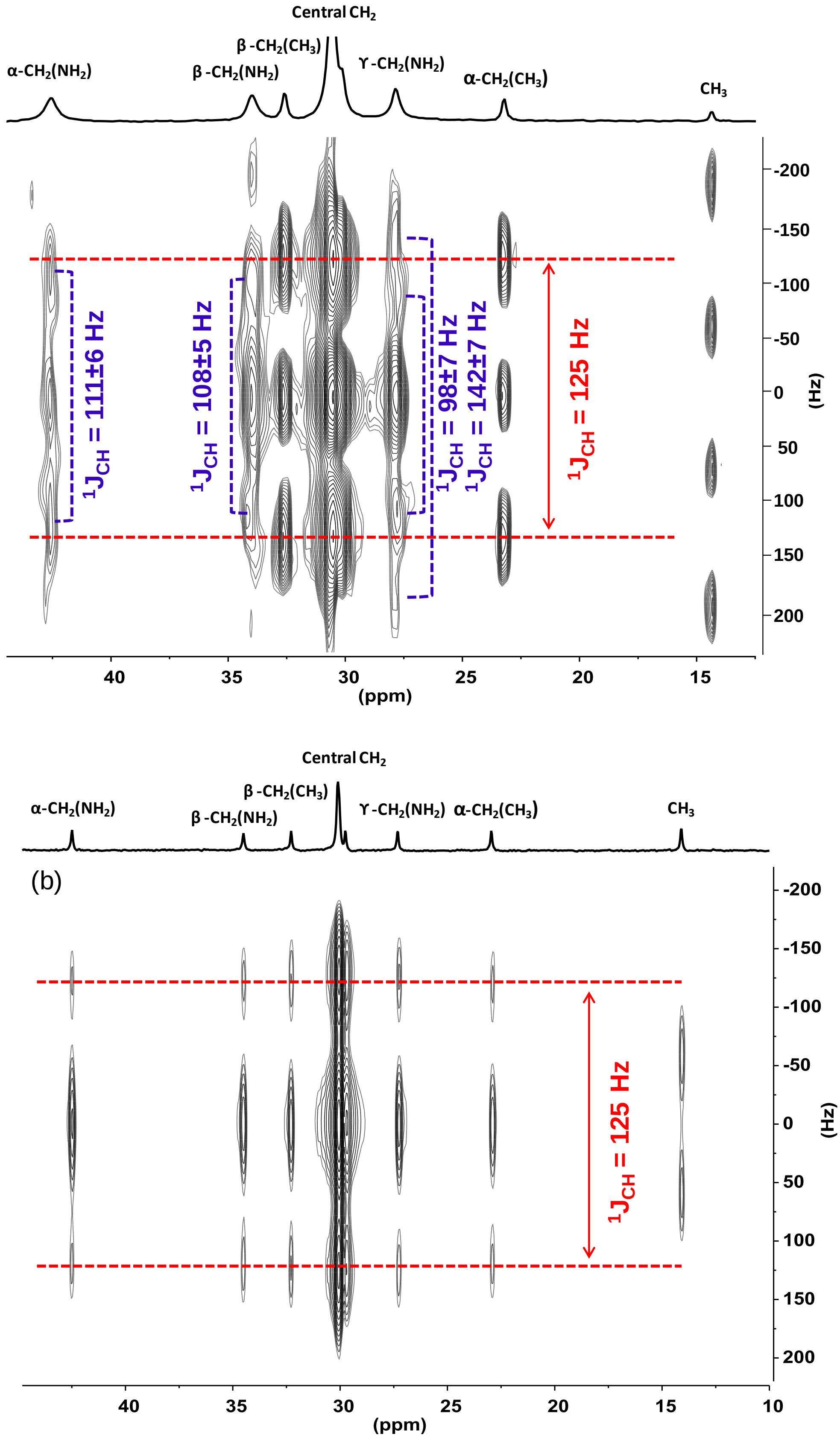
S5: ^{13}C DP MAS spectra of ZnO@DDA 0.2 eq (a) and 1 eq. (b) of DDA.



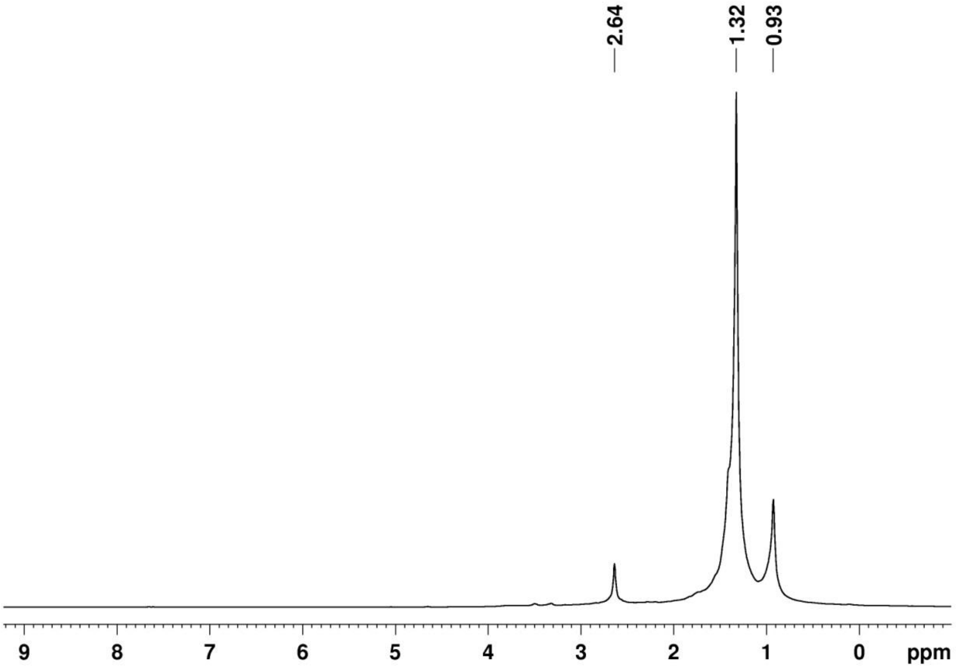
S6: Deconvolution of the γ-$CH_2(NH_2)$ signals in the ^{13}C DP MAS spectrum of ZnO@DDA (1 eq. DDA).



S7: ^{13}C ME-CP MAS spectra of (a) DDA alone and of (b) ZnO@DDA (0.2 eq. DDA) at 293K. A scaling factor of 0.58 was determined from a ^{13}C ME-CP MAS performed on a glycine sample with D_{CH} set to 21.5 KHz for the CH_2 group (Kharkov, B. B.; Chizhik, V. I.; Dvinskikh, S. V. *J. Phys. Chem. C*, 2014, 118 28308–13).

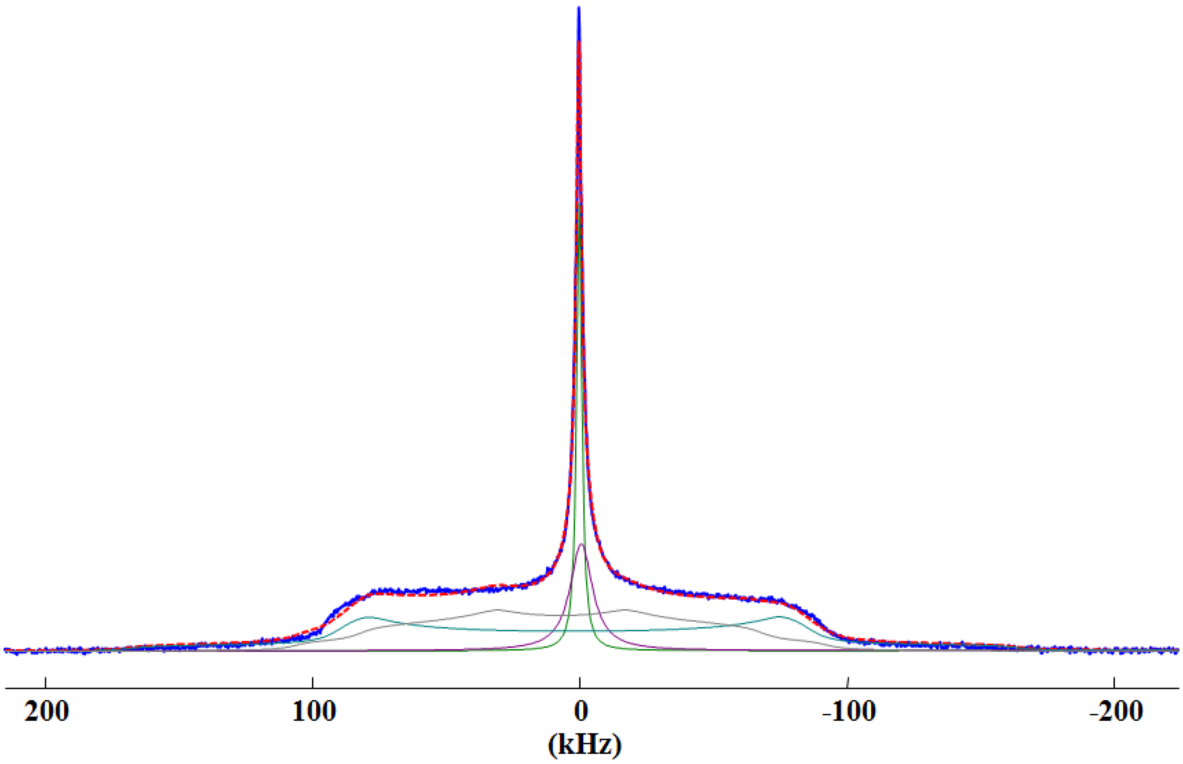


S8: (a) 2D CP J-resolved MAS spectra of ZnO@DDA (0.2 eq. DDA) at 293K and (b) 2D J-resolved MAS spectra DDA alone at 303K.



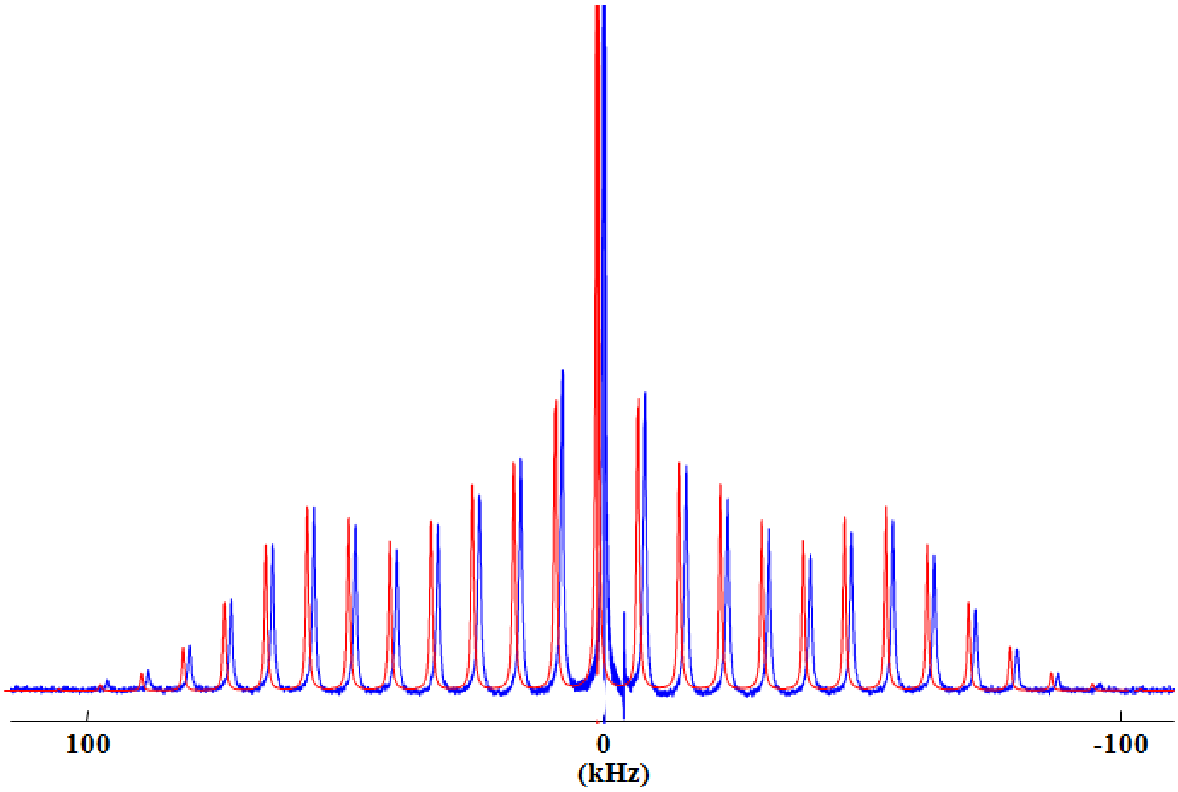
S9: ^{1}H MAS spectrum of ZnO@DDA (0.2 eq. DDA).

The ^{1}H MAS spectrum of ZnO@DDA is dominated by three signals: at 2.64 ppm, between 1.4-1.3 ppm, and at 0.93 ppm associated to respectively α-$CH_2(NH_2)$, central CH_2, and terminal CH_3 protons of the mobile DDA molecules. Very small residual solvent and impurities signals are also detected.

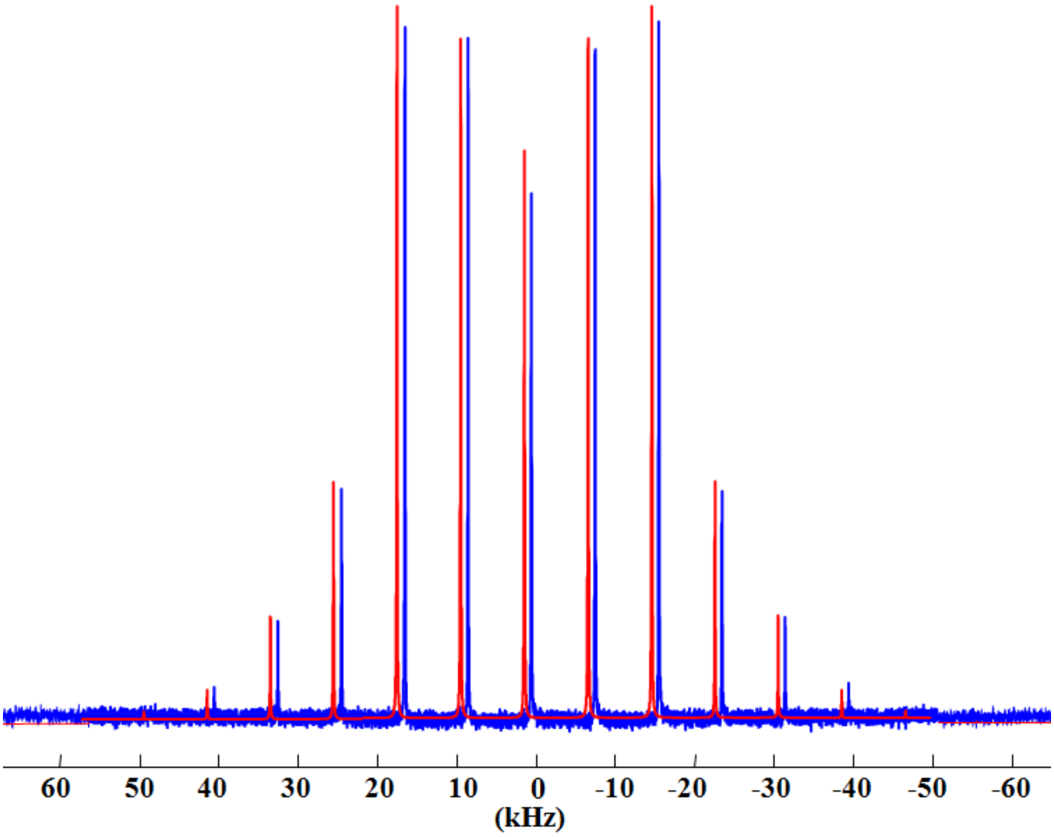


S10: Experimental (blue) and simulated (red) static ^{2}H spin-echo spectrum of ZnO^{D}@DDA (0.2 eq. DDA).

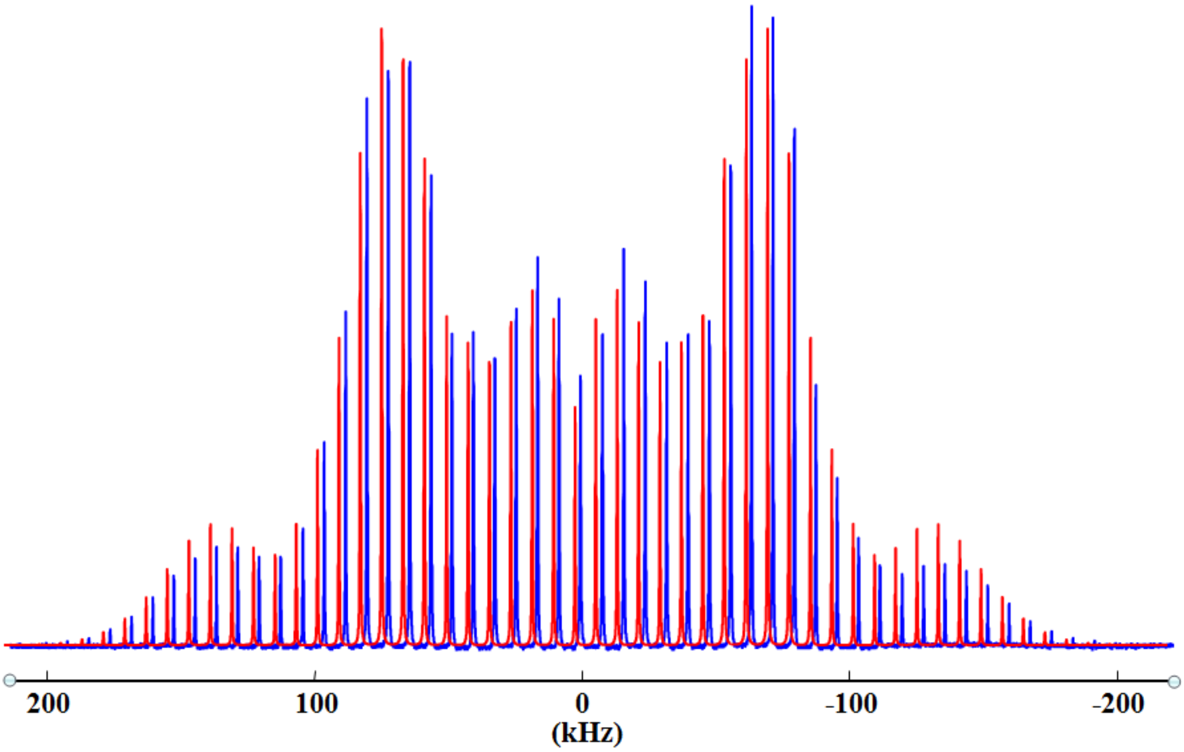
The static ^{2}H NMR spectra showed a broad contribution without singularities and a sharp one. The first one can be attributed to the presence of rigid amorphous species with significant quadrupole coupling constant (QCC) while the sharp one can be attributed to the presence of more mobile species. At least four superimposed contributions are necessary to fit the spectrum: i) two components for the rigid contribution with respectively QCC = 220 (± 20) kHz and 130 (± 20) kHz and asymmetry parameters $\eta = 0.10$ (± 0.05) and 0.50 (± 0.1) and ii) two Lorentzian lines with linewidth of respectively 1000 and 4500 Hz for the mobile contribution. A ratio of rigid *versus* mobile species of about 80/20 (±5) can be estimated from this deconvolution. The rigid component is too broad to extract further information notably precise chemical shifts. ^{2}H MAS offers considerable advantages over ^{2}H static measurements by providing greater sensitivity and the possibility obtaining more accurate isotropic shifts by simulation (Poupko, R.; Olender, Z.; Reichert, D.; Luz, Z. *J. Magn. Reson. A* **1994**, *106*, 113-115).



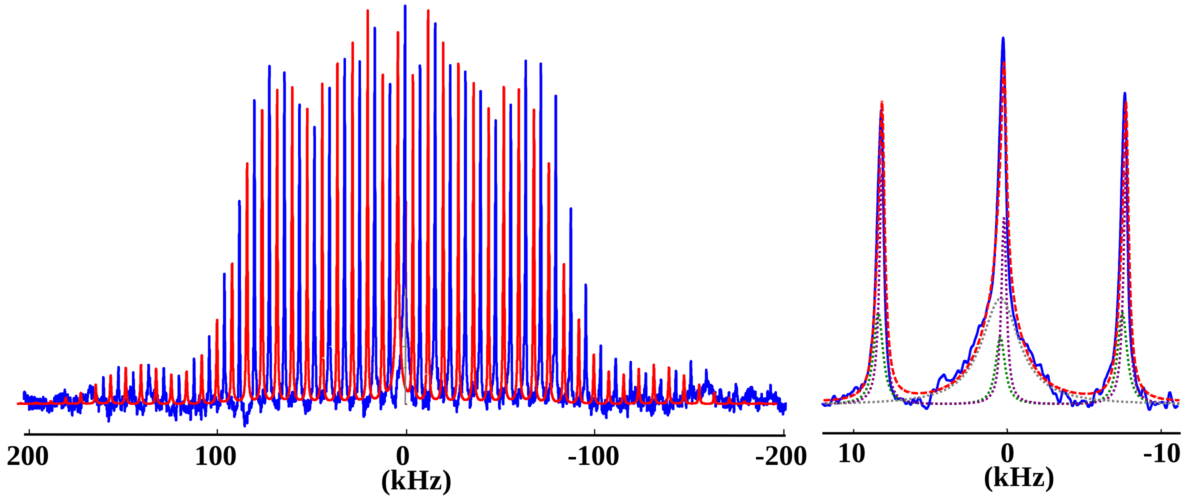
S11: Experimental (blue) and simulated (red) ^{2}H MAS (8 kHz) spectrum of DDA-d.



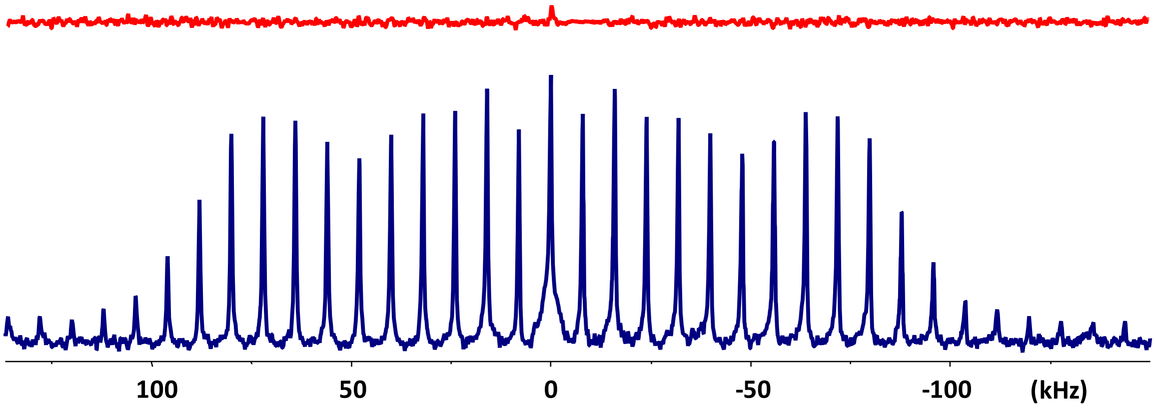
S12: Experimental (blue) and simulated (red) ^{2}H MAS (8 kHz) spectra of DDA^{+}.Cl^{-}-d.



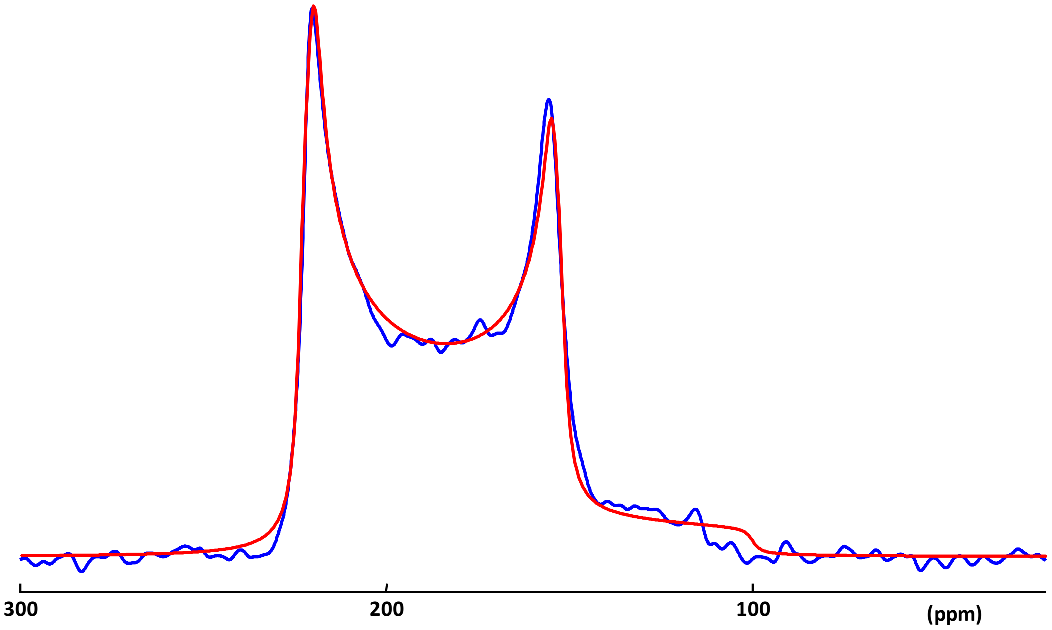
S13: Experimental (blue) and simulated (red) ^{2}H MAS spectrum of bared ZnO.



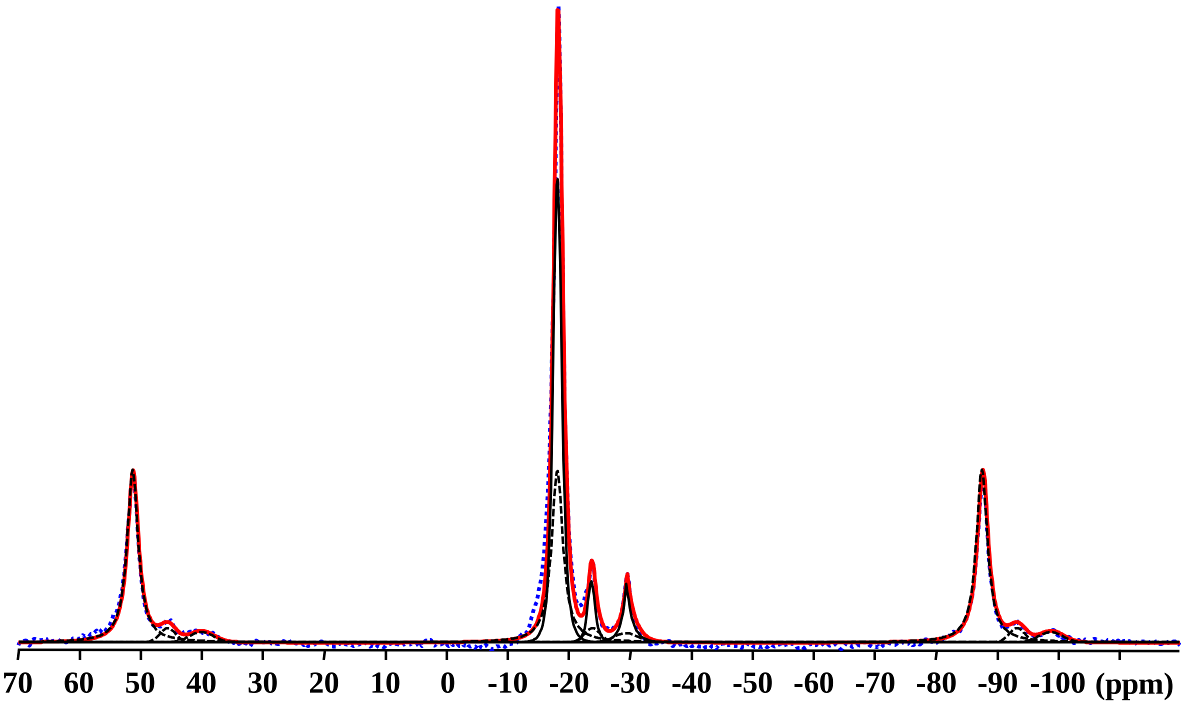
S14: Experimental (blue) and simulated (red) ^{2}H MAS (8 kHz) spectrum of bared ZnO^D.



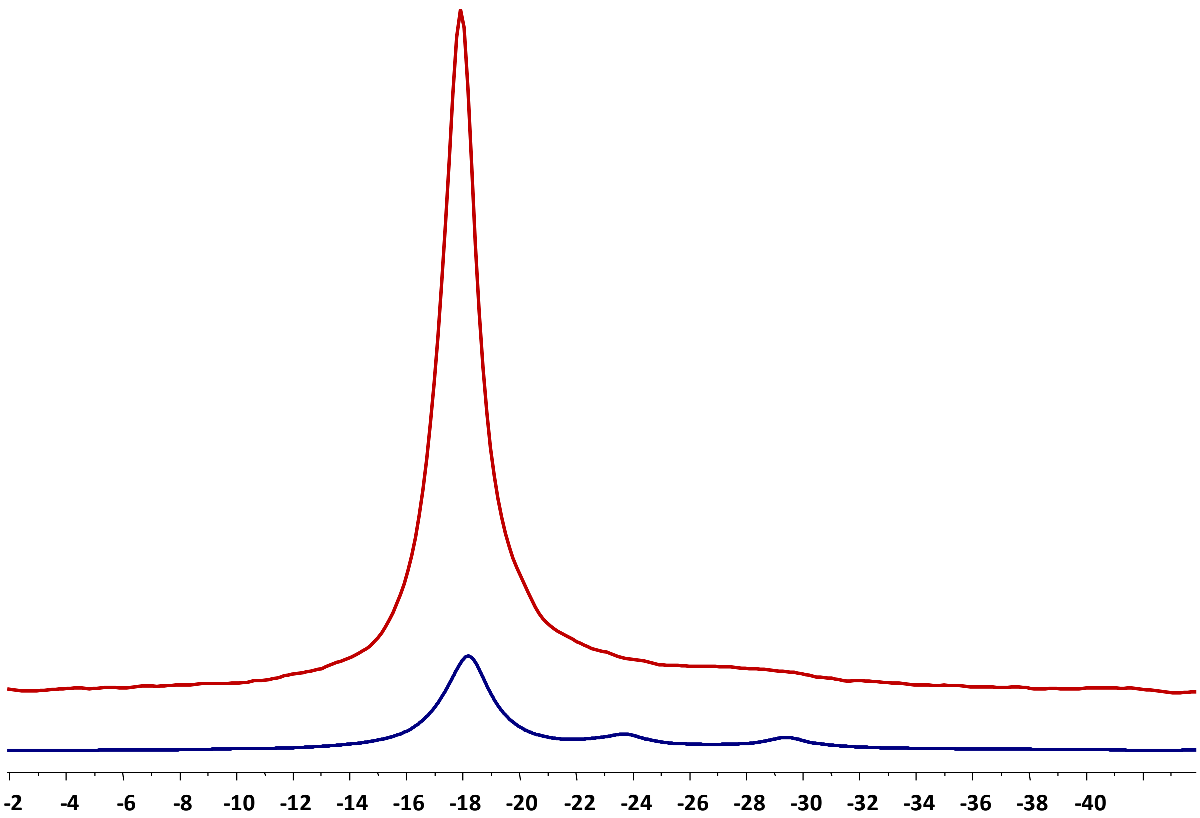
S15: ^{2}H MAS spectra of bared ZnO^{D} before (bottom) and after one night exposed to humid air (top).



S16: Experimental (blue) and simulated (red) ^{67}Zn Hahn-echo MAS spectra of commercial ZnO powder at 9.4 T.



S17: Experimental (blue) and simulated (red) 1D ^{17}O MAS at 20 T of vacuum dried ZnO^{Oex}@DDA (0.2 eq. DDA). Central transition (in black) were simulated with the Czjzek model. The presence of spinning side bands of the satellite transition under the central transitions were taken into account. The intensity of the n=0 spinning side bands of the satellite transitions were deduced from the n=±1 spinning sideband ones.(Y. Champouret, Y. Coppel, M. L. Kahn, *J. Am. Chem. Soc*, **2016**, *138*, 16322-16328). The whole ^{17}O ZnO signal can be reproduced with three resonances at -17.9(±0.1), -23.5(±0.2) and -29.2(±0.2) ppm with average quadrupolar coupling (QC) values of respectively 85(± 10) kHz, 80(± 10) kHz, and 95(± 5) kHz.



S18: Full ^{17}O MAS spectra at 20.0 T of sample ZnO@DDA (0.2 eq. DDA) exposed 12 hours to ^{17}O-enriched water (sample ZnO^{Oex}@DDA, blue) and of sample ZnO^{Osy}@DDA (red).

S19: Determination of the proportion of Zinc atoms located at the surface of ZnO NCs

The % of Zn atoms at the surface of NCs, %Zn(surf), is equal to the ratio between the number of Zn atoms of the basal planes, Zn(BP), plus the number of Zn atoms of the lateral planes, Zn(LP), and the overall number of Zn atom in a NC, Zn(Tot).

$$\mathrm{Zn(BP)} = \frac{3}{2}\frac{d^2}{a^2} \quad \mathrm{Zn(LP)} = 3\frac{dL}{ac} \quad \text{and} \quad \mathrm{Zn(Tot)} = \frac{3\sqrt{3}}{4}\frac{d^2L}{a^2\,\mathrm{c}\cos 30}$$

which leads to

$$\%\mathrm{Zn(surf)} = \left(\frac{c}{L} + \frac{2a}{d}\right) \times 100$$

In the case of isotropic ZnO NCs of ca 8 nm, d = L = 8 nm, *a* and *c* are the unit cell for hexagonal wurtzite ZnO structure with *a* = 0.33 nm and *c* = 0.52 nm.

Consequently, %Zn(surf) ≈ 15 %