

## Electronic Supplemental Information (ESI)

### Spatial distribution of organic functional groups supported on mesoporous silica nanoparticles (2): a study by $^1\text{H}$ triple-quantum fast-MAS solid-state NMR

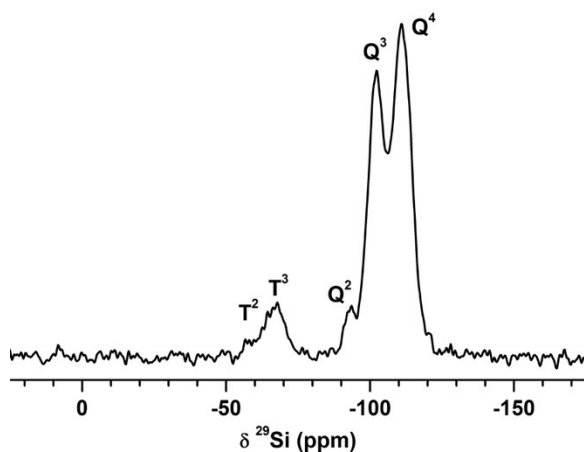
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#### S1. $^{29}\text{Si}$ DPMAS NMR

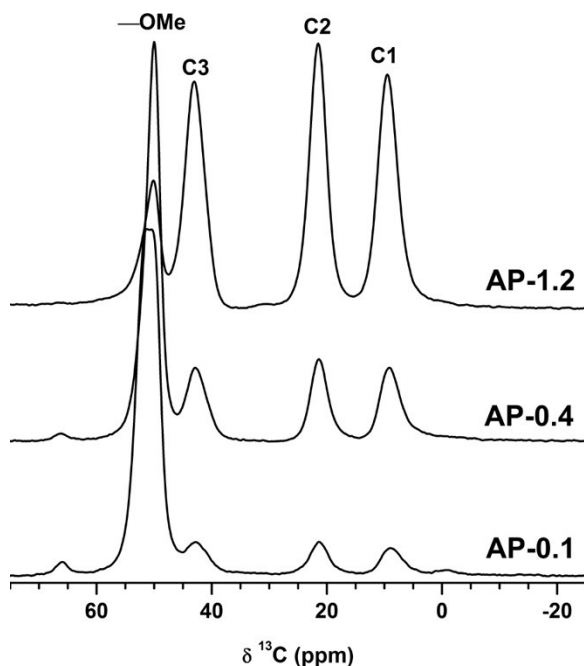
The  $^{29}\text{Si}$  direct polarization magic-angle spinning (DPMAS) experiment was performed on an Agilent NMR spectrometer, equipped with a 5-mm double-resonance magic-angle spinning (MAS) probe and operated at 9.4 T. The AP-1.2 was packed in the MAS zirconia rotor and spun at 8 kHz. The spectrum was taken with the RF magnetic field  $\nu_{\text{RF}}(^{29}\text{Si}) = 50$  kHz for a  $\pi/2$  pulse,  $\nu_{\text{RF}}(^1\text{H}) = 50$  kHz for a SPINAL-64  $^1\text{H}$  decoupling during the acquisition, recycle delay  $\tau_{\text{RD}} = 300$  s, and the number of scans  $\text{NS} = 296$ . The  $^{29}\text{Si}$  chemical shift was referenced with respect to tetramethylsilane (TMS) at 0 ppm. Based on the integration of silicon sites, we estimated that 8.7 % of Si atoms in this sample were bound to carbon, corresponding to an aminopropyl concentration of 1.2 mmol/g.



**Figure S1.**  $^{29}\text{Si}$  DPMAS spectrum of AP-1.2.

## S2. DNP-enhanced $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR

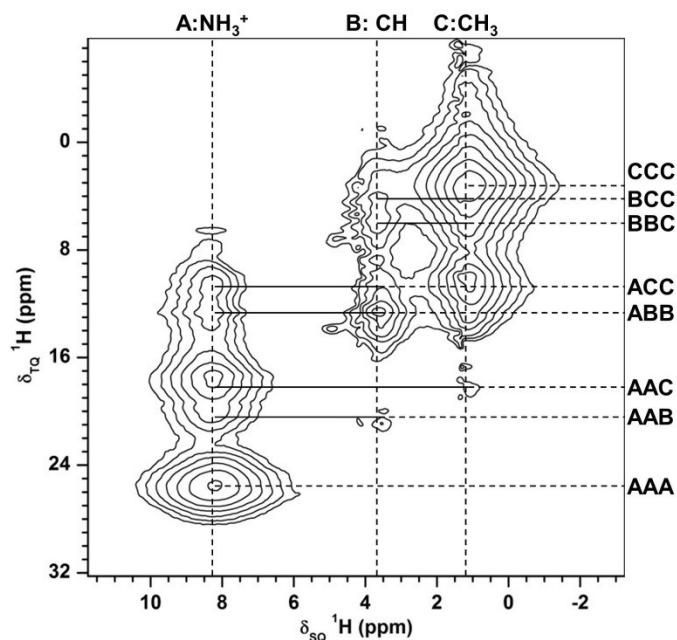
The DNP-enhanced  $^{13}\text{C}\{^1\text{H}\}$  cross-polarization (CP)MAS experiment was carried out on a Bruker Biospin DNP NMR spectrometer, operated at 9.4 T, equipped with a gyrotron generating microwaves at 264 GHz. Samples were impregnated with 10 mM AMUPol [1] dissolved in water, packed in 3.2-mm sapphire rotors and spun at a 10 kHz at a temperature of  $\sim 110$  K. The spectra were taken with the RF magnetic field  $\nu_{\text{RF}}(^{13}\text{C}) \sim 70$  kHz during cross-polarization,  $\nu_{\text{RF}}(^1\text{H}) = 100$  kHz during short pulse and SPINAL-64 decoupling,  $\nu_{\text{RF}}(^1\text{H}) = 80$  kHz during CP, contact time  $\tau_{\text{CP}} = 2$  ms, recycle delay  $\tau_{\text{RD}} = 3$  s, and the number of scans  $\text{NS} = 256$ . The  $^{13}\text{C}$  chemical shifts were referenced with respect to tetramethylsilane (TMS) at 0 ppm.



**Figure S2.** DNP-enhanced  $^{13}\text{C}\{^1\text{H}\}$  CPMAS spectra of AP-MSNs samples.

### S3. 2D $^1\text{H}$ TQ/SQ correlation spectrum of L-alanine·HCl.

The pulse sequence for the TQ/SQ correlation experiment was tested on L-alanine·HCl and verified by comparing the spectrum with that shown in an earlier paper by Spiess et al.[2]



**Figure S3.** 2D  $^1\text{H}$  TQ/SQ correlation spectrum of L-alanine·HCl. The spectrum was obtained using  $\nu_R = 36$  kHz,  $\nu_{RF}(^1\text{H}) = 100$  kHz,  $\tau_{\text{exc/rec}} = 4\tau_R$  (111.1  $\mu\text{s}$ ),  $\tau_{Z\text{-fil}} = 0.5$  ms,  $\tau_{RD} = 1.0$  s, 160 rows with  $\Delta t_1 = 27.778$   $\mu\text{s}$ , NS = 24, AT = 2.1 h.

### References

- [1] Sauvée, C.; Rosay, M.; Casano, G.; Aussenac, F.; Weber, R.T.; Ouari, O.; Tordo, P. “Highly efficient, water-soluble polarizing agents for dynamic nuclear polarization at high frequency” *Angew. Chem. Int. Ed.* **2013**, 52, 10858–10861.
- [2] Schnell, I.; Lupulescu, A.; Hafner, S.; Demco, D.E.; Spiess, H.W. “Resolution enhancement in multiple-quantum MAS NMR spectroscopy”, *J. Magn. Reson.* **1998**, 133, 61-69.