

Supplementary Information

Highly ordered mesostructured material containing regularly distributed phenols: preparation and characterization at a molecular level through ultra-fast magic angle spinning proton NMR spectroscopy.

Arthur Roussey,^a David Gajan,^a Tarun K. Maishal,^a Anhurada Mukerjee,^a Laurent Veyre,^a Anne Lesage,^b Lyndon Emsley,^{*b} Christophe Copéret,^{*c} and Chloé Thieuleux^{*a}

^a Université de Lyon, Institut de Chimie de Lyon, C2P2, CNRS–Université Lyon 1–ESCPE Lyon, ESCPE Lyon, F-308-43 Boulevard du 11 novembre 1918, F-69616, Villeurbanne Cedex, France.
^b Université de Lyon, CNRS/ENS Lyon/UCB Lyon 1, Centre de RMN à Très Hauts Champs, 5 rue de la Doua, 69100 Villeurbanne, France.

^c Department of Chemistry, Wolfgang-Pauli-Str. 10, ETH Zürich, CH-8093 Zürich, Switzerland.

General Information.

Reactions of passivation/depassivation were carried out under inert atmosphere using dried and freshly distilled solvents. All the materials were analyzed after drying under high-vacuum at 135°C overnight. *p*-bromophenol, TEOS, HMDS, Pluronic P123, TMSBr and dry triethylamine were bought from Sigma-Aldrich.

Nuclear Magnetic Resonance Spectroscopy.

One-dimensional CP/MAS ²⁹Si and ¹³C solid-state NMR spectra were respectively recorded on a Bruker Avance 300 and 500 MHz using conventional double resonance 4 mm CP-MAS probe. For these experiments, the MAS frequency was set to 10 kHz and the CP contact times was 2ms. The ²⁹Si spectrum of **MatPhOH** was recorded on a Bruker Avance 500 MHz at a MAS frequency of 5 kHz with a contact time of 2ms.

The one- and two-dimensional proton solid-state NMR experiments were recorded using a 1.3 mm MAS probe on Bruker Avance III 800 MHz (for MatPhOH) and 900 MHz (for **MatSiMe₃PhOSiMe₃** and **MatSiMe₃PhOH**) spectrometers at the High Field NMR Center of Lyon. For all the experiments the MAS frequency was set to 60 kHz.

The two-dimensional proton double-quantum (DQ) – single quantum (SQ) correlation spectra were recorded according to the following general scheme: excitation of DQ coherences, *t*₁ evolution, reconversion into observable magnetization, Z-filter, and detection. DQ excitation and reconversion were achieved using the BACK-to-BACK (BABA) pulse sequence¹⁻³. The length of the BABA excitation and reconversion block was set to 33.34 μs (2 BABA cycles). Quadrature detection in ω₁ was achieved using the States-TPPI method⁴. A recycle delay of 3 s was used. A total of 32 *t*₁ increments of 16.67 μs were recorded with 128 and 512 scans for spectrum (a) (800 MHz) and for spectra (b) and (c) (900 MHz) respectively.

Transmission electronic microscopy.

Conventional TEM micrographs were performed at the “Centre Technologique des Microstructures”, UCBL, Villeurbanne, France, using a Philips 120 CX electron microscope. The acceleration voltage was 120 kV. The samples were prepared by dispersing a drop of the ethanol suspension of a ground sample on a Cu grid covered by a carbon film.

X-Ray Diffraction.

Small-Angle X-ray diffraction (XRD) on powder was carried out with a Bruker D8 Avance diffractometer (33 kV & 45 mA) with CuKα radiation (λ = 0.154 nm) in the “Centre de diffractométrie H. Longchambon”, UCBL, Lyon, France. The diffraction patterns were collected in the 2θ angle range [0.5°-10.0°] at a scanning rate of 0.1°/min. The interplane spacings, d(hkl) for different Miller indices (hkl) were calculated using the Bragg’s law (nk = 2dsinθ). The lattice parameter (a₀) for the 2D hexagonal structured mesoporous material is given by a₀ = 2d(100)/√3

Nitrogen adsorption-desorption measurements.

The Nitrogen adsorption and desorption measurements were achieved at 77 K using an ASAP 2020 Micromeritics

system. Before N₂ adsorption, the samples were outgassed at 10⁻⁴ Pa at 408 K for 12 h. The pore diameter distribution and the mean pore diameter (dp) were calculated using Barrett–Joyner–Halenda (BJH) method. The specific surface area (S_{BET}) was calculated by Brunauer–Emmett–Teller (BET) equation. The pore wall thickness (ep) of the sample was calculated using the following formula: $ep = \sqrt{3d(100)/2} - dp$.

Synthesis of the precursor Me₃Si-O-Ph-Si(OEt)₃ (adapted from ref. 5).

Catalytic amount of saccharin (140 mg, 0.80 mmol) and 4-bromophenol (16 g, 92 mmol) was dissolved in dry dichloromethane (200 mL). Under reflux conditions, hexamethyldisilazane (20 mL, 96 mmol) was added rapidly. The solution was refluxed for 3h. After elimination of the volatiles, the colorless oil was dissolved in THF. Mg (15g, 0.63 mol) and TEOS (150 mL, 0.72 mol) were taken in THF (200 mL). A pinch of iodine was added into the solution and then the former solution of the bromophenol derivative (20 g, 82 mmol) was dropwise added at reflux condition (80 °C). After 2h of stirring, THF was removed and excess pentane (200 mL) was added. The resulting mixture was filtrated and evaporated under vacuum to afford a colorless oil. (17 g, 63%). ¹H NMR: 7.52 (d, 2H, J = 9 Hz), 6.86 (d, 2H, J = 9 Hz), 3.84 (q, 6H), 1.22 (t, 9H), 0.27 (s, 9H). ¹³C{¹H} NMR: 157, 136, 129, 119, 58, 18, 0.

Synthesis of the phenol-functionalized material, MatPhOH.

2.95 g of P123 dissolved in an aqueous HCl solution (240 mL, pH 1.5) was added in a mixture of TEOS (6.8 g, 32.6 mmol) and PhOSiMe₃ (0.35g, 1.2 mmol) at room temperature. The reaction mixture was stirred for 2 hours giving rise to a micro-emulsion (transparent mixture). To the reaction mixture heated at 45 °C, a small amount of NaF (50 mg, 1.2 mmol) was added under stirring. The mixture was left at 45°C under stirring for 72 h. The resulting solid was filtered and washed with water, acetone, ethanol and ether. The surfactant was removed by treatment in pyridine (30mL), water (30 mL) and 2M HCl (5 mL)⁶. The solid was then filtered, washed with water, acetone and ether and dried at 135 °C under vacuum. 2.2 g of **MatPhOH** was obtained as a white solid (75%). ¹H MAS solid state NMR (800MHz, d1 = 3s, 64 scans): 7.5, 6.6, 3.8, 1.8, 1.1, 0 ppm. ¹³C CP-MAS solid state NMR (300MHz, d1 = 30s, 2951 scans): 158, 135, 120, 113 ppm. ²⁹Si CP-MAS solid state NMR (500MHz, MAS 5kHz, d1 = 10s, 30000 scans, experimental time = ca. 3.5 days! -70, -92, -101, -110 ppm.

Synthesis of the fully passivated material, MatSiMe₃PhOSiMe₃.

2 g of dry **MatPhOH** was suspended in dry toluene (50 mL) and dry triethylamine (21 mL). Then, TMSBr (10g, 7.4 eq.) was slowly added at room temperature. The mixture was stirred overnight, filtrated, washed with toluene, ethanol, ether and dried under vacuum (2.1g, 98%). ¹H MAS solid state NMR (900MHz, d1= 3s, 64 scans): 7.4, 6.6, 3.7, 1.1, 0 ppm. ¹³C CP-MAS solid state NMR (300MHz, d1 = 2s, 30621 scans): 157, 136, 123, 119, 59, 17, 0 ppm. ²⁹Si CP-MAS solid state NMR (300MHz, d1 = 4s, 6056 scans): 12, -101, -110 ppm.

Synthesis of the phenol-functionalized passivated material, MatSiMe₃PhOH.

2 g of dry **MatSiMe₃PhOSiMe₃** was suspended in dry methanol (50 mL). The mixture was stirred for 1h at room temperature, filtrated and washed with ether. ¹H MAS solid state NMR (900MHz, d1 = 3s, 64 scans): 7.5, 6.7, 3.8, 1.1, 0 ppm. ¹³C CP-MAS solid state NMR (500MHz, d1 = 2s, 41752 scans): 158, 136, 119, 114, 57, 50, 16, 0 ppm. ²⁹Si CP-MAS solid state NMR (300MHz, d1 = 8s, 10000 scans): 12, -102, -110 ppm.

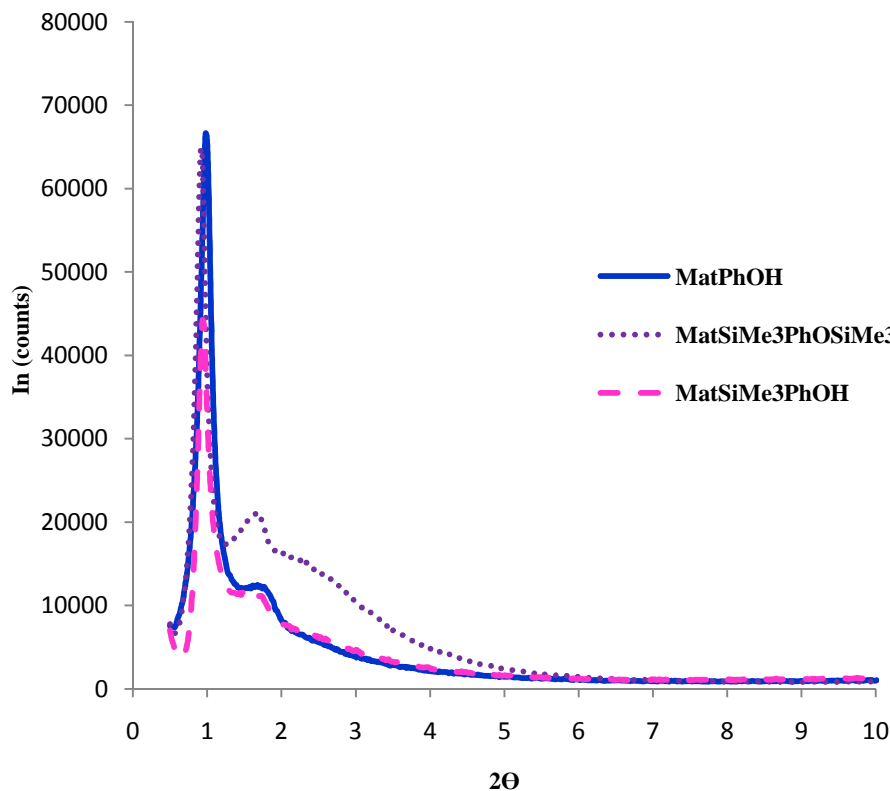
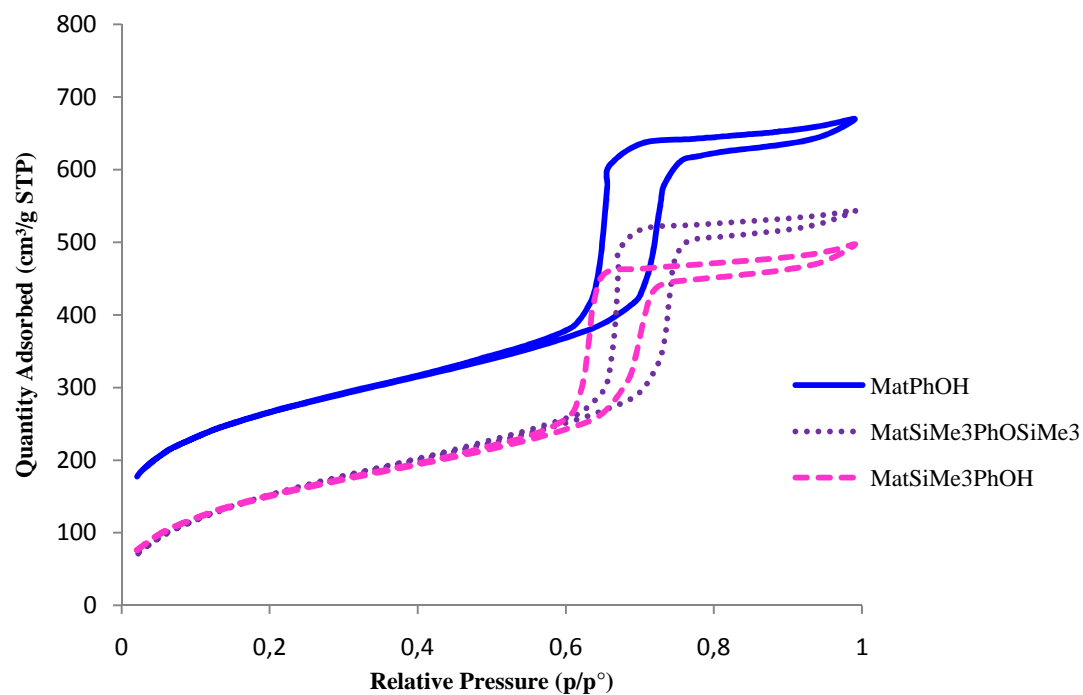


Figure S1. Small angle X-Ray diffraction patterns of the materials.

	Surface Area (m ² /g) ^a	Pore volume (cm ³ /g) ^b	Microporous volume (cm ³ /g) ^c	Average pore diameter d _p (nm) ^b	Lattice parameter a ₀ (nm) ^d	Wall thickness (e _p =a ₀ -d _p , nm)
MatPhOH	925	0,96	0,07	8	10,6	4
MatSiMe ₃ PhOSiMe ₃	590	0,93	0,002	6	11,2	4
MatSiMe ₃ PhOH	565	0,83	0,02	6	11,0	5

Table S2. Characteristics of the materials; ^a Calculated with the BET method; ^b Calculated with the BJH method on the adsorption branch of the isotherm; ^c Calculated with the t-plot method; ^d Calculated from the XRD pattern $a_0 = (2 d_{100})/\sqrt{3}$.



b)

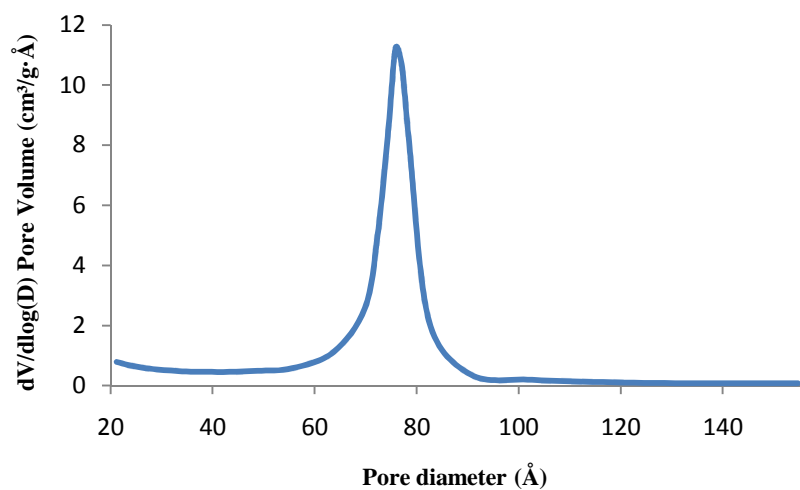


Figure S3. a) Nitrogen adsorption-desorption isotherms at 77K;
b) Pore size distribution of MatPhOH (adsorption).

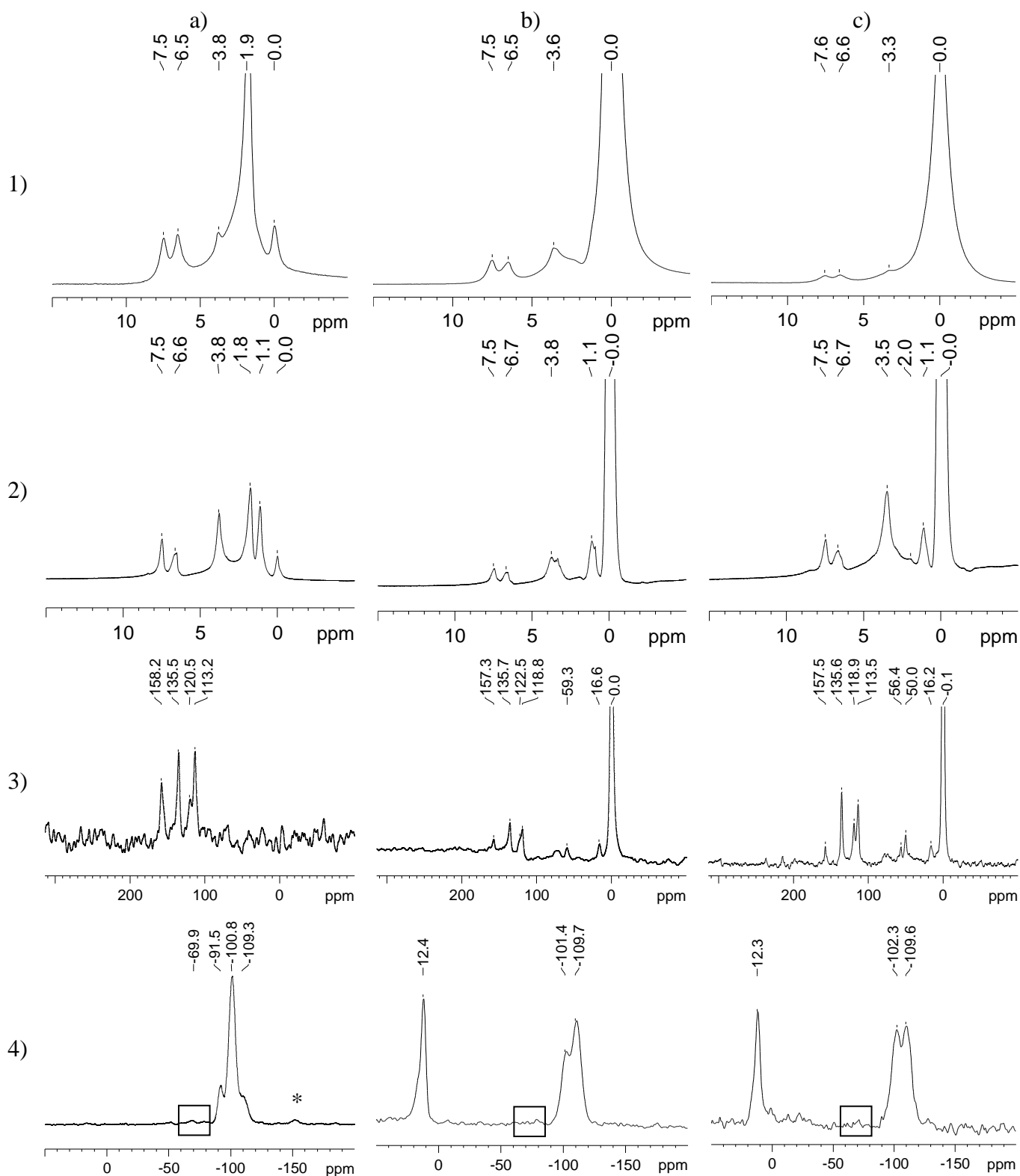


Figure S4. Comparison of 1) ¹H MAS 10 kHz, 2) ¹H MAS 60 kHz, 3) ¹³C CP/MAS 10 kHz and 4) ²⁹Si CP/MAS 10 kHz (5kHz for a) of a) MatPhOH, b) MatSiMe₃PhOSiMe₃ and c) MatSiMe₃PhOH. The squares in line 4 underline the -70 ppm region of the spectra where signals associated with silicon T sites are usually observed.

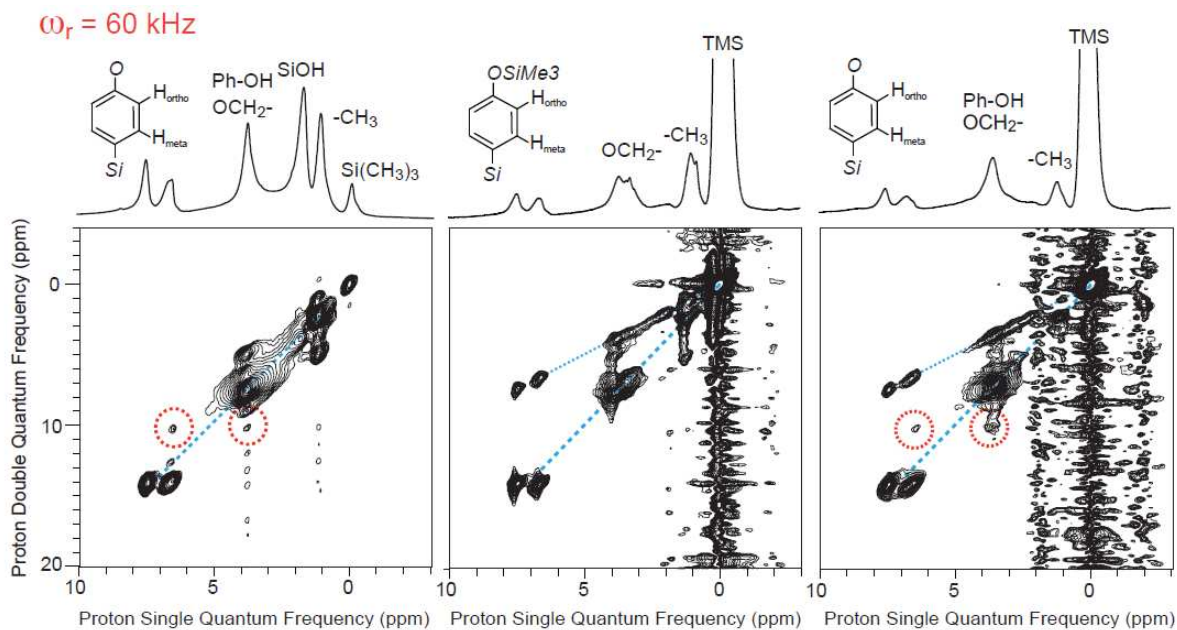
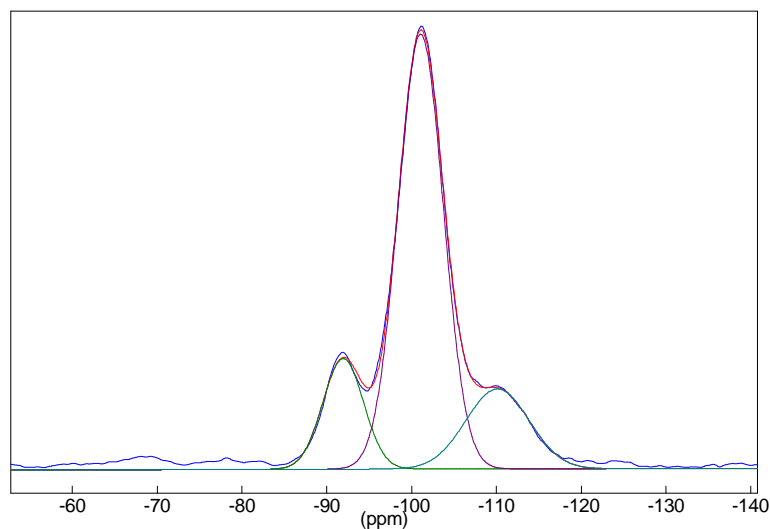


Figure S5. 2D DQ ^1H - ^1H MAS NMR correlation spectra of MatPhOH (left), Mat_{TMS}PhOTMS (middle) and Mat_{TMS}PhOH. (right). The base contour level is at 0.5% level in each spectra.



Peaks	δ (ppm)	Area (%)	Contribution
Q ²	-91 ppm	15.38 %	2
Q ³	-101 ppm	67.28 %	3
Q ⁴	-111 ppm	17.34 %	4

$$\text{Condensation} = \frac{\sum \text{Area} (\%) \times \text{Contribution}}{100\% Q^4} \quad (100\% Q^4 = 4)$$

$$\text{Condensation} = 75.5\%$$

Figure S6. Deconvolution of the ^{29}Si spectrum of MatPhOH and calculation of the condensation of the silica matrix.

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