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Supplementary Information

Sensitivity enhancement *via* multiple contacts in the {^{1}H-^{29}Si}-^{1}H cross polarization experiment: A case study of modified silica nanoparticle surfaces

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Part 1, Details of solid-state NMR pulse sequences.
Part 2, Supplementary data.

Supplementary Information

Part 1, Solid-State NMR pulse sequences and experiments.

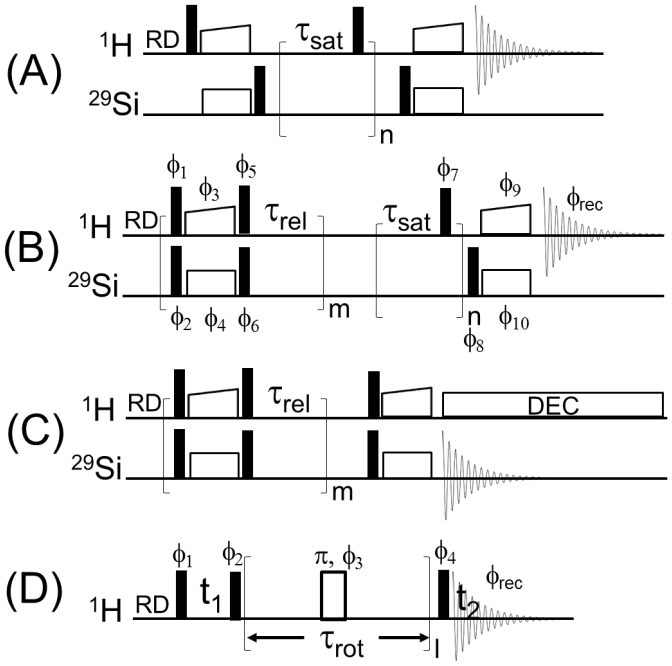
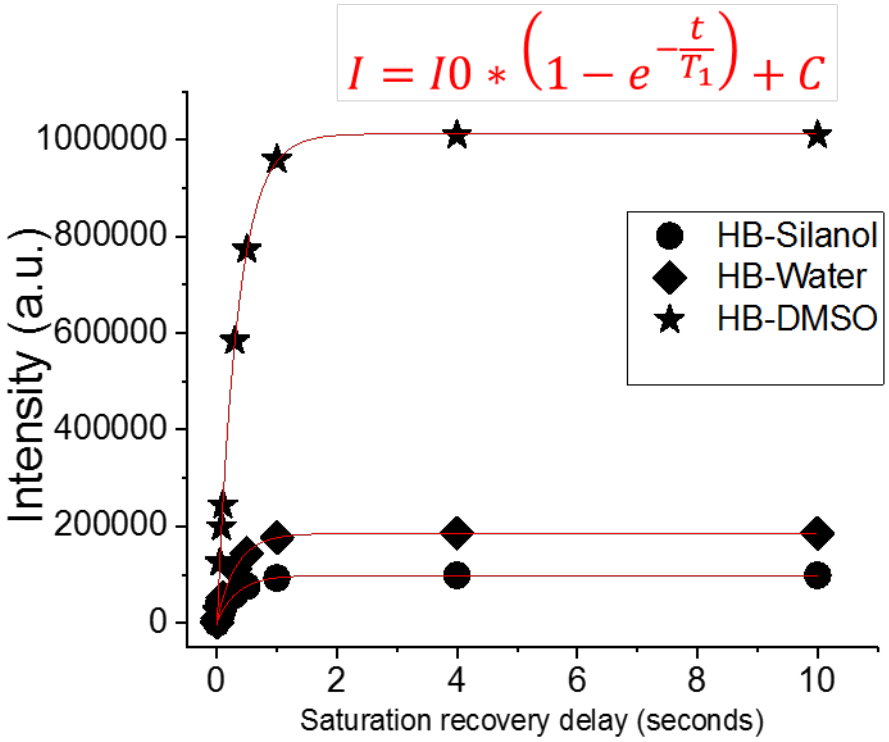


Fig. S1 Pulse sequences. (A) { ^{1}H- ^{29}Si}- ^{1}H double cross-polarization inverse detection (DCPi), phases of pulses and receiver are the same as given in Babonneau's work.[1] (B) { ^{1}H- ^{29}Si}- ^{1}H multiple cross-polarization reverse detection (MCPi), phases of pulses and receiver are as follows: $\phi_1 = \phi_2$ = {x, x, -x, -x}, $\phi_3 = \phi_4$ = {y}, $\phi_5 = \phi_6$ = {-x, -x, x, x}, ϕ_7 = {x}, ϕ_8 = {x, -x}, ϕ_9 = {x*4, -x*4, y*4, -y*4}, ϕ_{10} = {y}, ϕ_{rec} = {x, -x, x, -x, -x, x, -x, x, y, -y, y, -y, -y, y, -y, y}. (C) { ^{1}H-}- ^{29}Si multiple cross-polarization (multiCP). The phases of pulses and receiver are the same as given in the original work.[2] (D) ^{1}H- ^{1}H radio frequency driven recoupling correlation spectroscopy (RFDR), phases of pulses and receiver are as follows: ϕ_1 = {x, -x}, ϕ_2 = {x*8, -x*8}, ϕ_3 = {{x, y, x, y, y, x, y, x}}, ϕ_4 = {x, x, -x, -x, y, y, -y, -y}, ϕ_{rec} = {x, -x, x, -x, y, -y, -y, y, -x, x, x, -x, -y, y, y, -y}. The phase cycling of the RFDR part (ϕ_3) was adopted from Griffin's work.[3]

Part 2, Supplementary data.



Groups	$T_{1,H}$ / seconds
Silanol (7.5 ppm)	0.336 ± 0.005
water (4.63 ppm)	0.329 ± 0.008
DMSO (3.16 ppm)	0.348 ± 0.004

Fig. S2 Proton spin-lattice relaxation constant (T_1^H) measurement of the DMSO-h_6-adsorbed SiNP using standard saturation recovery pulse sequence, where delay between two consecutive 90° pulses (τ_{sat}) = 1 ms, total number of 90° pulses (n) = 64. The T_1's were obtained by fitting the peak intensities to a single exponential function (embedded in the figure). The fitting was performed using the software OriginPro 2018 (64-bit) SR1. The standard errors were estimated by the fitting errors.

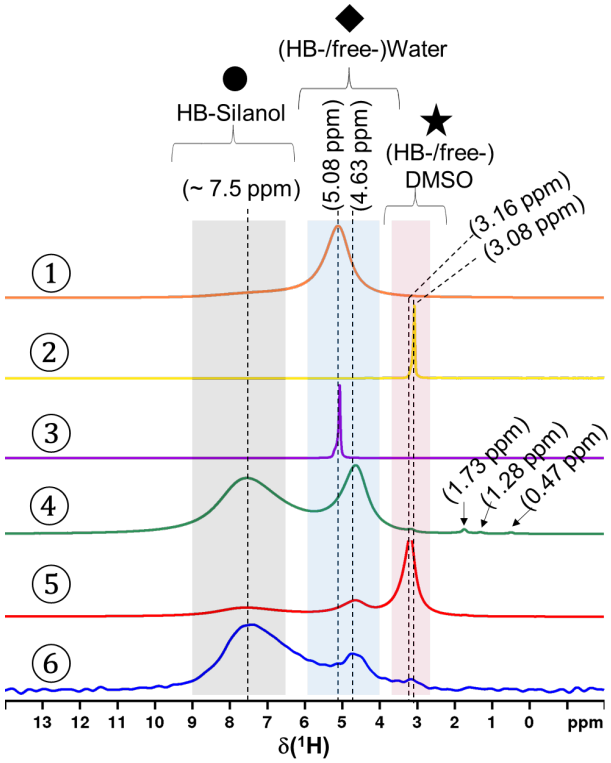


Fig. S3 ^{1}H reference spectra used for the chemical shift assignments of silanol, water and DMSO. These spectra were obtained from the ^{1}H onepulse (① to ⑤) and {^{1}H-^{29}Si}-^{1}H (⑥) DCPi ssNMR experiments. Samples used for obtaining these spectra are ①"SiNP-as received", ②liquid DMSO-H6, ③liquid water, ④DMSO-d_6-adsorbed SiNP and ⑤&⑥DMSO-H_6-adsorbed SiNP, respectively. For spectra ① to ③, RD = 2 s and NS = 4. For spectra ④&⑤, RD = 4 s and NS = 4. For spectrum ⑥, RD = 4 s , NS = 2048, t_{cp1} = t_{cp2} = 5 ms.

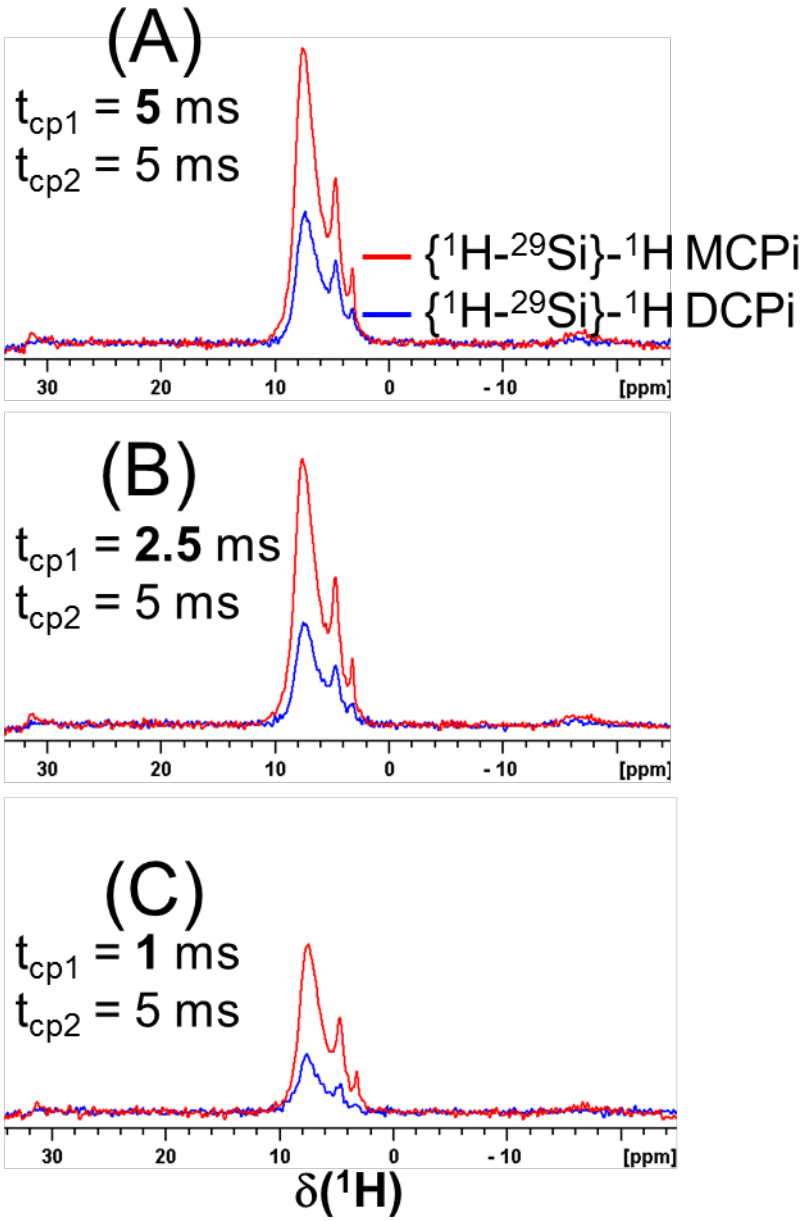


Fig. S4 The sensitivity comparison between {^{1}H-^{29}Si}-^{1}H MCPi and DCPi (RD = **0.44** s, t_{cp1} = 1.0, 2.5 & 5.0 ms, t_{cp2} = 5 ms, *m* = 3 for MCPi). Sample is DMSO-adsorbed SiNP (SiNP: DMSO-h_6 = 0.20 g : 0.11 g).

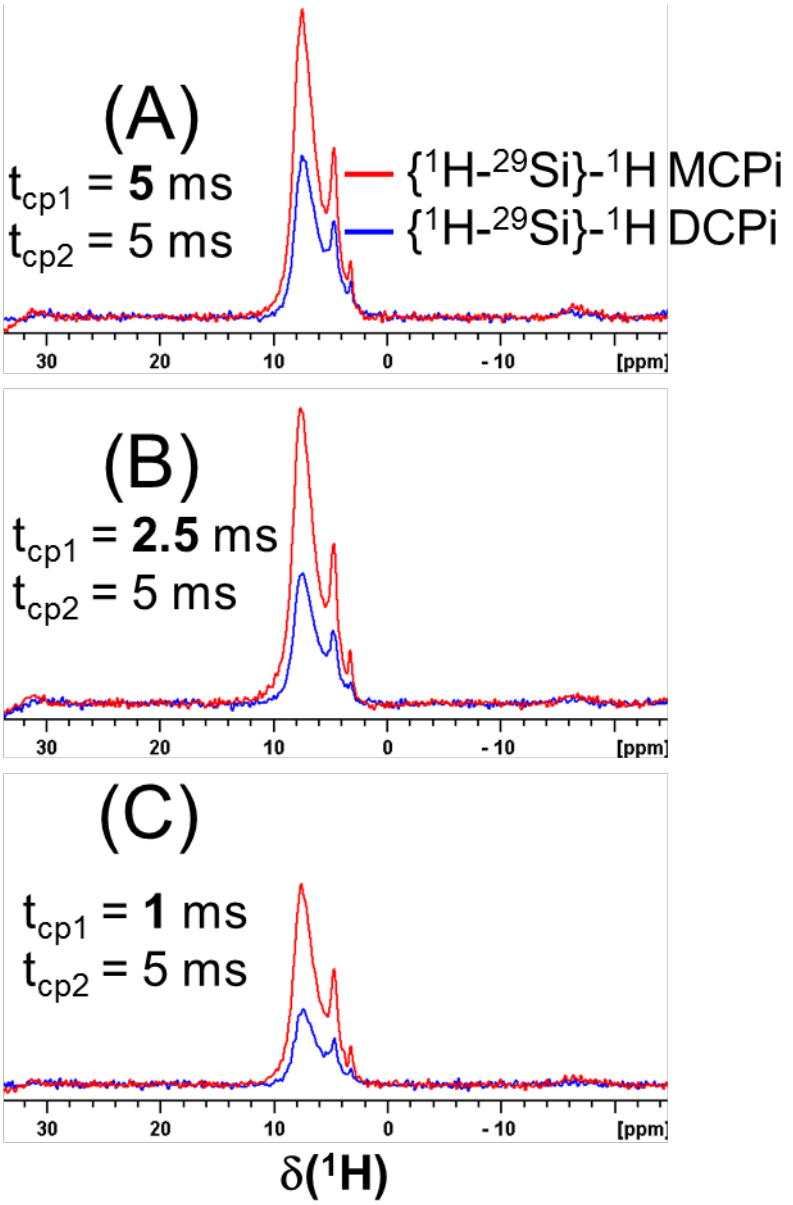


Fig. S5 The sensitivity comparison between {^{1}H-^{29}Si}-^{1}H MCPi and DCPi (RD = **4.0 s**, t_{cp1} = 1.0, 2.5 & 5.0 ms, t_{cp2} = 5 ms, *m* = 3 for MCPi). Sample is DMSO-adsorbed SiNP (SiNP: DMSO-h_6 = 0.20 g : 0.11 g).

Supplementary Information

Table S1. Comparison of the signal-to-noise ratio (S/N) between MCPi and DCPi sequences for DMSO-adsorbed SiNP (SiNP: DMSO-h_6 = 0.20 g : 0.11 g).

	DCPi Experiment (**RD = 0.44 s**)			
t_{cp1}/ms	Experiment time per scan, Expt/s	S/N for Silanol peak (6.5 to 8.0 ppm)	S/N for water peak (4.0 to 5.0 ppm)	S/N for DMSO peak (2.9 to 3.5 ppm)
1.00	0.5600	17.61	8.51	2.10
2.50	0.5615	29.43	16.93	6.00
5.00	0.5640	37.62	23.70	9.94
	MCPi Experiment (**RD = 0.44 s**)			
1.00	2.6620	41.70	23.43	9.94
2.50	2.6665	59.84	33.25	14.87
5.00	2.6740	82.18	45.92	20.83
Note: the noise region was defined from 15 to 25 ppm.				

Table S2. Comparison of the signal-to-noise ratio (S/N) between MCPi and DCPi sequences for DMSO-adsorbed SiNP (SiNP: DMSO-h_6 = 0.20 g : 0.11 g).

	DCPi Experiment (**RD = 4.0 s**)			
t_{cp1}/ms	Experiment time per scan, Expt/s	S/N for Silanol peak (6.5 to 8.0 ppm)	S/N for water peak (4.0 to 5.0 ppm)	S/N for DMSO peak (2.9 to 3.5 ppm)
1.00	4.1200	18.95	11.51	3.93
2.50	4.1215	35.83	19.86	5.74
5.00	4.1240	48.69	28.96	10.83
	MCPi Experiment (**RD = 4.0 s**)			
1.00	6.2220	62.73	36.08	11.93
2.50	6.2265	66.44	35.96	11.90
5.00	6.2340	94.04	51.84	17.17
Note: the noise region was defined from 15 to 25 ppm.				

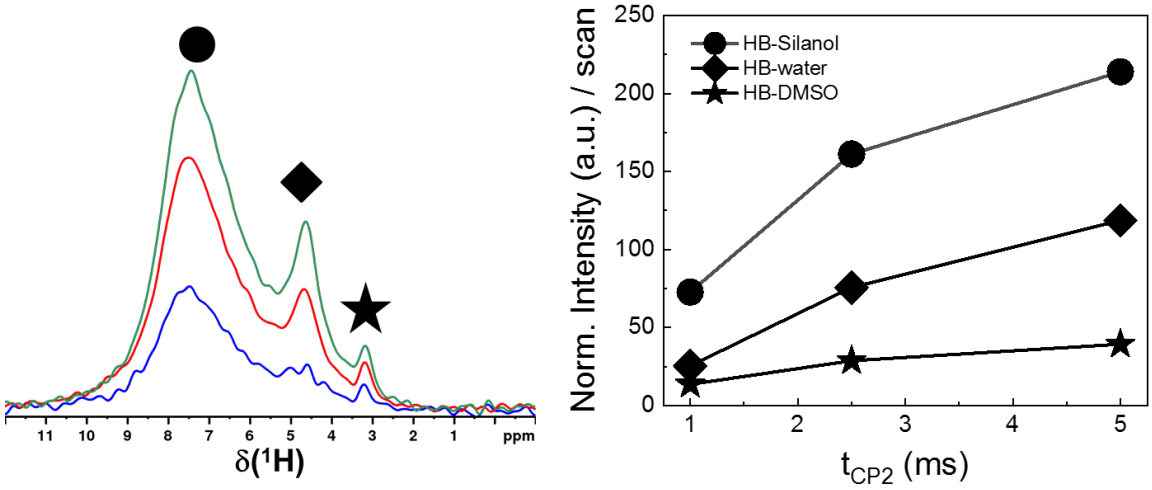


Fig. S6 The sensitivity dependence on t_{cp2} in the {^{1}H-^{29}Si}-^{1}H MCPi experiment (t_{cp1} = 5 ms, t_{cp2} = variable, m = 3). Sample is DMSO-adsorbed SiNP (SiNP: DMSO-h_6 = 0.20 g : 0.11 g).

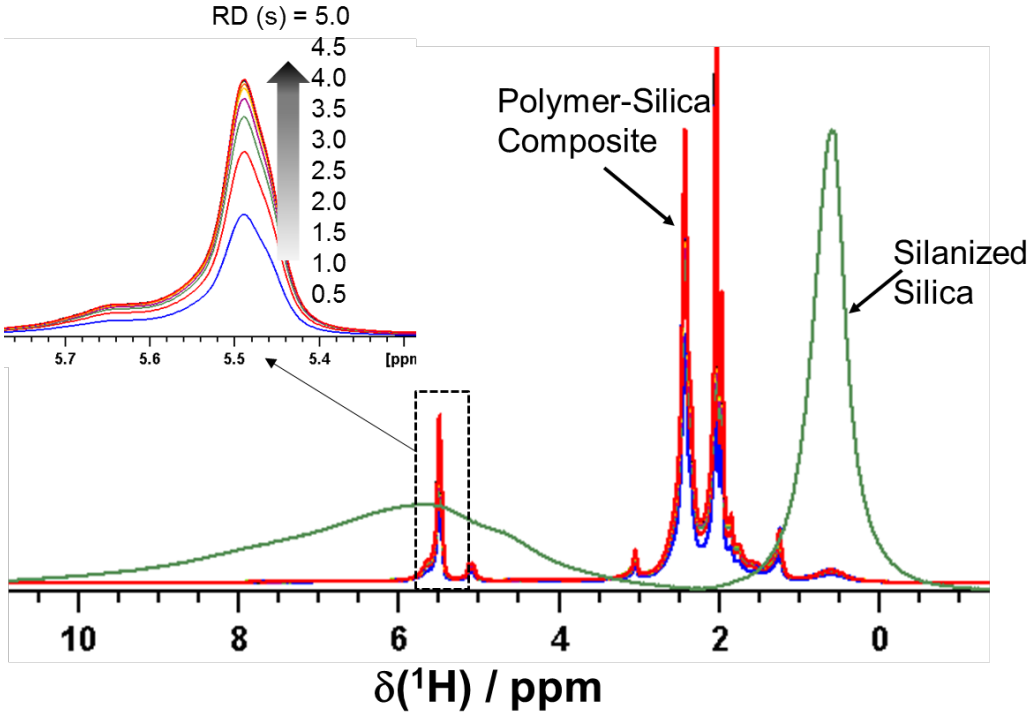


Fig. S7 ^{1}H one-pulse spectra of silanized silica (RD = 4.0 s) and polymer-silica composite (RD = 0.5 to 5.0 s).

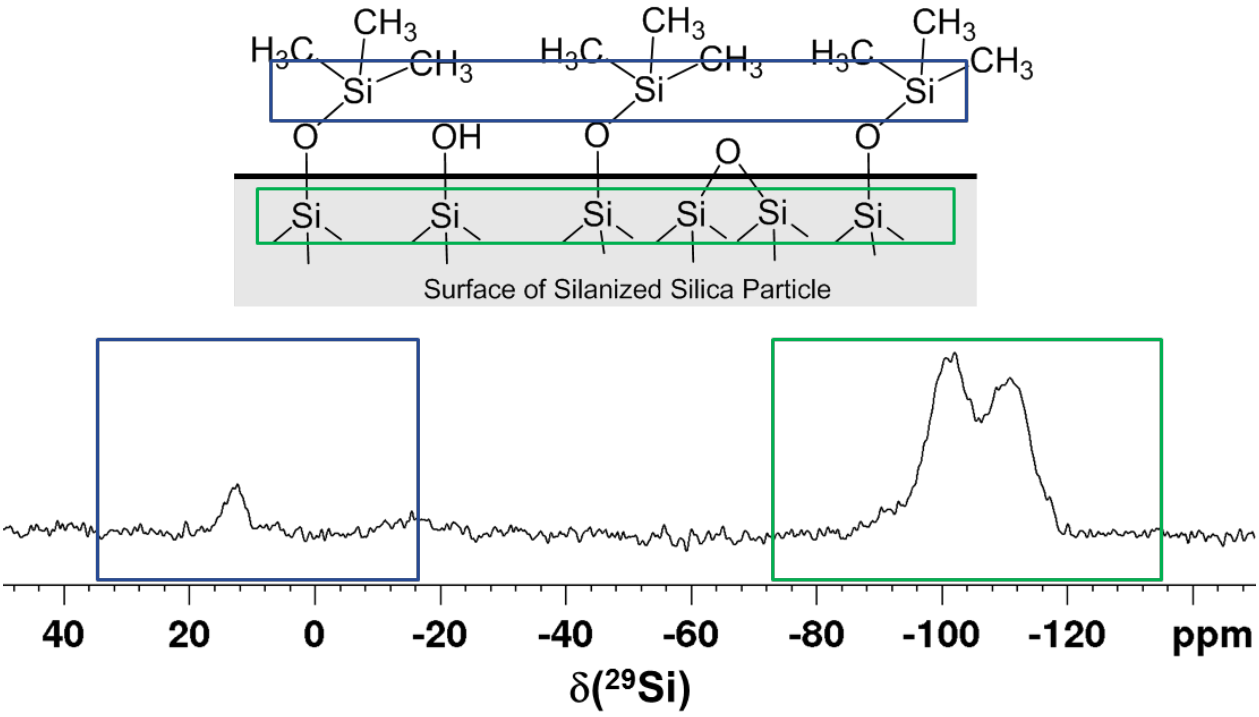


Fig. S8 ^{29}Si multiCP spectrum of the polymer-silica composite obtained by the pulse sequence of Fig. S1C. Acquisition parameters: MAS speed = 14 kHz, RD = 4.0 s, τ_{rel} = 0.7 s, contact time = 5 ms, multiCP looping number m = 2 (*i.e.* 3 contacts in total) and accumulation of 662 scans.

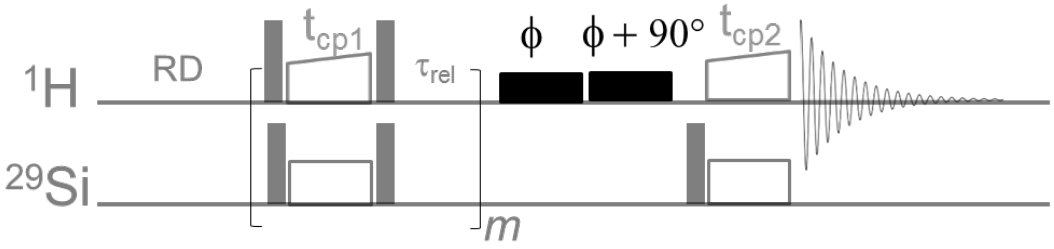


Fig. S9 For the sample containing large organic molecule, the saturation pulse train of Fig. S1A & B was replaced by a more efficient scheme, which consists of two long out-of-phase pulses at low power (each pulse duration is 500 ms and pulse power level is 1 Watts, respectively). This saturation scheme has been reported previously.[4, 5]

Table S3. The signal-to-noise ratio (S/N) of the DCPi/MCPi spectra of the polymer-silica composite.

m=	Experiment time per scan, Expt/s	S/N for silanol peak (5.5 to 8.0 ppm)	S/N for water peak (3.0 to 5.0 ppm)	S/N for silane peak (0.0 to 1.0 ppm)
1	5.0600	8.06	13.95	24.12
3	7.1700	11.65	18.14	36.05
6	9.2850	16.05	26.57	49.21
Note: the noise region was defined from 15 to 25 ppm.				

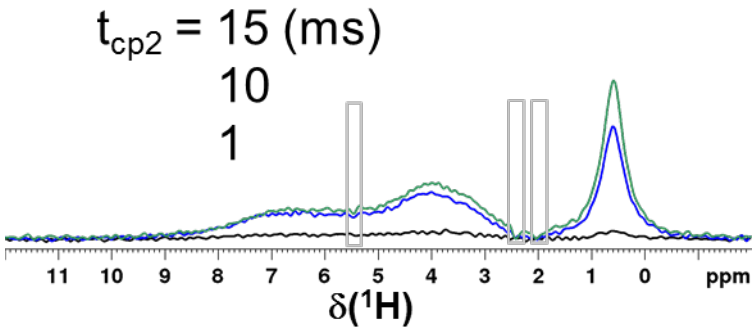


Fig. S10 {^{1}H-^{29}Si}-^{1}H MCPi spectra of the polymer-silica composite obtained by a slightly modified pulse sequence (Fig. S9): RD= 4.0 s, t_{cp1} = 5 ms, τ_{rel} = 0.7 s, m = 3 and t_{cp2} = 1 ms (black), 10 ms (blue) and 15 ms (green). Grey boxed are the regions where the polyisoprene signals would be expected.

References:

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