Supporting Information for:

Silica–surface reorganization during organotin grafting evidenced by ¹¹⁹Sn DNP SENS: a tandem reaction of gem-silanols and strained siloxane bridges

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General Considerations.

All experiments related to surface-modifications were carried out under an inert argon atmosphere. Allyltributylstannane was purchased from Aldrich. Toluene and pentane were dried by passage through two columns of activated alumina. Toluene- d_8 was dried over Na/benzophenone and degassed by three freeze-pump-thaw cycles. Gas chromatography was performed on an Agilent 7980A GC with flame ionization detection. Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer. Elemental analyses were performed by the Mikroanalytisches Labor Pascher, Remagen, Germany.

General Procedure for Bu₃Sn(allyl) grafting on dehydroxylated silica

Dehydroxylated silica (Aerosil-200, Degussa, 200 mg) was suspended in toluene- d_8 (1 mL) containing allyltributylstannane (0.1 mL) and heated to 110 °C for 3 days in a sealed rotafloe under static argon. The volatile contents were transferred to an NMR tube containing ferrocene as an internal standard, and the propene and butane were quantified using ¹H NMR spectroscopy. The solid was washed washed with toluene (2 x 4 mL) and pentane (10 mL). The solid was dried on a high vac line (10⁻⁵ mbar) and stored in an Ar filled glovebox.

DNP Solid-state NMR Experiments. DNP solid-state NMR experiments were performed on a 400 MHz (¹H/electron Larmor frequencies) Bruker Avance III solid-state NMR spectrometer equipped with a 263 GHz gyrotron. The sweep coil of the main superconducting coil was set so that microwave irradiation occurred at the positive enhancement maximum of TOTAPOL. A low temperature triple resonance 3.2 mm probe configured for ¹H-¹¹⁹Sn-¹³C was employed for most DNP experiments. DNP enhanced ²⁹Si CPMAS experiments were performed with the same 3.2 mm probe configured in double resonance ¹H-²⁹Si mode. Sample temperatures during DNP experiments were around 110 K. DNP enhancements were measured by comparing the intensity of spectra acquired with and without continuous wae microwave irradiation. Typically 20 mg of powdered material was impregnated with 20 μ L of 16 or 14 mM TEKPol tetrachloroethane solution. Impregnated materials were then packed into sapphire rotors. CPMAS experiments were performed with a linearly ramped spin lock pulse on ¹H which varied in amplitude from 50 kHz to 100 kHz. ¹¹⁹Sn spin lock rf fields were then optimized to obtain maximum signal. SPINAL-64 heteronuclear ¹H decoupling was employed during acquisition.¹ ¹H *e*-DUMBO-1₂₂ homo-nuclear dipolar decoupling was applied with an rf field of 100 kHz during *t*₁ of hetero-nuclear ¹H-X dipolar CP HETCOR experiments. Echo re-constructed ¹¹⁹Sn CP-CPMG solid-state NMR spectra (Figure 2 of main text) were obtained by summing each of the echoes in the CPMG train in the time domain.^{2, 3} The FID was then truncated to a single summed echo, apodized with a centered Gaussian function and spectra were then Fourier transformed and phased by applying a large first order phase correction. Additional details on NMR experiments are provided in the figure captions.

Table S1. Quantification of Volatiles

Dehydroxylation	Propene (mmol/g)	Butane (mmol/g)
Temp		
300	0.56	0.0003
500	0.28	0.0004
700	0.25	0.02
800	0.11	0.006
1000	0.088	0.005

Dehydroxylation	‰ _{wt} Sn	‰ _{wt} C	‰ _{wt} H
Temperature			
300 °C	5.12	6.42	1.25
500 °C	4.89	6.07	1.15
700 °C	4.19	5.62	1.06
800 °C	1.43	2.02	0.41
1000 °C	1.35	1.85	0.35

 Table S2. Elemental analysis of Bu₃Sn(allyl)@SiO₂



Figure S1. a) ²⁹Si CPMAS NMR of Bu₃Sn(allyl)@SiO₂₋₇₀₀ acquired at 298 K in a 4 mm rotor at 5 kHz spinning. The recycle delay was 4 s between scans and 40000 scans were collected; b) ²⁹Si CPMAS NMR of SiO₂₋₇₀₀ acquired at 298 K in a 4 mm rotor at 5 kHz spinning. The recycle delay was 4 s between scans and 40 k scans were collected.



Figure S2. ²⁹Si solid-state NMR of SiO_{2-800} acquired at 298 K in a 4 mm rotor at 5 kHz spinning. The recycle delay was 5 s between scans and 40000 scans were collected.



Figure S3. ²⁹Si solid-state NMR of SiO₂₋₁₀₀₀ acquired at 298 K in a 4 mm rotor at 5 kHz spinning. The recycle delay was 5 s between scans and 40000 scans were collected.



Figure S4. DNP enhanced ²⁹Si CPMAS NMR of Bu₃Sn(allyl)@SiO₂₋₇₀₀ (20 mg) impregnated with 20 μ L of 14.1 mM Tekpol TCE solution. Spectra were acquired at ca. 110 K with a 3.2 mm sapphire rotor and a 10 kHz MAS frequency. 272 scans were acquired with a 4 s recycle delay. The arrow indicates the expected position of silicon T sites. The absence of T sites indicates that there was no transfer of butyl groups to silicon.



Figure S5. 400 MHz DNP SENS spectra of SnBu₃@SiO₂(700°C) (20 mg) impregnated with 20 µL of 14.1 mM Tekpol in TCE. $\omega_r/2\pi$ = 12500 Hz **1**) ¹H MAS NMR, 8 scans, recycle delay of 2 s, microwave on (a) and microwave off (b). **2**) ¹³C CPMAS, the recycle delay was 4.5 s, the contact time was 0.5 ms (a) microwave on, 64 scans; (b) microwave off 64 scans. **3**) ¹H-¹³C HETCOR, the recycle delay was 4.5 s, the contact time was 250 µs, 4 scans, 80 t_1 increments. **4**) ¹¹⁹Sn CPMAS (a) and CPMG (b,c), the recycle delay was 4.5 s, the contact time was 2 ms: (a) 128 scans, CPMAS spectra microwave on; (b) CPMG, 32 scans, microwave on; (c) CPMG, 128 scans, microwave off. **5**) ¹H-¹¹⁹Sn HETCOR, the recycle delay was 4.5 s, the contact time was 500 µs, 64 scans, 80 t_1 increments.



Figure S6. 400 MHz DNP SENS spectra of SnBu₃@SiO₂(800°C) (20 mg) impregnated with 20 μ L of 16 mM Tekpol in TCE. $\omega_r/2\pi$ = 12500 Hz **1**) ¹H MAS NMR, 8 scans, recycle delay of 3 s, microwave on (a) and microwave off (b). **2**) ¹³C CPMAS, the recycle delay was 3 s, the contact time was 1.5 ms (a) microwave on, 32 scans; (b) microwave off 32 scans. **3**) ¹H-¹³C HETCOR, the recycle delay was 4.5 s, the contact time was 500 μ s, 8 scans, 64 t_1 increments. **4**) ¹¹⁹Sn CPMAS (a) and CPMG (b,c), the recycle delay was 4 s, the contact time was 2 ms: (a) 1024 scans, CPMAS spectra microwave on; (b) CPMG, 1024 scans, microwave on; (c) CPMG, 128 scans, microwave off.



Figure S7. 400 MHz DNP SENS spectra of SnBu₃@SiO₂(1000°C) (20 mg) impregnated with 20 μ L of 16 mM Tekpol in TCE. $\omega_r/2\pi$ = 12500 Hz **1**) 1H MAS NMR, 8 scans, recycle delay of 3 s, microwave on (a) and microwave off (b). **2**) ¹³C CPMAS, the recycle delay was 3 s, the contact time was 1.5ms (a) microwave on, 32 scans; (b) microwave off 32 scans. **3**) ¹¹⁹Sn CPMG (a,b), the recycle delay was 4 s, the contact time was 2ms: (b) CPMG, 512 scans, microwave on; (c) CPMG, 128 scans, microwave off.



Figure S8. 400 MHz DNP SENS spectra of SnBu₃@SiO₂(300°C) (20mg) impregnated with 20 µL of 14.1mM Tekpol in TCE. $\omega_r/2\pi = 12500$ Hz 1) 1H MAS NMR, 8 scans, recycle delay of 2s, microwave on (a) and microwave off (b). 2) ¹³C CPMAS, the recycle delay was 4s, the contact time was 0.5ms: (a) microwave on, 32 scans; (b) microwave off 512 scans. 3) ¹H-¹³C HETCOR, the recycle delay was 4s, the contact time was 250µs, 8 scans, 80 t_1 increments. 4) ¹¹⁹Sn CPMAS (a) and CPMG (b,c), the recycle delay was 4 s, the contact time was 2 ms: (a) CPMAS spectra microwave on, 512 scans; (b) CPMG, 512 scans, microwave on; (c) CPMG, 256 scans, microwave off. 5) ¹H-¹¹⁹Sn HETCOR, the recycle delay was 4 s, the contact time was 250 µs, 32 scans, 80 t_1 increments.

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Figure S9. 400 MHz DNP SENS spectra of SnBu₃@SiO₂(500°C) (20mg) impregnated with 20 μ L of 14.1mM Tekpol in TCE. $\omega_r/2\pi = 12500$ Hz **1)** 1H MAS NMR, 8 scans, recycle delay of 2 s, microwave on (a) and microwave off (b). **2)** ¹³C CPMAS, the recycle delay was 4 s, the contact time was 0.5 ms: (a) microwave on, 64 scans; (b) microwave off 128 scans. **3)** ¹H-¹³C HETCOR, the recycle delay was 4 s, the contact time was 250 μ s, 4 scans, 80 t_1 increments. **4)** ¹¹⁹Sn CPMAS (a) and CPMG (b,c), the recycle delay was 4 s, the contact time was 2 ms: (a) 128 scans, CPMAS spectra microwave on; (b) CPMG, 128 scans, microwave off. **5)** ¹H-¹¹⁹Sn HETCOR, the recycle delay was 4 s, the contact time was 500 μ s, 32 scans, 80 t_1 increments.



Figure S10. 400 MHz DNP SNS spectra of **(a)** Sn(allyl)Bu₃ SiO₂ (300°C), 512 scans, the recycle delay was 4 s, the contact time was 2 ms; **(b)** Sn(allyl)Bu₃ (500°C), 128 scans, the recycle delay was 4 s, the contact time was 2 ms; **(c)** Sn(allyl)Bu₃ (300°C), 32 scans, the recycle delay was 4.5 s, the contact time was 2 ms; **(d)** Sn(allyl)Bu₃ SiO₂ (300°C), 1024 scans, the recycle delay was 4.5 s, the contact time was 2 ms; **(e)** Sn(allyl)Bu₃ SiO₂ (1000°C), 512 scans, the recycle delay was 4.5 s, the contact time was 2 ms; **(e)** Sn(allyl)Bu₃ SiO₂ (1000°C), 512 scans, the recycle delay was 4.5 s, the contact time was 2 ms; **(a)** Sn(allyl)Bu₃ SiO₂ (1000°C), 512 scans, the recycle delay was 4.5 s, the contact time was 2 ms. All spectra were measured with $\omega_r/2\pi = 12500$ Hz.

Table S3. Summary of the different enhencement and T1 relaxation (measured with a ${}^{1}H/{}^{13}C$ CPMAS saturation recovery sequence) obtain with Bu₃Sio₂@SiO₂ 300, Bu₃Sio₂@SiO₂ 500 and Bu₃Sio₂@SiO₂ 700.

	Bu ₃ Sio ₂ @SiO ₂ 300	Bu ₃ SiO ₂ @SiO ₂ 500	Bu ₃ Sio ₂ @SiO ₂ 700
ε(1H)	93	90	116
E(13C solvent)	101	87	116
ε(¹³ C Surface)	64	52	97
ε(¹¹⁹ Sn)	>58	>50	>56
T_1 (¹ H solvent) ^a	3.1 s	2.8 s	3.1 s
T_1 (¹ H surface) ^a	3.2 s	3.1 s	3.4 s

	Bu ₃ Sio ₂ @SiO ₂ 800	Bu ₃ SiO ₂ @SiO ₂ 1000
ε(1H)	147	88
E(¹³ C solvent)	59	>88
ε(¹³ C Surface)	57	>88
ε(¹¹⁹ Sn)	>57	>71
$\hat{T}_1 (^1 \text{H})$	4.1 s	3.2 s

^aProton longitudinal relaxation times were measured with a saturation recovery pulse sequence with ¹³C CPMAS signal detection. The "solvent" and "surface" T_1 's correspond to the proton T_1 measured for the TCE and butyl resonances.



Figure S11. Infrard spectra of (allyl)SnBu₃@SiO₂ recorded on silica dehydroxylated at the temperatures shown in the figure.

Computational Details.

The monografted tin [\equiv SiOSnBu₃] species and the *bis*-grafted tin species: [=Si(OH)OSnBu₃], [=Si(O)₂SnBu₂], and [(\equiv SiO)₂SnBu₂] were all modeled using cluster models. All of these clusters were terminated with –OSi(OH)₃ groups. The geometries were initially optimized by means of the Gaussian 09 program package⁴ at B3LYP level⁵⁻⁷ using the LANL2DZ pseudopotential⁸ with *d* polarization functions for the Sn atom⁹ and the 6-31G(d,p) basis set for Si, O, C and H atoms. Gibbs free energies were calculated as implemented in Gaussian 09. In order to account for dispersion effects, the Sn complexes were re-optimized by means of the M06 density functional.¹⁰

For the monografted tin [\equiv SiOSnBu₃] species we also calculated the chemical shift on one additional structure (see Figure S10).

For all the optimized geometries from Gaussian 09, the ¹¹⁹Sn shieldings were calculated for the cluster geometries at the B3LYP level including relativistic effects with the ZORA method¹¹⁻¹³ at spin-orbit (SO) level with the TZP basis set using the NMR module^{14, 15} of the ADF code.¹⁶⁻¹⁸ We used B3LYP instead of M06 since meta-GGA's and meta-hybrids (e. g. M06) should not be used in combination with NMR chemical shielding calculations. The results are wrong due to an incorrect inclusion of GIAO terms. A similar methodology was successfully implements for chemical shift calculation for a series of Sn compounds.¹⁹ Calculated ¹¹⁹Sn chemical shielding values were converted to chemical shift values by comparison to the calculated isotropic chemical shielding of SnMe₄.



Figure S12. Additional structure of the [\equiv SiOSnBu₃] monografted species, with a ¹¹⁹Sn chemical shift = 82 ppm

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