

## Supporting Information

### Monolayer Doping of Silicon through Grafting a Tailored Molecular Phosphorus Precursor onto Oxide-Passivated Silicon Surfaces

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## SI 1. General procedures and Methods

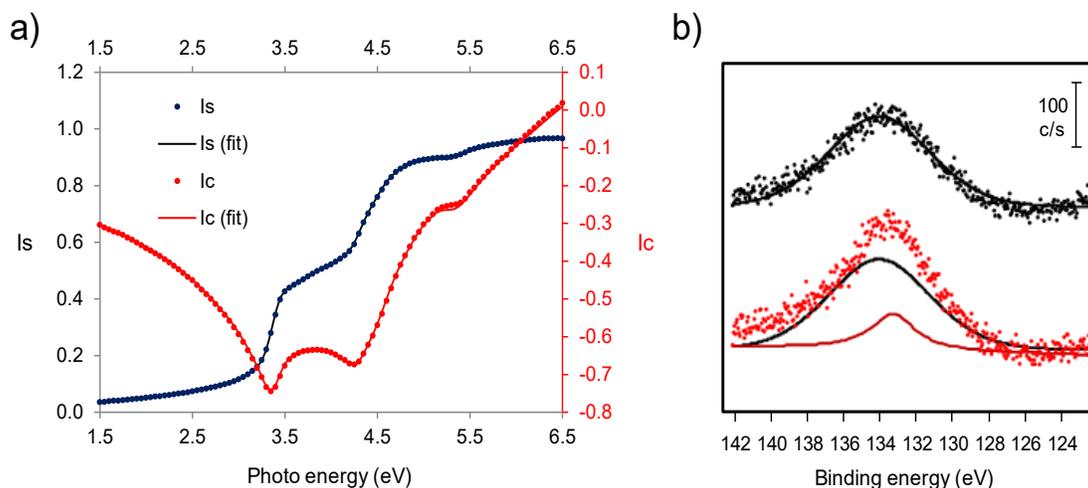
### Experimental

*Samples preparation.* All experiments, otherwise stated, were carried out under dry and oxygen free Ar atmosphere using either standard Schlenk or glovebox techniques for the organic synthesis. For syntheses and treatments of surface species, reactions were carried out using high vacuum lines ( $10^{-5}$  mbar). Elemental analyses were performed at “Mikroanalytisches Labor Pascher” in Germany. Toluene, and pentane were dried using an MBraun solvent purification system, contacted with molecular sieves 4 Å and degassed under vacuum. Hepta-isobutyl-POSS triol (POSS-OH), phosphorus trichloride ( $\text{PCl}_3$ ), diethyl-benzyl phosphonate (DEBP), ethyl-tosylate and triethylamine ( $\text{Et}_3\text{N}$ ) were purchased from Sigma Aldrich.  $\text{PCl}_3$  and  $\text{Et}_3\text{N}$  were distilled prior to use. The  $\text{SiO}_2/\text{Si}$  wafers were 30 cm in diameter, *p*-doped ( $10^{15}$  B.cm<sup>-3</sup>) and double-face polished. Wafers with native oxide (~1.5 nm) were used as received. Chemical oxides (~0.7 or ~0.9 nm) were grown on silicon wafers in a SU-3100 from DNS, in clean rooms of LETI, CEA Grenoble. RTP and ICP-MS analyses on wafers were also performed in clean rooms (CEA Grenoble). RTP annealing experiments were done in a JetFirst 200 (Jipelec) using BT or HT type optical pyrometer and 2 K type (Chromel/Alumel) Ø 0.127 mm thermocouples.

*Conventional NMR experiments.* Liquid-state NMR spectra were recorded using a Bruker Spectrospin 300 MHz spectrometer. For *conventional solid-state NMR*, 40 to 50 mg of material was packed in 4.0 mm zirconia NMR rotor under inert atmosphere. NMR spectra were acquired either on a 300 MHz (<sup>29</sup>Si) or 500 MHz (<sup>1</sup>H/<sup>13</sup>C/<sup>31</sup>P) ultrashielded Bruker NMR spectrometer. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>29</sup>Si spectra were recorded using a 4.0 mm cross-polarization (CP) magic angle spinning (MAS) probe with a sample temperature of 294 K and sample spinning frequencies between 5 to 10 kHz. Standard CP was used to record <sup>29</sup>Si and <sup>13</sup>C spectra.

*DNP SENS experiments.* 12.5 to 14.7 mg of material was wetted with 20 to 25  $\mu\text{l}$  of a solution of 16 mM TEKPol in 1,1,2,2-tetrachloroethane. The impregnated powder was then packed into a 3.2 mm NMR rotor, under air. A sapphire NMR rotor was used to maximize microwave penetration throughout the sample. The rotor was capped with a zirconia drive cap and quickly inserted into the DNP spectrometer. Several insert and eject cycles were performed to guarantee good glass quality as well as de-oxygenation of the sample. All spectra were acquired on a Bruker Avance I or Avance III 400 MHz DNP NMR spectrometer equipped with a 263 GHz gyrotron microwave system ( $B_0 = 9.4 \text{ T}$ ,  $\omega_{\text{H}}/2\pi = 400 \text{ MHz}$ ,  $\omega_{\text{P}}/2\pi = 162.0 \text{ MHz}$ ).<sup>1</sup> The field sweep coil of the NMR magnet was set so that MW irradiation occurred at the DNP enhancement maximum of TOTAPOL, with an estimated 8 W power of the MW beam at the output of the probe waveguide.  $^1\text{H}$  and  $^{31}\text{P}$  DNP-SENS spectra were recorded using a triple resonance low-temperature CPMAS probe with a sample temperature of 105 K and sample spinning frequencies between 8 to 12.5 kHz. SPINAL-64 heteronuclear decoupling<sup>2</sup> was applied during acquisition ( $\omega_{\text{H}}/2\pi = 100 \text{ kHz}$ ). Standard CP was used for  $^{31}\text{P}$  spectra where SPINAL-64 proton decoupling was applied during the acquisition. Processing of the spectra and fitting of the chemical shift anisotropy (CSA) parameters was done using the Topspin software package.  $^1\text{H}$ ,  $^{13}\text{C}$  and chemical shifts are referenced to TMS at 0 ppm.

*Ellipsometric measurements.* The  $\text{SiO}_2/\text{Si}$  model used to fit ellipsometric data (Figure S1-a) was considered to be a relevant model for the POSS-P, which contains a silica-like scaffold. Comparison of the very good fits obtained for reference and grafted samples shows an increase of about 1.0 ( $\pm 0.2$ ) nm of thickness after deposition of POSS-P. Such an increase of thickness is similar to the calculated projected radius of POSS-P ( $\sim 0.8 \text{ nm}$ ), and is consistent with monolayer formation previously reported for other B- or P-species.<sup>3,4</sup> we thus assumed that a monolayer of surface species was formed after grafting POSS-P.



**Figure S1.** (a) Ellipsometric data (dots) and corresponding fit (lines), obtained for POSS-P/SiO<sub>2</sub>/Si wafer, (b) XPS analysis with P 2p region before (black dots) and after (red dots) grafting POSS-P onto SiO<sub>2</sub>/Si.

*XPS analysis.* XPS spectra were recorded on a VersaProbe II spectrometer from Physical Electronics equipped with a 180° hemispherical electron energy analyzer, and using a high-resolution monochromatic Al-K $\alpha$  line X-ray source at 1486.7 eV. A pass energy of 23 eV was used for core level analysis leading to an overall energy resolution of 0.6 eV. The photoelectron take-off angle was 45°, yielding an integrated sampling depth of approximately 5 nm. Measurements were made at ambient temperature, at a pressure lower than 10<sup>-8</sup> Pa in the analysis chamber. All spectra were referenced against the C 1s level peak at a binding energy of 284.8 eV. The spectra were analyzed using the CASA XPS software. XPS samples were prepared as follows: SiO<sub>2</sub>/Si wafer<sub>(140)</sub> were immersed into a 80  $\mu$ M pentane solution of POSS-P under argon, and the temperature was raised to 30°C until pentane evaporation, giving POSS-P adsorbed onto wafer<sub>(140)</sub>. Subsequent rinsing with pentane removed physisorbed species and led to chemisorbed POSS-P/wafer<sub>(140)</sub>.

Figure S1-b. shows P 2p region of POSS-P/SiO<sub>2</sub>/Si (red dots) and SiO<sub>2</sub>/Si (black dots) samples. The broad plasmon loss peak of silicon centered at 134 eV is visible on the black spectrum (black line), and partly overlaps the P 2p photopeak of P species on the red spectrum which is highlighted by the red line. An unresolved P 2p<sub>3/2</sub>, 2p<sub>3/2</sub> photopeak centered at ~133.3 eV is thus observed (red solid line), and is assigned to P(V) species,<sup>4</sup> chemisorbed on the substrate.<sup>4-6</sup>

*Other analyses:* An Agilent ICP-MS-MS 8800 was used for the ICP-MS measurements with the following parameters: analysis hot plasma mode (1500W), O<sub>2</sub> as reacting gas (mass 31 (P) on detector n°1, mass 47 (P + O<sub>2</sub>) on detector n°2). Time of flight SIMS analyses were performed on a TOF SIMS 5 instrument from IONTOF. FTIR spectra recorded in diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) mode were obtained on a Nicolet 6700 FT-IR spectrometer equipped with a HgCdTe (MCT) detector cooled with liquid N<sub>2</sub>. The samples were loaded into a custom DRIFT cell equipped with CaF<sub>2</sub> windows under inert atmosphere (glovebox). Typically, 32 to 64 scans were acquired (4 cm<sup>-1</sup> resolution).

*Synthesis of hepta-isobutyl-polyhedral oligomeric silsesquioxane phosphorus triester (POSS-P).*

In a schlenk was prepared a 20 mL-toluene solution of POSS-OH (1.159 g, 1.46 mmol) and Et<sub>3</sub>N (0.730 mL, 3.3 eq.) under gentle stirring. A 10 mL-toluene solution of PCl<sub>3</sub> (0.145 ml, 1.60 mmol, 1.1 eq.) was then added dropwise over 10 min. A white slurry immediately appeared, and the solution was left to react for 2 h. Volatiles were removed *in vacuo*, and the remaining solid was suspended in pentane and filtrated over Celite®. Recrystallisation of the resulting solution (-30 °C, overnight) yielded crystals collected in two crops, which were dried under vacuum to give pure **POSS-P** as a white powder. Yield: 34% (0.411 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): δ<sub>H</sub>= 2.1 (m, 1H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.1 (d, 6H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 0.8 (d, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (ppm): δ<sub>C</sub>= 25.9 (2C, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 24.3 (1C, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 23.0 (1C, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (ppm): δ<sub>Si</sub>= -66.3 (3Si, Si-O-P), -67.4, -67.5, -70.5, -71.1 (4Si, Si-O-Si). <sup>31</sup>P NMR (ppm): δ<sub>P</sub>= 84.7.

*Synthesis of tosylate tributyl-ethylphosphonium (TBEP).* In a 100 mL Schlenk flask blown with argon, 12.223 g of ethyl-tosylate (61.0 mmol) were diluted in 44 mL of toluene. Then, 14 mL of tributylphosphine (11.3 g; 56.1 mmol, 0.9 eq) were added to the solution. A water cooler was adapted to the flask and the mixture was heated up and left to be stirred at 90 °C overnight (12 h). All volatiles were then taken *in vacuo*. The flask was cooled down to RT (24 °C) and the resulting white solid was then suspended in dry diethyl ether and filtered. The product was heated up to 90°C and melted down, and all volatiles were taken *in vacuo*. The flask was again allowed to cool down to RT (24 °C) and stored in the glovebox. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, ppm): δ<sub>H</sub>= 0.97 (m, 9H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.28 ppm (m, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.52 ppm (large peak, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>CH<sub>3</sub>), 2.34 ppm (s;3H; CH<sub>3</sub>-Tos), 2.45 (m, 12H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 7.14 ppm (d, 10 Hz, 2H, H<sub>Ar\_Tos</sub>), 7.81 ppm (d; 10 Hz; 2H, H<sub>Ar\_Tos</sub>). <sup>31</sup>P NMR (ppm): δ<sub>P</sub>= 34.6.

## Study on silica nanoparticles (NPs).

*Preparation of partially dehydroxylated silica at 700 °C (SiO<sub>2-(700)</sub>). Representative procedure.*

Silica (Aerosil Degussa, 200 m<sup>2</sup>.g<sup>-1</sup>) was compacted using distilled water and dried at 110°C for 5 days in an oven. The obtained compacted solids were broken down in a mortar and sieved to yield agglomerates of about 50 meshes (particles of ca. Ø ≈ 20 nm). The thus-obtained powder was calcined for 5 h under air at 500 °C (6 °C.min<sup>-1</sup>), partially dehydroxylated at 500°C in secondary vacuum (10<sup>-5</sup> mbar) for 12 h, then at 700 °C for 10 h, and finally stored in the glovebox. **S<sub>BET</sub>** (m<sup>2</sup>.g<sup>-1</sup>): 197. **IR** (cm<sup>-1</sup>): 3747 (isolated SiOH), 3600 (large peak, very low intensity, bonded SiOH).

*Preparation of partially dehydroxylated silica at 500 °C (SiO<sub>2-(500)</sub>). SiO<sub>2-(500)</sub> was prepared according to the representative procedure. **S<sub>BET</sub>** (m<sup>2</sup>.g<sup>-1</sup>): 198. **IR** (cm<sup>-1</sup>): 3745 (isolated SiOH), 3600 (large peak, low intensity, bonded SiOH).*

*Preparation of silica dehydrated at 140 °C (SiO<sub>2-(140)</sub>). Silica powder was loaded in a reactor, put under secondary vacuum (10<sup>-5</sup> mbar) and heated up to 140 °C for 17 h, and stored in the glovebox. **S<sub>BET</sub>** (m<sup>2</sup>.g<sup>-1</sup>): 196. **IR** (cm<sup>-1</sup>): 3741 (isolated SiOH), 3660 & 3540 (large peaks, medium intensity, bonded SiOH).*

*Dosing SiOH groups on SiO<sub>2-(140)</sub>. Representative procedure.* A small Schlenk was loaded with SiO<sub>2-(140)</sub> (267.4 mg) and equipped with a pressure equalizing dropping funnel loaded with ~2 ml of pentane. About 1.0 ml of BuMgCl•Et<sub>2</sub>O was added, mixed with pentane and slowly added onto silica. After 30 min under gentle stirring, the gas phase was transferred to an expansion flask (6678 ml). After 16 h, the gas phase (300 µl) was analyzed by GC (KCl alumina column, 40°C (isotherm), injector 280°C). Results (~4.6 OH/nm<sup>2</sup>) were averaged on 3 measurements.

*Grafting of POSS-P on SiO<sub>2-(500)</sub>*. Representative procedure.

POSS-P (244 mg,  $3.0 \times 10^{-4}$  mol) was solubilized in pentane (10 mL) and was subsequently contacted with SiO<sub>2-(500)</sub> (488 mg,  $\sim 3.2 \times 10^{-4}$  mol surface silanol) at 25 °C for 2.5 h, under gentle stirring. After filtration, the solid was washed 3 times with pentane, and all volatile compounds were removed *in vacuo*. The resulting solid **POSS-P/SiO<sub>2-(500)</sub>** was dried under high vacuum ( $10^{-5}$  mbar) and the grafted species were then stored under Argon. **IR** (cm<sup>-1</sup>): 3745 (weak, remaining isolated SiOH), 3703 (perturbed, H-bonded SiOH), 3326 (broad), 2960, 2934, 2909 & 2876 (ν(C-H)), 2450 & 2425 (ν(P-H)), 1468 (δ(C-H)). **<sup>1</sup>H NMR** (ppm): δ<sub>H</sub>= 6.9 (d, very weak, *H*-P, J<sub>PH</sub>~700 Hz), 1.9 (CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 0.9 (CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> and CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (CP-MAS, ppm): δ<sub>C</sub>= 23 (broad). **<sup>31</sup>P NMR** (HP-Dec, ppm): δ<sub>P</sub>= -19; -26 (sh). **<sup>29</sup>Si NMR** (CP-MAS, ppm): δ<sub>Si</sub>= -66 (T<sub>3</sub>-type Si, POSS cage), 92, 101 & 110 (Q-type Si, SiO<sub>2</sub> network). **Elemental analysis**: 4.85 wt % C, 0.91 wt % H, 0.47 wt % P, 42.4 wt % Si, *i.e.* H/C(at/at)= 2.3 (th. 2.3), C/P= 26.7 (th 28.0) and P/Si (×100)= 1.00.

*Grafting of POSS-P on SiO<sub>2-(700)</sub>*. **POSS-P/SiO<sub>2-(700)</sub>** was prepared according to the representative procedure, with 264 mg of SiO<sub>2-(700)</sub> ( $\sim 6.1 \times 10^{-5}$  mol surface silanols) and 52 mg of POSS-P ( $6.5 \times 10^{-5}$  mol). **IR** (cm<sup>-1</sup>): 3746 (remaining isolated SiOH), 3715 (perturbed, H-bonded SiOH), 3250 (broad), 2958, 2938, 2909 & 2877 (ν(C-H)), 2450 & 2425 (ν(P-H)), 1468 (δ(C-H)). **<sup>31</sup>P CP-MAS DNP-SENS** (ppm): δ<sub>P</sub>= -3, -16. **Elemental analysis**: 0.76 wt % P.

*Grafting of POSS-P on SiO<sub>2-(140)</sub>*. **POSS-P/SiO<sub>2-(140)</sub>** was prepared according to the representative procedure, with 312 mg of SiO<sub>2-(140)</sub> and 225 mg of POSS-P ( $2.7 \times 10^{-4}$  mol). **IR** (cm<sup>-1</sup>): 3690 (perturbed, H-bonded SiOH), 3430 (broad), 2960, 2934, 2909 & 2876 (ν(C-H)), 2450 & 2425 (ν(P-H)), 1468 δ(C-H). **<sup>1</sup>H NMR** (ppm): δ<sub>H</sub>= 2.0 (-CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 0.9 (-CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> and -CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (CP-MAS, ppm): δ<sub>C</sub>= 23. **<sup>31</sup>P NMR** (HP-Dec, ppm): δ<sub>P</sub>= -19, -26 (sh). **<sup>29</sup>Si NMR** (CP-MAS, ppm): δ<sub>Si</sub>= -66 (T<sub>3</sub>-type Si, POSS cage), 92, 101 & 110 (Q-type Si, SiO<sub>2</sub> network). **Elemental analysis**: 0.59 wt % P.

*Grafting of diethyl-benzyl phosphonate (DEBP) on SiO<sub>2-(700)</sub>. DEBP/SiO<sub>2-(700)</sub> was prepared according to the representative procedure, with 567 mg of SiO<sub>2-(700)</sub> ( $\sim 0.13 \times 10^{-3}$  mol surface silanols) and  $\sim 37$  mg of DEBP ( $\sim 0.16 \times 10^{-3}$  mol). IR (cm<sup>-1</sup>): 3744 (remaining isolated SiOH), 3625 (perturbed, H-bonded SiOH), 3158 (broad), 3092, 3069 & 3036  $\nu$ (Csp<sub>2</sub>-H), 2986, 2938, 2915, 2878  $\nu$ (Csp<sub>3</sub>-H), 1605 & 1588 ( $\delta$ (Csp<sub>2</sub>-H)), 1497 ( $\delta$ (Csp<sub>3</sub>-H)). **Elemental analysis:** 4.57 wt % C, 1.04 wt % P.*

*Adsorption of p-tosylate tributyl-ethylphosphonium (TBEP) on SiO<sub>2-(700)</sub>. TBEP/SiO<sub>2-(700)</sub> was prepared according to the representative procedure, with 310 mg of SiO<sub>2-(700)</sub> ( $\sim 6.6 \times 10^{-5}$  mol surface silanols) and  $\sim 34$  mg of TBEP ( $\sim 0.16 \times 10^{-3}$  mol). IR (cm<sup>-1</sup>): 3745 (remaining isolated SiOH), 3150 (broad), 2967, 2932, 2912, 2877  $\nu$ (C-H). **Elemental analysis:** 5.61 wt % C, 0.68 wt % S, 0.65 wt % P.*

*Thermal treatment of POSS-P/SiO<sub>2-(500)</sub> under air (oxidative atmosphere): 340 mg of POSS-P/SiO<sub>2-(500)</sub> were loaded in a quartz reactor and calcined at 500 °C under a flow of dry air (temperature ramp: 6 °C.min<sup>-1</sup>, air flow: 50 mL.min<sup>-1</sup>). IR (cm<sup>-1</sup>): 3746 (isolated SiOH), 3671  $\nu$ (P-OH). <sup>31</sup>P NMR (HPDec, ppm):  $\delta_P = -24, -37$ . <sup>29</sup>Si NMR (CP-MAS, ppm):  $\delta_{Si} = 92, 101 \text{ \& } 110$  (Q-type Si, SiO<sub>2</sub> network). **Elemental analysis:** 0.13 wt % C; 0.14 wt % H; 0.48 wt % P, 44.0 wt % Si, *i.e.* C/P(at/at)= 0.7 and P/Si ( $\times 100$ )= 0.99.*

*Thermal treatment of POSS-P/SiO<sub>2-(500)</sub> under argon (inert conditions): 310 mg of POSS-P/SiO<sub>2-(500)</sub> were loaded in a quartz reactor and calcined at 500 °C under a flow of argon (temperature ramp: 6 °C.min<sup>-1</sup>, argon flow:  $\sim 50$  mL.min<sup>-1</sup>). IR (cm<sup>-1</sup>): 3704, 3316, 2960, 2934, 2909, 2876, 2460 ( $\nu$ (P-H)), 2250 ( $\nu$ (Si-H)), 1468 ( $\nu$ (C-H)). <sup>31</sup>P NMR (HP-Dec, ppm):  $\delta_P = 108$  (8%),  $-19$  (92%). <sup>29</sup>Si NMR (CP-MAS, ppm):  $\delta_{Si} = -57$  (T<sub>2</sub>-type Si-OH, POSS cage),  $-66$  (T<sub>3</sub>-type Si, POSS cage), 92, 101 & 110 (Q-type Si, SiO<sub>2</sub> network). **Elemental analysis:** 4.64 wt % C; 0.86 wt % H; 0.48 wt % P, 41.3 wt % Si, *i.e.* C/P(at/at)= 25.0 and P/Si ( $\times 100$ )= 1.05.*

*Thermal treatment of DEBP/SiO<sub>2-(700)</sub> under air (oxidative atmosphere):* 200 mg of **DEBP/SiO<sub>2-(700)</sub>** were loaded in a quartz reactor and calcined at 500 °C under a flow of dry air (temperature ramp: 6 °C.min<sup>-1</sup>, air flow: 50 mL.min<sup>-1</sup>). **IR** (cm<sup>-1</sup>): 3746 (isolated SiOH), 3671 ν(P-OH).  
**Elemental analysis:** 0.16 wt % C; 0.14 wt % P.

*Thermal treatment of TBEP/SiO<sub>2-(700)</sub> under air (oxidative atmosphere):* 310 mg of **TBEP/SiO<sub>2-(700)</sub>** were loaded in a quartz reactor and calcined at 500 °C under a flow of dry air (temperature ramp: 6 °C.min<sup>-1</sup>, air flow: 50 mL.min<sup>-1</sup>). **IR** (cm<sup>-1</sup>): 3746 (isolated SiOH), 3671 ν(P-OH).  
**Elemental analysis:** 0.44 wt % C; 0.25 wt % P.

### **Surface chemistry on wafers.**

*Grafting of POSS-P on wafers.* In the glovebox, a toluene or pentane solution of **POSS-P** (~80 μM) was prepared by solubilizing the POSS-P compound into 45 mL of solvent at 25 °C. Then, the wafer pieces (2.5×8 cm<sup>2</sup>) were immersed into the solution and left to react for 2 hours. The wafer pieces were then washed 3 times with toluene (5 mL) and/or with pentane (5 mL) before being dried *in vacuo*.

*Preparation of “control” wafers.* A wafer pieces was dipped in the neat solvent (45 mL) for 2 hours. Then, the solution was removed and all volatiles were removed *in vacuo* before putting the sample inside the glovebox. Finally, the wafer was annealed in the same conditions as its corresponding P-grafted counterpart.

## SI 2. DFT calculations

**Details of the calculations.** The *tert*-butyl groups on P-POSS were replaced with methyl groups in the calculations. All structures used for the NMR calculations were optimized with the B3-LYP hybrid density functional, as implemented in Gaussian 09 (Revision C.01).<sup>7</sup> The IGLO-II basis set<sup>8</sup> was used on all atoms. NMR shielding tensors were computed at the same level, using the Gauge-Independent Atomic Orbital (GIAO) method. The experimental <sup>31</sup>P chemical shifts are referenced to aqueous H<sub>3</sub>PO<sub>4</sub>, which is not easily described by computational methods. Therefore, following recommendation from others,<sup>9,10</sup> all chemical shifts ( $\delta$ ) were referenced to gaseous PH<sub>3</sub>, using the experimental value vs. H<sub>3</sub>PO<sub>4</sub> ( $\delta_{\text{exp}}(\text{PH}_3) = -266.1$  ppm) as follows:

$$\delta_{\text{calc}} = \sigma_{\text{calc}}(\text{PH}_3) - \sigma_{\text{calc}} - \delta_{\text{exp}}(\text{PH}_3).$$

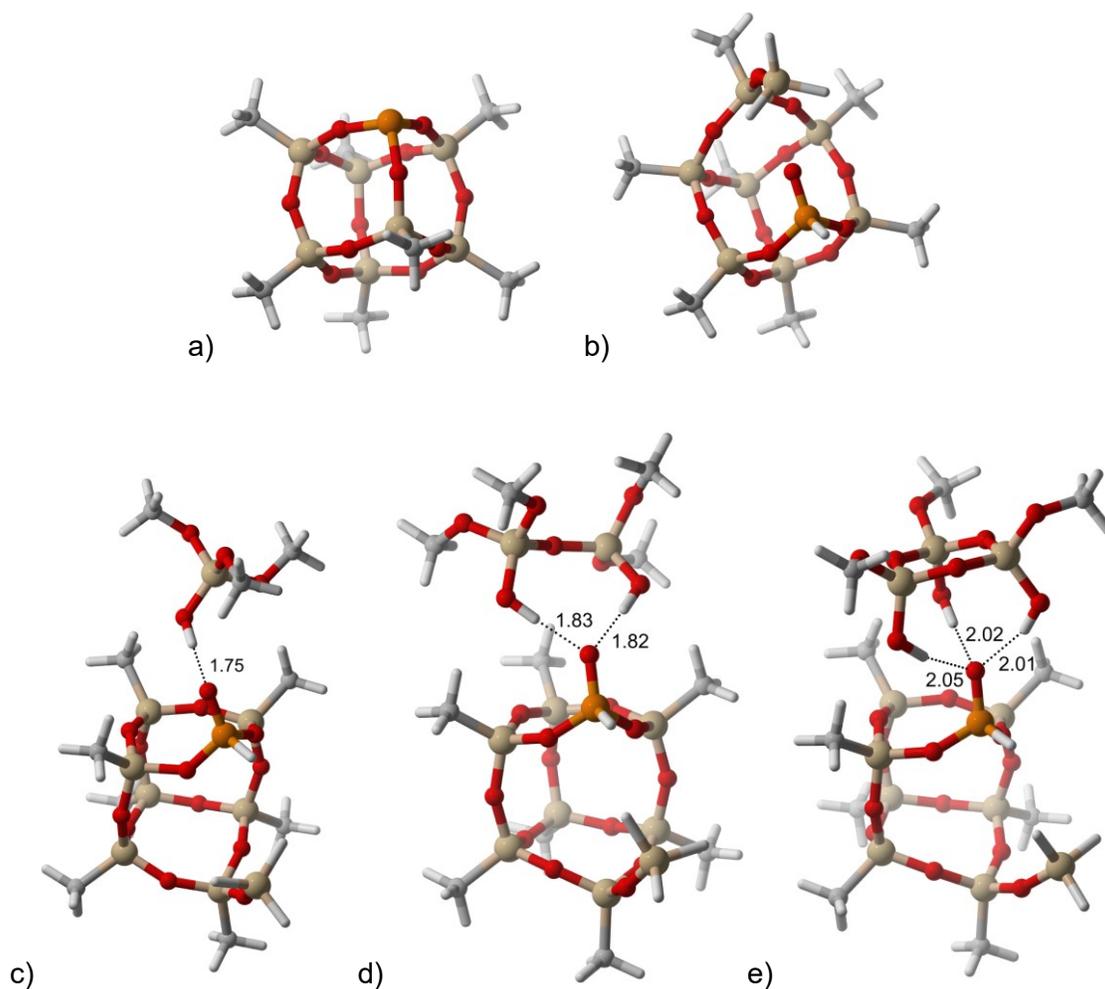
The isotropic chemical shift ( $\delta_{\text{iso}}$ ), the span ( $\Omega$ ), and the skew ( $\kappa$ ) were calculated according to the Herzfeld-Berger<sup>11</sup> convention:

$$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$$

$$\Omega = \delta_{11} - \delta_{33}$$

$$\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$$

Harmonic vibrational frequencies were calculated at the B3-LYP/6-31G(d) level and scaled by a factor of 0.96.<sup>12</sup>



**Figure S2.** Optimized structures of a) P-POSS, b) POSS-Phosphonate, c) POSS-Phosphonate-silanol, d) POSS-Phosphonate-bis-silanol, e) POSS-Phosphonate-tris-silanol. Distances are given in Å. The figures were produced with the free Cylview software (CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (<http://www.cylview.org>)).

**Table S1.** Eigenvalues of the GIAO magnetic shielding tensor ( $\sigma_{11}$ ,  $\sigma_{22}$  and  $\sigma_{33}$ , in ppm), and corresponding isotropic shielding values ( $\sigma_{\text{iso}}$ , ppm) as calculated with Gaussian.

	$\sigma_{11}$	$\sigma_{22}$	$\sigma_{33}$	$\sigma_{\text{iso}}$
PH <sub>3</sub>	529.6623	587.267	587.3099	568.1
POSS-Me terminated	142.955	143.5882	402.3732	229.6
POSS-Phosphonate	236.7698	280.1999	498.3533	338.4
POSS-Phosphonate-silanol	242.0736	285.9143	461.2441	329.7
POSS-Phosphonate-bis-silanol	251.108	291.9551	448.1499	330.4
POSS-Phosphonate-tris-silanol	246.9235	294.996	436.2345	326.1

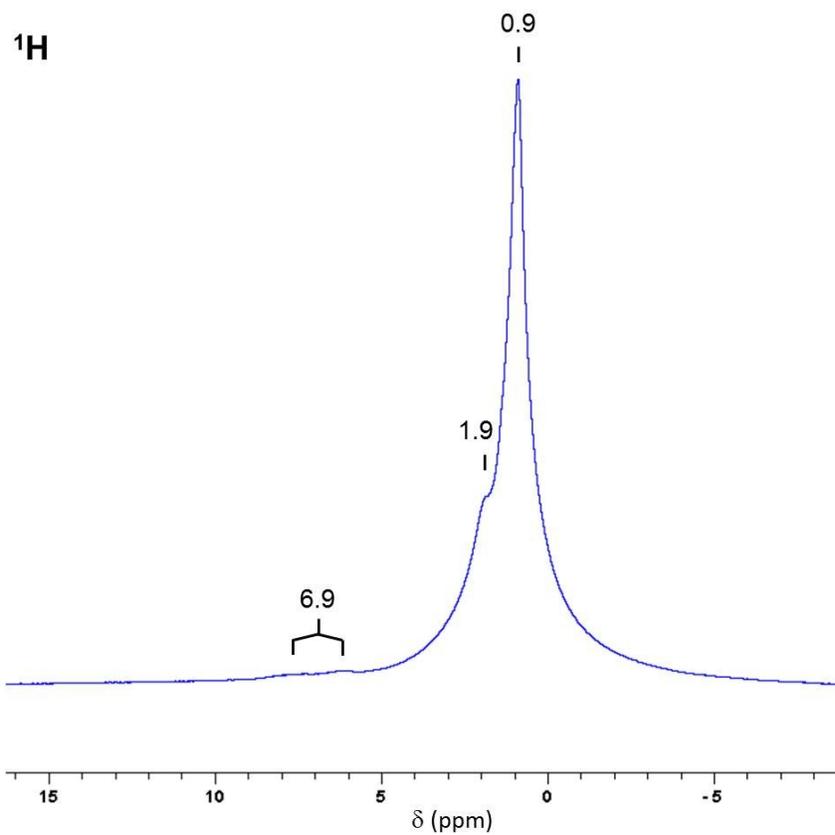
**Table S2.** Principal components of the chemical shift tensor ( $\delta_{11}$ ,  $\delta_{22}$  and  $\delta_{33}$  ppm), isotropic chemical shift ( $\delta_{\text{iso}}$ , ppm), span ( $\Omega$ , ppm) and skew ( $\kappa$ ).

	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	$\delta_{\text{iso}}$	$\Omega$	$\kappa$
PH <sub>3</sub>	-227.7	-285.3	-285.3	-266.1	57.6	-1.00
POSS-Me terminated	159.0	158.4	-100.4	72.3	259.4	1.00
POSS-Phosphonate	65.2	21.8	-196.4	-36.5	261.6	0.67
POSS-Phosphonate-silanol	59.9	16.1	-159.3	-27.8	219.2	0.60
POSS-Phosphonate-bis-silanol	50.9	10.0	-146.2	-28.4	197.0	0.59
POSS-Phosphonate-tris-silanol	55.1	7.0	-134.3	-24.1	189.3	0.49

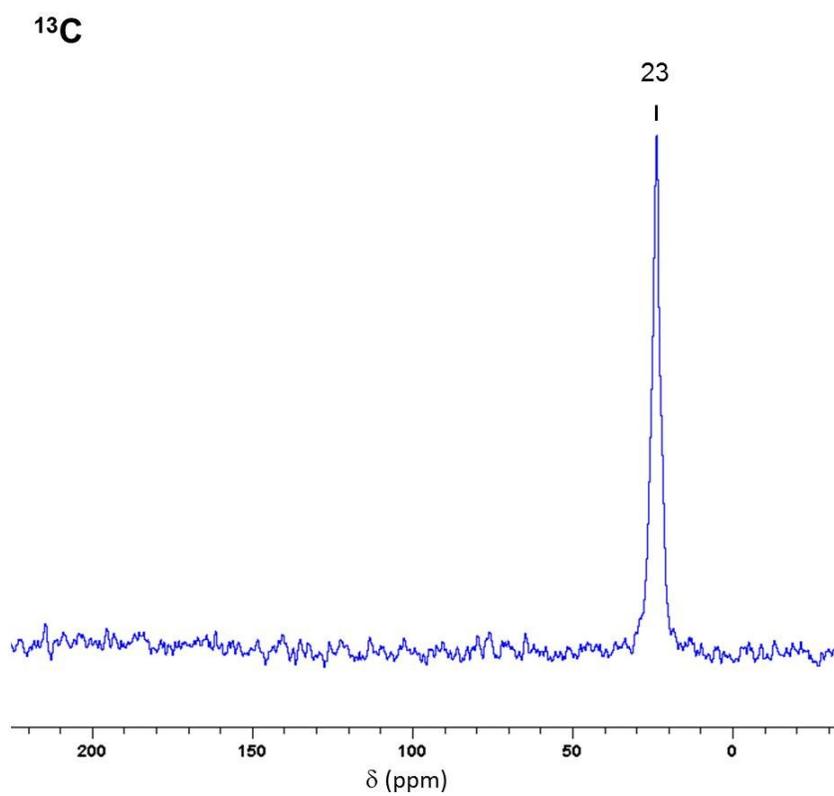
**Table S3.** Calculated P-H stretching frequency  $\nu(\text{P-H})$  ( $\text{cm}^{-1}$ ) and frequency shift  $\Delta\nu$  ( $\text{cm}^{-1}$ ) generated by the interaction with silanol groups.

	$\nu(\text{P-H})$	$\Delta\nu$
POSS-Phosphonate	2475	0
POSS-Phosphonate-silanol	2498	+23
POSS-Phosphonate-bis-silanol	2510	+35
POSS-Phosphonate-tris-silanol	2516	+41

**SI 3.**  $^1\text{H}$  MAS and  $^{13}\text{C}$  CP-MAS spectra of **POSS-P/SiO<sub>2</sub>-(500)**

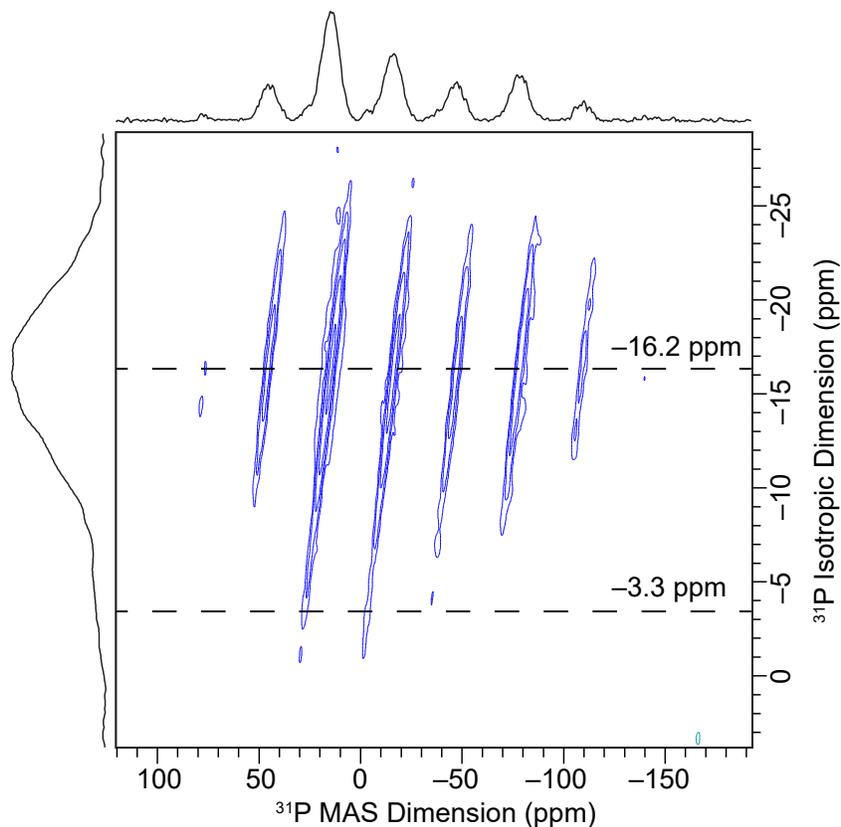


**Figure S3-1.**  $^1\text{H}$  MAS solid-state NMR spectrum of **POSS-P/SiO<sub>2</sub>-(500)** (500 MHz,  $\omega_{\text{rot}}/2\pi = 10$  kHz, 8 scans, recycle delay 5 s).

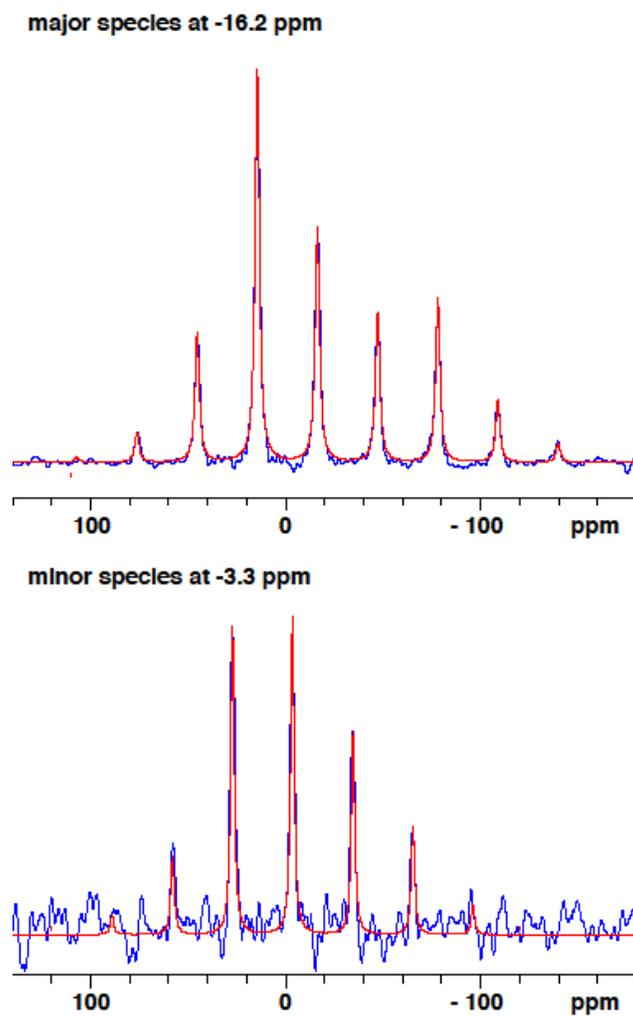


**Figure S3-2.** <sup>13</sup>C CP-MAS solid-state NMR spectrum of **POSS-P/SiO<sub>2</sub>-(500)** (500 MHz,  $\omega_{\text{rot}}/2\pi = 10$  KHz, 4 k scans, recycle delay of 2 s, 2 ms contact time).

**SI 4.** DNP enhanced 2D  $^{31}\text{P}$  magic angle turning (MAT) correlation spectrum of **POSS-P/SiO<sub>2</sub>(700)**.

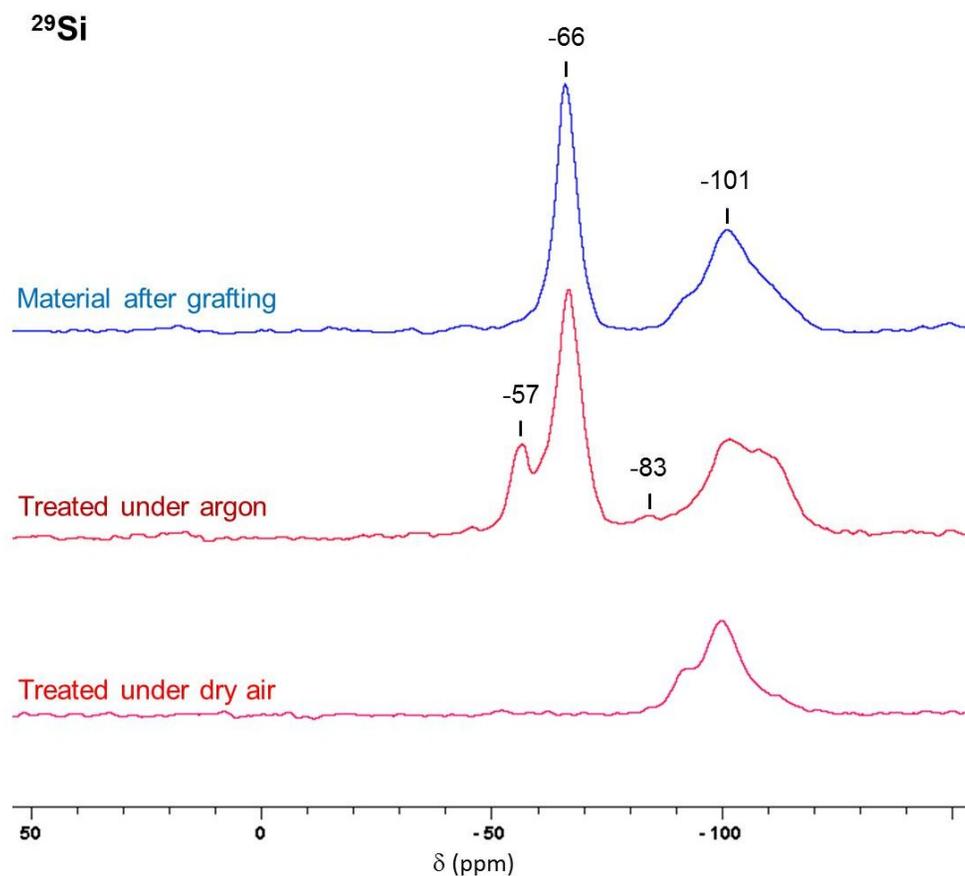


**Figure S4-1.** DNP enhanced 2D  $^{31}\text{P}$  magic angle turning (MAT) isotropic-anisotropic chemical shift correlation spectrum of POSS-P/SiO<sub>2</sub>(700). Slices at isotropic chemical shifts were extracted at -3.3 ppm and -16.2 ppm and are shown in Figure S4-2. The spectrum was acquired with a MAS frequency of 5000 Hz, 14 scans, a 3.0 s polarization delay between scans, 48  $t_1$  increments and a  $t_1$  increment of 158.33 ms. The five p pulse MAT sequence of Grant and co-workers was used.<sup>13</sup> Echo-anti-echo acquisition was used to obtain a pure adsorption mode 2D spectrum.



**Figure S4-2.** Slices at isotropic chemical shifts of  $-3.3$  ppm (lower traces) and  $-16.2$  ppm (upper traces) from the 2D  $^{31}\text{P}$  MAT solid-state NMR spectrum (Figure S4-1) and fits of the sideband manifolds (red traces) to obtain the CS tensor parameters (Figure S4-2).

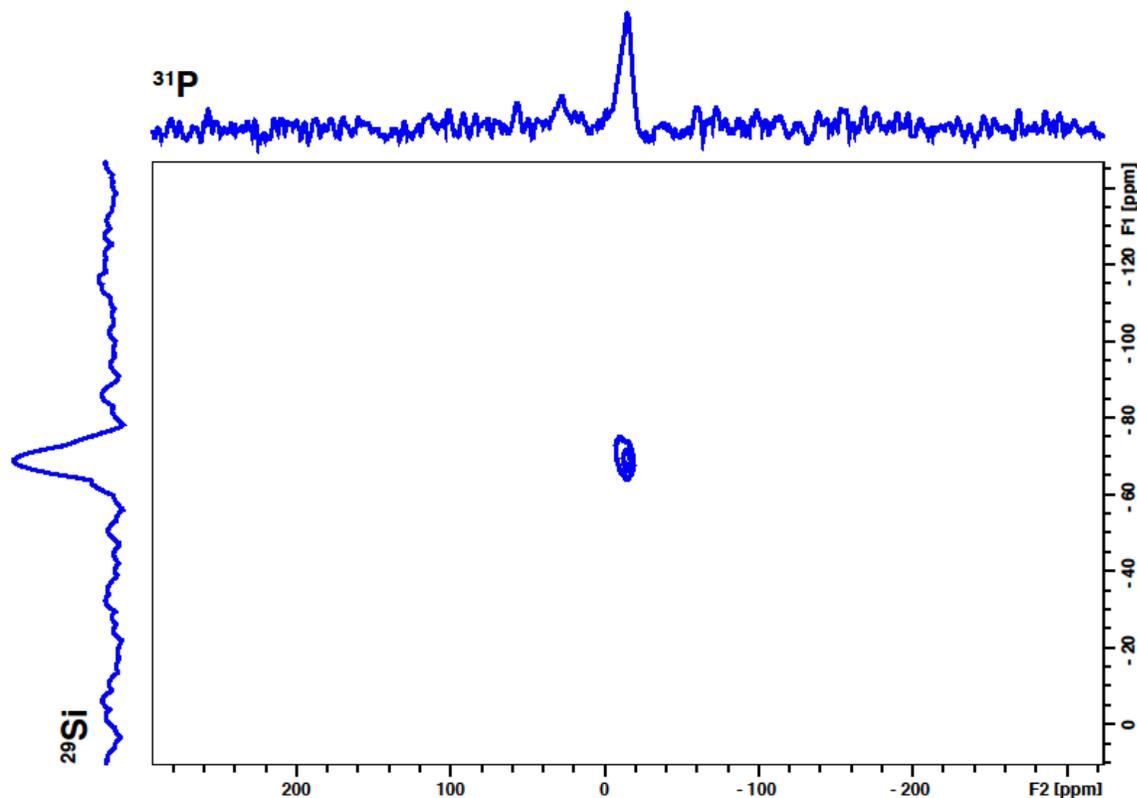
**SI 5.**  $^{29}\text{Si}$  CP-MAS NMR spectra of **POSS-P/SiO<sub>2-(500)</sub>** after grafting and inert or oxidative post-treatment.



**Figure S5.**  $^{29}\text{Si}$  CP-MAS solid state NMR spectra of **POSS-P/SiO<sub>2-(500)</sub>** after grafting, and treated under argon (inert) or dry air (oxidative atmosphere). 300 MHz,  $\omega_{\text{rot}}/2\pi = 5$  KHz, 27 k scans, recycle delay of 2 s, 2 ms contact time.

Spectrum of the sample treated under argon (inert conditions): the peak at -57 ppm ( $T_2$ -type Si-OH of POSS) shows that the POSS cage is partially opened. The peak of low intensity at -83 ppm reveals the presence of  $T_3$ -like Si-H of POSS,<sup>14</sup> consistent with the release of small amounts of  $C_3/C_4$  alkenes,<sup>15</sup> observed from  $\sim 380$  °C, and generating Si-H groups (see  $\nu(\text{Si-H}) \sim 2250$   $\text{cm}^{-1}$  on the IR spectrum (main text)).

**SI 6.** DNP enhanced 2D  $^{29}\text{Si}$ - $^{31}\text{P}$  NMR correlation spectrum of **POSS-P/SiO<sub>2</sub>-(700)**.

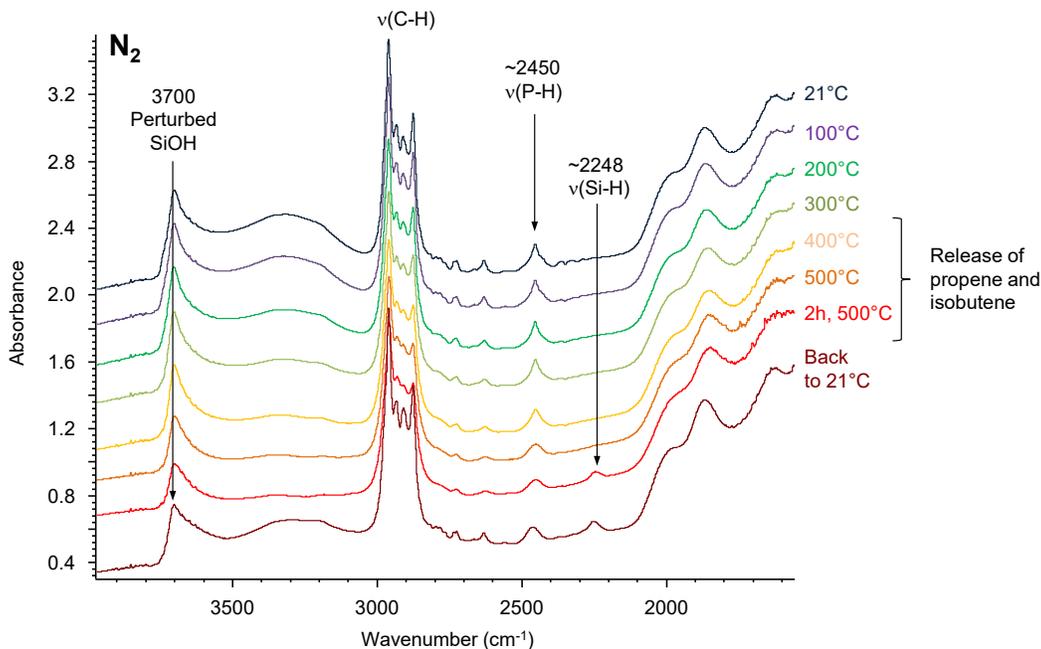


**Figure S6.** DNP enhanced 2D transferred echo double resonance (TEDOR)  $^{29}\text{Si}$ - $^{31}\text{P}$  correlation spectrum.  $^{29}\text{Si}$  was polarized with a CP step (6 ms contact time), then allowed to evolve for  $t_1$ . The  $^{29}\text{Si}$  polarization was then transferred to  $^{31}\text{P}$  for detection with REDOR recoupling. 80 total rotor cycles of recoupling (6.4 ms) was used for  $^{29}\text{Si}$ - $^{31}\text{P}$  coherence transfer. The States-TPPI procedure was employed to obtain phase sensitive detection. The spectrum was acquired with a MAS frequency of 12500 Hz, 24 scans per  $t_1$  increment, a rotor synchronized 80.0  $\mu\text{s}$   $t_1$  increment and 24 total  $t_1$  increments.

**SI 7.** Stability of surface species upon inert or oxidative thermal treatment, and followed by *in-situ* IR coupled with GC/MS.

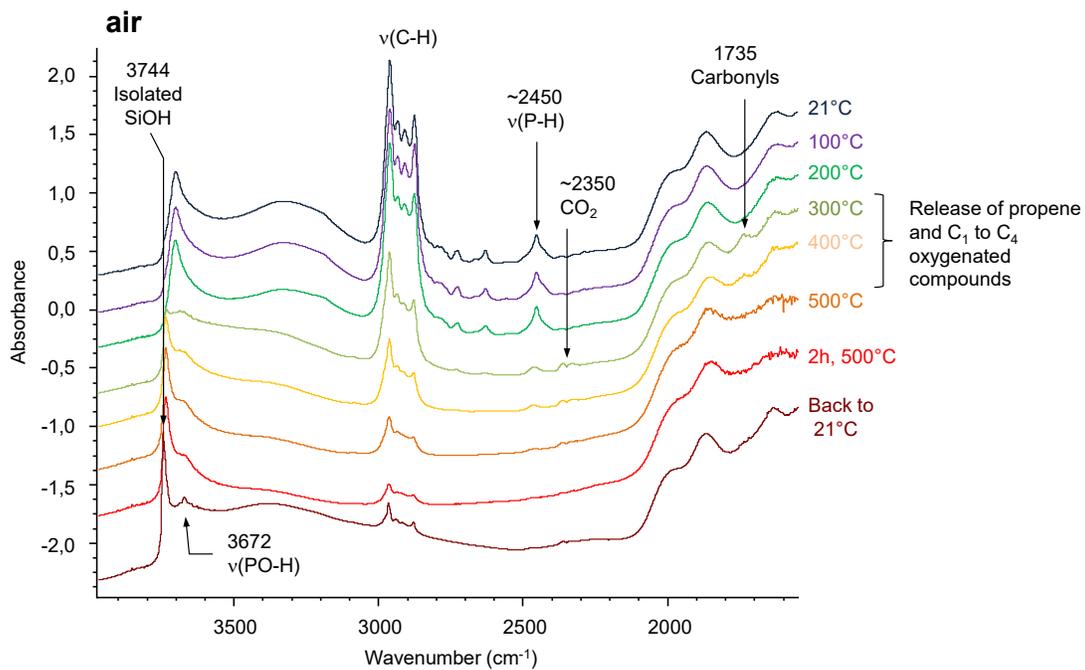
**Details:** FT-IR spectra recorded in DRIFT mode were obtained on a Nicolet 6700 FT-IR spectrometer. The samples were loaded into a custom DRIFT cell equipped with ZnSe windows under inert atmosphere (glovebox). Typically, 4 spectra per minute were acquired, with 64 scans ( $4\text{ cm}^{-1}$  resolution). POSS-P/SiO<sub>2</sub> (typically 20 mg) was decomposed under a flux (10 ml/min) of dry gas (air or N<sub>2</sub>), with a heating rate of  $3^{\circ}\text{C}\cdot\text{min}^{-1}$ , from  $\sim 20^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ , and maintained at  $500^{\circ}\text{C}$  for 2h before being cooled to the starting temperature. Gases, released during thermal treatment, were collected and analyzed by GC/MS for identification.

**Decomposition under inert atmosphere (N<sub>2</sub>):**



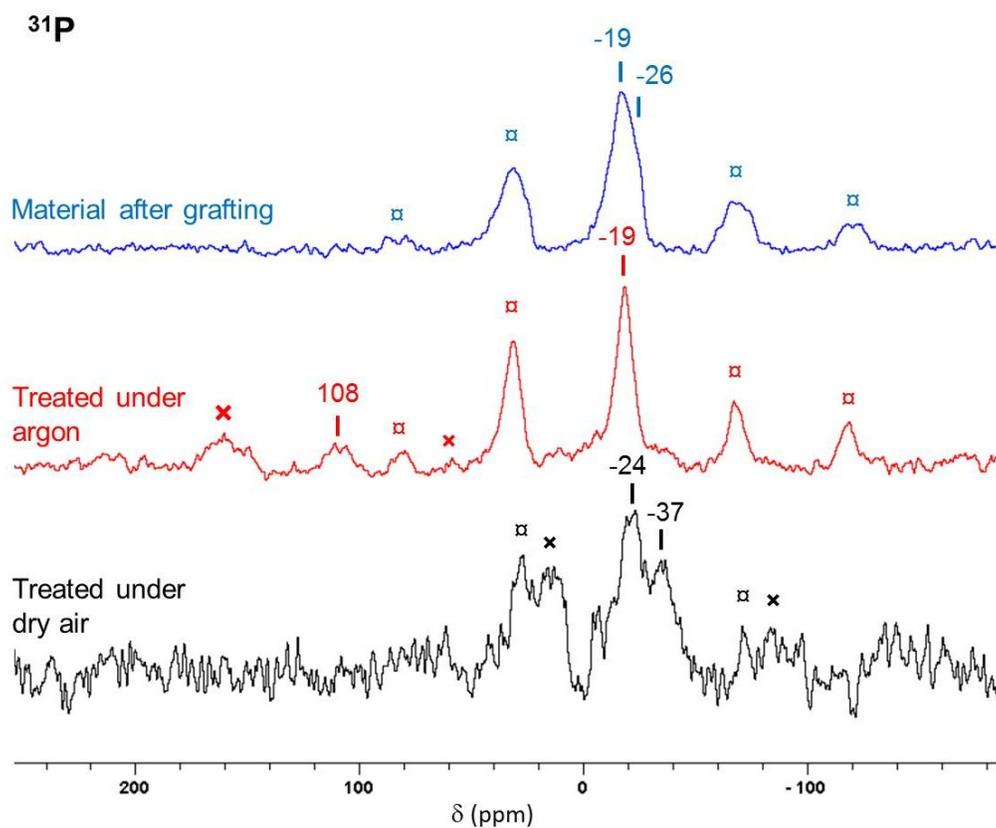
**Figure S7-1.** IR (DRIFT) spectra of POSS-P/SiO<sub>2</sub> decomposed under dry and O<sub>2</sub>-free N<sub>2</sub>, between 21°C and 500°C.

### Decomposition under oxidative atmosphere (air):



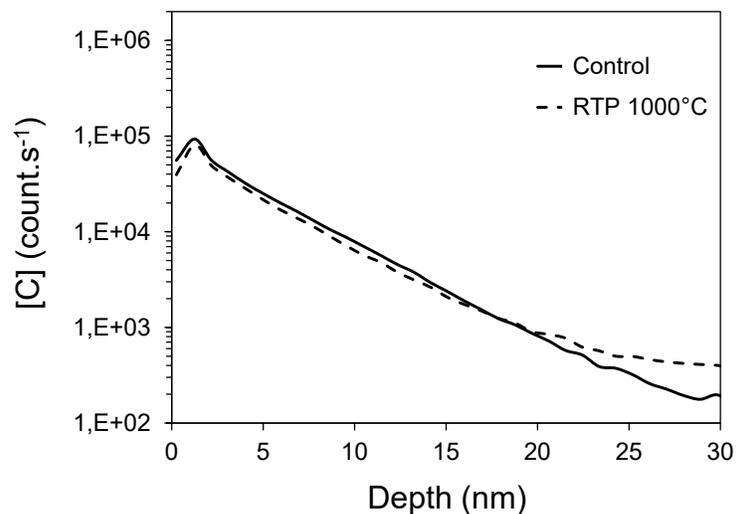
**Figure S7-2.** IR (DRIFT) spectra of POSS-P/SiO<sub>2</sub> decomposed under dry air, between 21°C and 500°C.

**SI 8.**  $^{31}\text{P}\{^1\text{H}\}$  pulse-acquire MAS spectra of **POSS-P/SiO<sub>2-(500)</sub>** after grafting and inert or oxidative post-treatment.



**Figure S8.**  $^{31}\text{P}$  pulse-acquire,  $^1\text{H}$  decoupled MAS solid state NMR spectra of **POSS-P/SiO<sub>2-(500)</sub>** after grafting, and treated under argon (inert) or dry air (oxidative atmosphere). 500 MHz,  $\omega_{\text{rot}}/2\pi = 10$  KHz, from 1 k to 3 k scans, recycle delay 40 s, except for the sample treated under dry air (100 s).  $\square$  and  $\times$  denote spinning side bands.

### SI 9. Secondary ion mass spectrometry (SIMS) depth profiles of carbon in silicon



**Figure S9.** Secondary ion mass spectrometry (SIMS) depth profile of carbon from P-grafted wafers and a reference (control) non-doped wafer annealed in the same conditions (spike 1s, 1000°C, 1.5 nm SiO<sub>2</sub>).

The tail observed on both depth profiles of carbon in silicon (control and sample) is an artifact coming from the use of a Cs<sup>+</sup> ion beam for sputtering.

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