Supporting information of
Fast room-temperature functionalization of silicon nanoparticles using alkyl silanols

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S1 Experimental details

DMSO (anhydrous, ≥99.9%), pentane (anhydrous, ≥99%), triethoxysilane (95%), sodium L-ascorbate (≥99.0%), diethyl ether, allyl(chloro)dimethylsilane (97%), 1-thio-β-D-glucose tetraacetate (97%), hydrochloric acid (37% in water), sodium methoxide (0.5 M solution in methanol), chlorobenzene (≥99.5%), 2,2-dimethoxy-2-phenylacetophenone (99%), quinine for fluorescence (anhydrous, ≥98%), magnesium sulfate (anhydrous, 98%), and triethylamine (≥99%) were purchased from Sigma Aldrich. Toluene (≥99.5%) was purchased from Merck. 30 vol% sulfuric acid was purchased from Chem-Lab NV. n-Hexane (≥95%) and methanol (≥99.8%) were purchased from Biosolve. N-Decyldimethylchlorosilane (97%) and (3,3,3-trifluoropropyl)dimethylchlorosilane (97%) were purchased from abcr. Wherever water is mentioned, milli-Q water should be read, produced using a Milli-Q Integral 3 system (Millipore). DMSO was immediately placed in a glovebox upon arrival, and both DMSO and methanol were (further) dried with activated molecular sieves before use. All other chemicals were used as received.

Silanols were prepared on a 5 ml scale in 100 mL round-bottom flasks. The volume of diethyl ether was 10x the volume of chlorosilane (50 mL), and the volume of hexane was equal to the volume of diethyl ether. Washing was done with 2 x 25 mL of ice-cold 0.5M HCl in water. Due to its susceptibility to dimerization, allyldimethylsilanol was prepared fresh for each experiment. For IR results, only notable peaks are mentioned.

Allyldimethylsilanol (1): Yield: 80%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 0.00 (s, 6H), 1.50 (d, J = 8.2 Hz, 2H), 4.81 (m, 2H), 5.46 (s, 1H), 5.77 (tdd, J = 17.0, 10.1, 8.1 Hz, 1H). IR (ATR): ν = 3289, 3079, 1631, 1254, 990, 932, 893 cm^{-1}. MS ($C_5H_{11}SiO$): calculated m/z = 115.0579 [M - H]$^-$, found 175.0246 [M+OAc]$^-$

n-Decyldimethylsilanol (2): Yield: 90%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = -0.03 (s, 6H), 0.45 (t, J = 7.5 Hz, 2H), 0.85 (t, J = 7.5 Hz, 3H), 1.24 (m, 16H), 5.22 (s, 1H). IR (ATR): ν = 3271, 2921, 1250 cm^{-1}. MS ($C_{12}H_{28}SiO$): calculated m/z = 215.1831 [M - H]$^-$, found 215.1836.

(3,3,3-Trifluoropropyl)dimethylsilanol (3): Yield: 83%. (400 MHz, DMSO-d$_6$): δ = 0.04 (s, 6H), 0.64 (m, 2H), 2.16 (m, 2H), 5.55 (s, 1H). IR (ATR): ν = 3277, 2962, 1259, 1203 cm^{-1}. MS ($C_5H_{11}F_3SiO$): calculated m/z = 171.0453 [M - H]$^-$, found 171.0457.

S2 NMR spectra

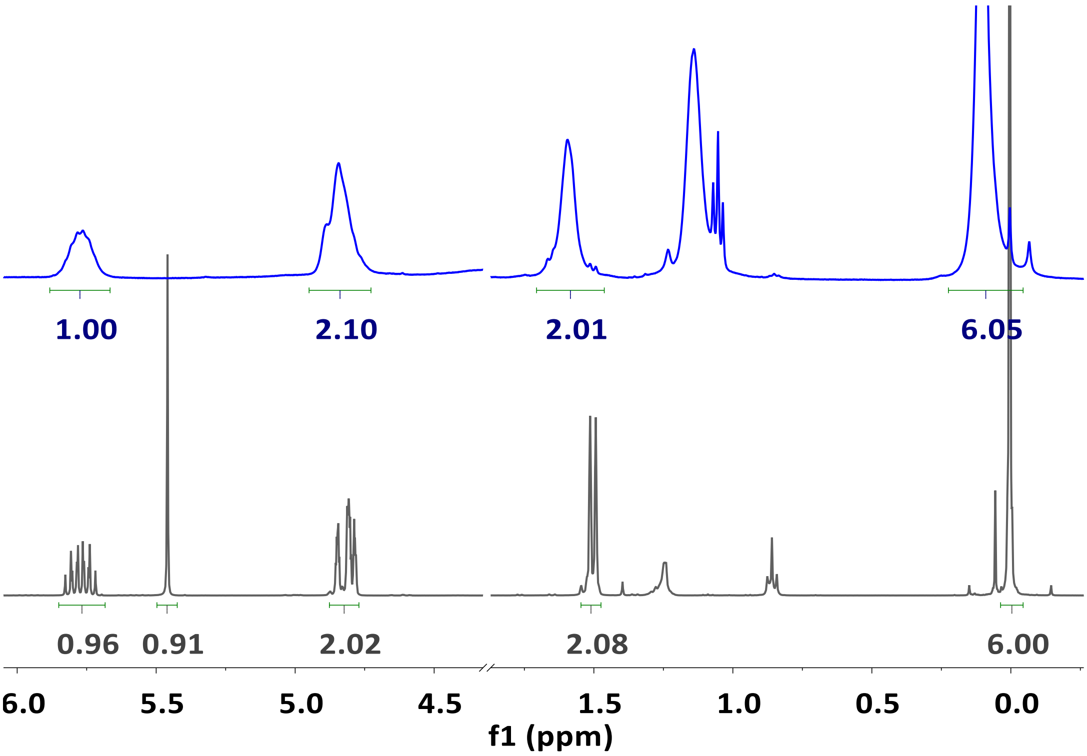


Figure S1: ^{1}H NMR spectrum of **1**-Si NPs (top) and pure unbound **1** (bottom) in DMSO-d_6.

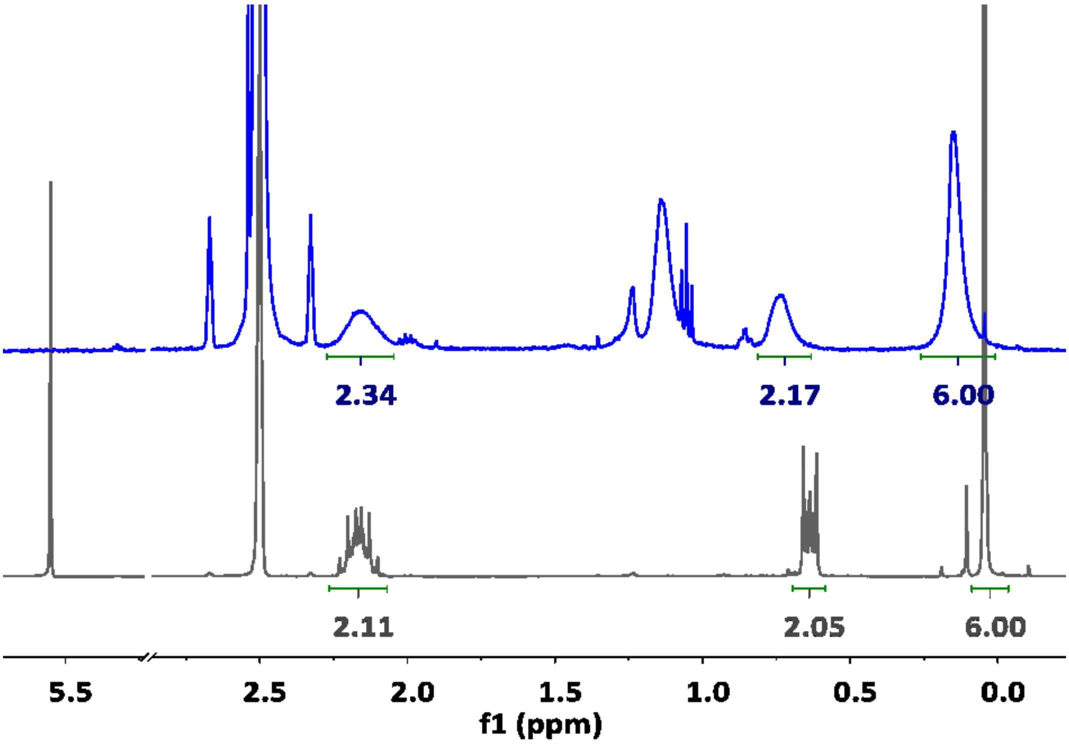


Figure S2: ^{1}H NMR spectrum of **3**-Si NPs (top) and pure unbound **3** (bottom) in DMSO-d_6.

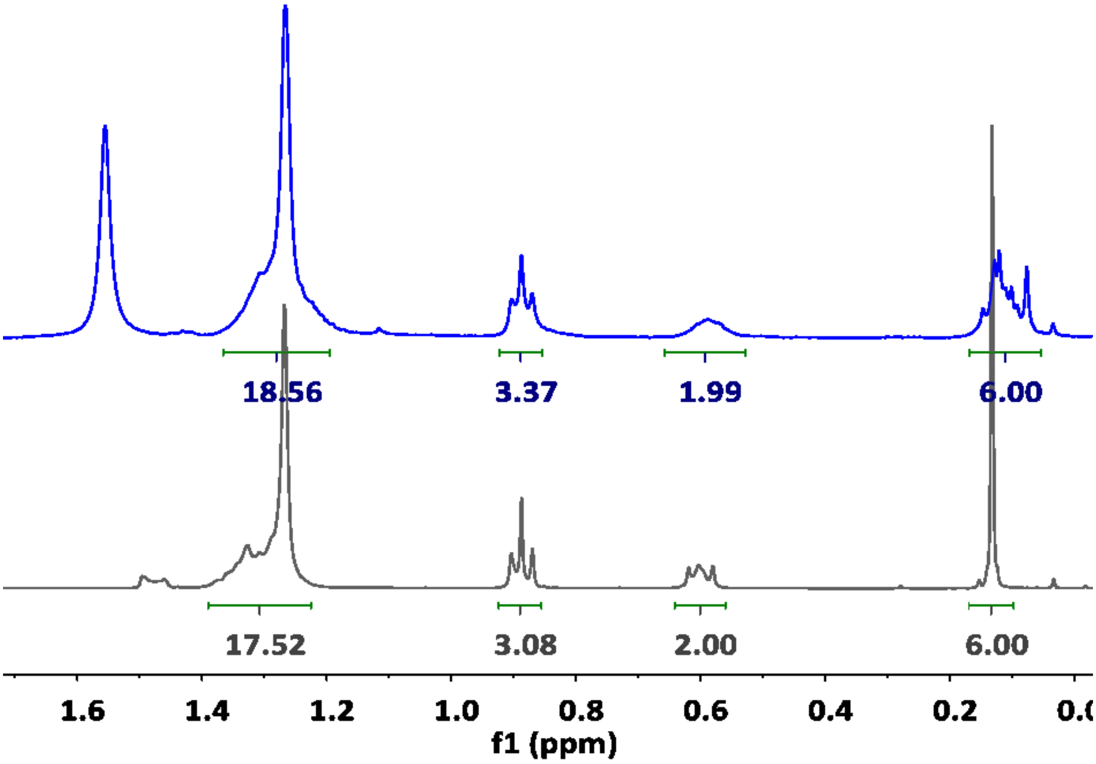


Figure S3: ^{1}H NMR spectrum of **2**-Si NPs (top) and pure unbound **2** (bottom) in $CDCl_3$.

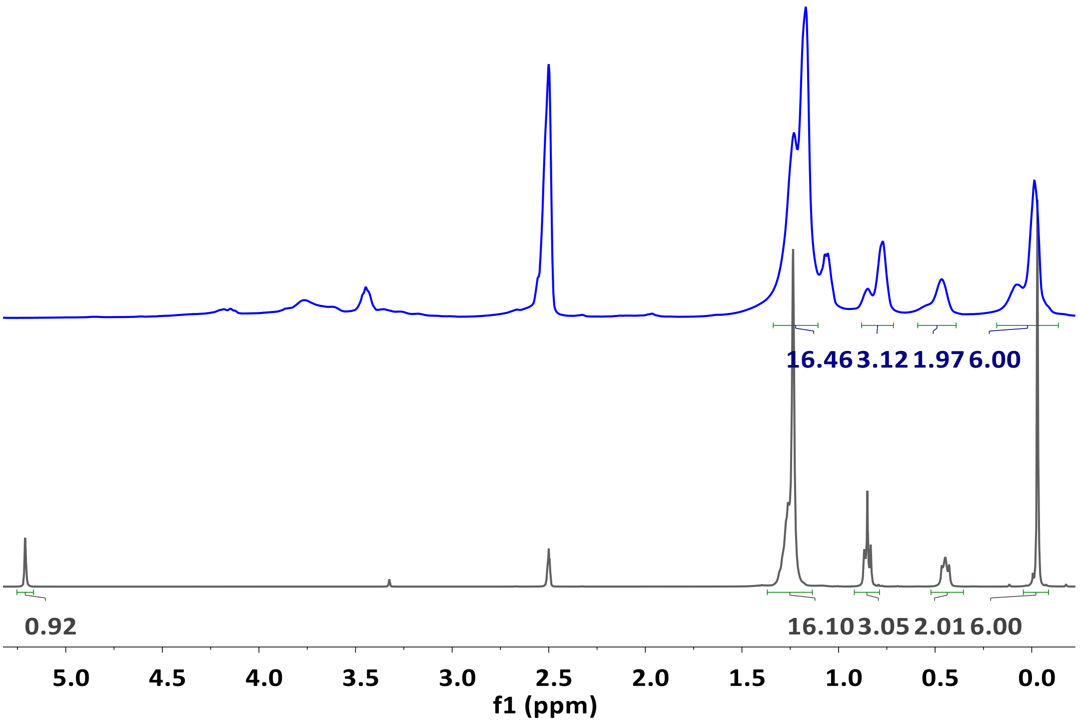


Figure S4: ^{1}H NMR spectrum of **2**-Si NPs (top) and pure unbound **2** (bottom) in DMSO-d_6.

S3 IR spectra

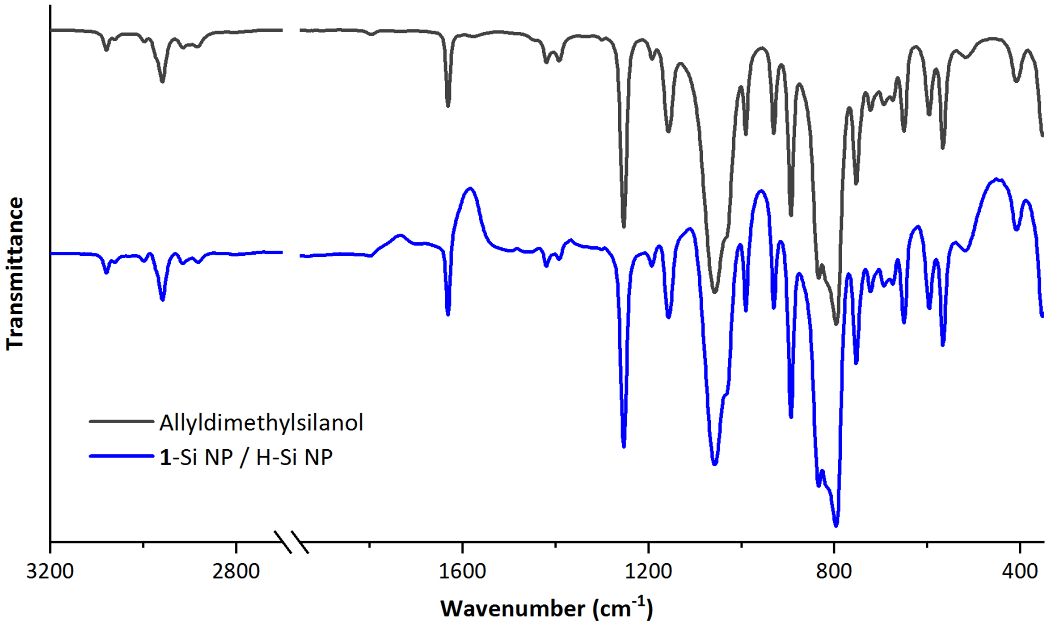


Figure S5: Top: ATR-IR spectrum of **1**. Bottom: ATR-IR difference spectrum between passivated and non-passivated Si NPs. As a background, (partially) oxidized H-Si NPs were used.

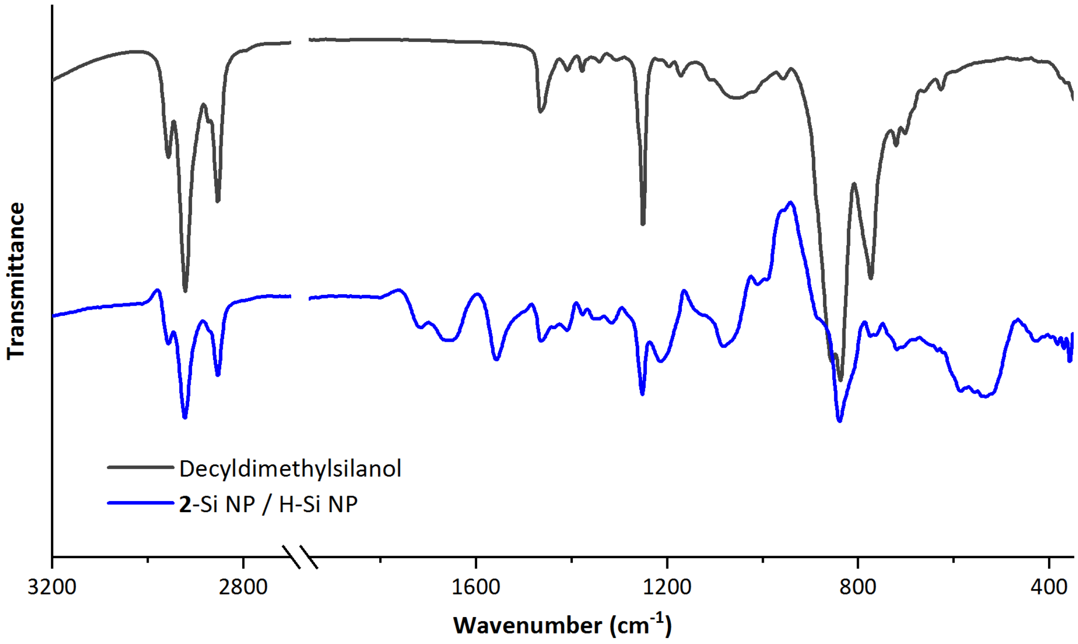


Figure S6: Top: ATR-IR spectrum of **2**. Bottom: ATR-IR difference spectrum between **2**-passivated and unpassivated Si NPs. As a background, (partially) oxidized H-Si NPs were used.

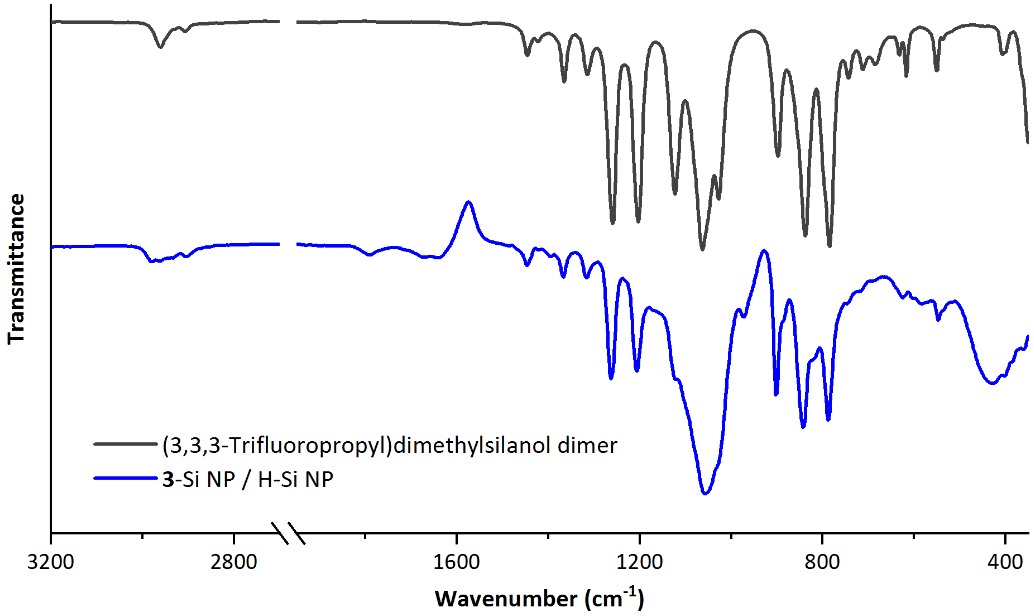
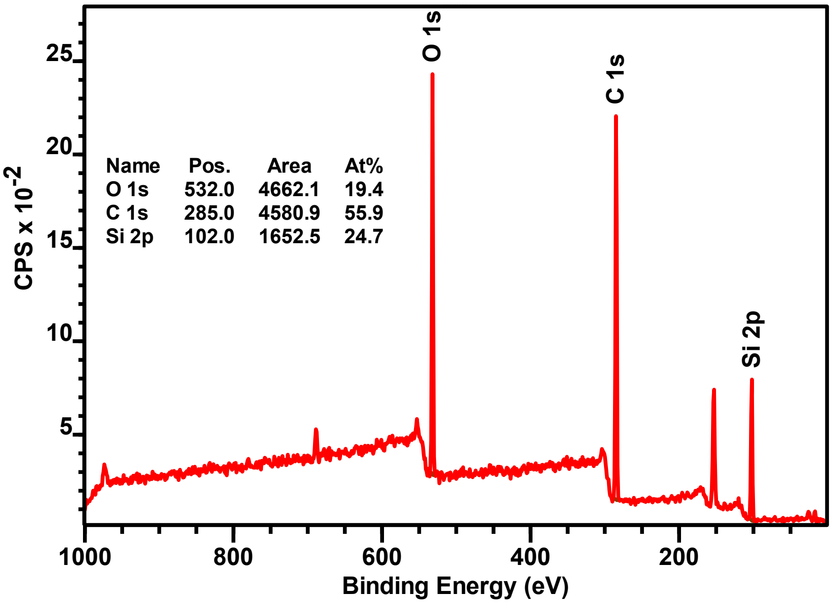


Figure S7: Top: ATR-IR spectrum of **3**$_2$. Bottom: ATR-IR difference spectrum between **3**-passivated and unpassivated Si NPs. As a background, (partially) oxidized H-Si NPs were used.

S4 XPS spectra



Name	Pos.	Area	At%
O 1s	532.0	4662.1	19.4
C 1s	285.0	4580.9	55.9
Si 2p	102.0	1652.5	24.7

Figure S8: XPS wide scan of **2**-Si NPs drop coated onto a cleaned gold surface. Spectra was calibrated on the C 1s peak, which was set to 285 eV.

As can be seen in Figure S8, the ratio of carbon to oxygen to silicon does not match with the predicted values. The silicon peak should be higher, and the C:O ratio should be 12:1. The increased oxygen ratio could indicate oxidation, yet the silicon narrow scan suggests this is not dominant. Therefore, the increased oxygen and carbon likely arise from environmental contaminants, as the XPS samples were prepared in a regular fume hood, instead of the glovebox. This is further confirmed by the presence of a small fluorine peak, likely derived from the Teflon tweezers used to handle the surfaces. Environmental contaminants can also be seen in the wide and carbon narrow scan of **3**-Si NPs (Figure S9 top row). The ratio in the carbon peaks belonging to $\underline{C}F_3$, $\underline{C}H_2$-CF_3, and Si-$\underline{C}$ / $\underline{C}$-C should be 1:1:3, respectively. Instead, the last peak is much higher due to the presence of atmospheric contaminants.

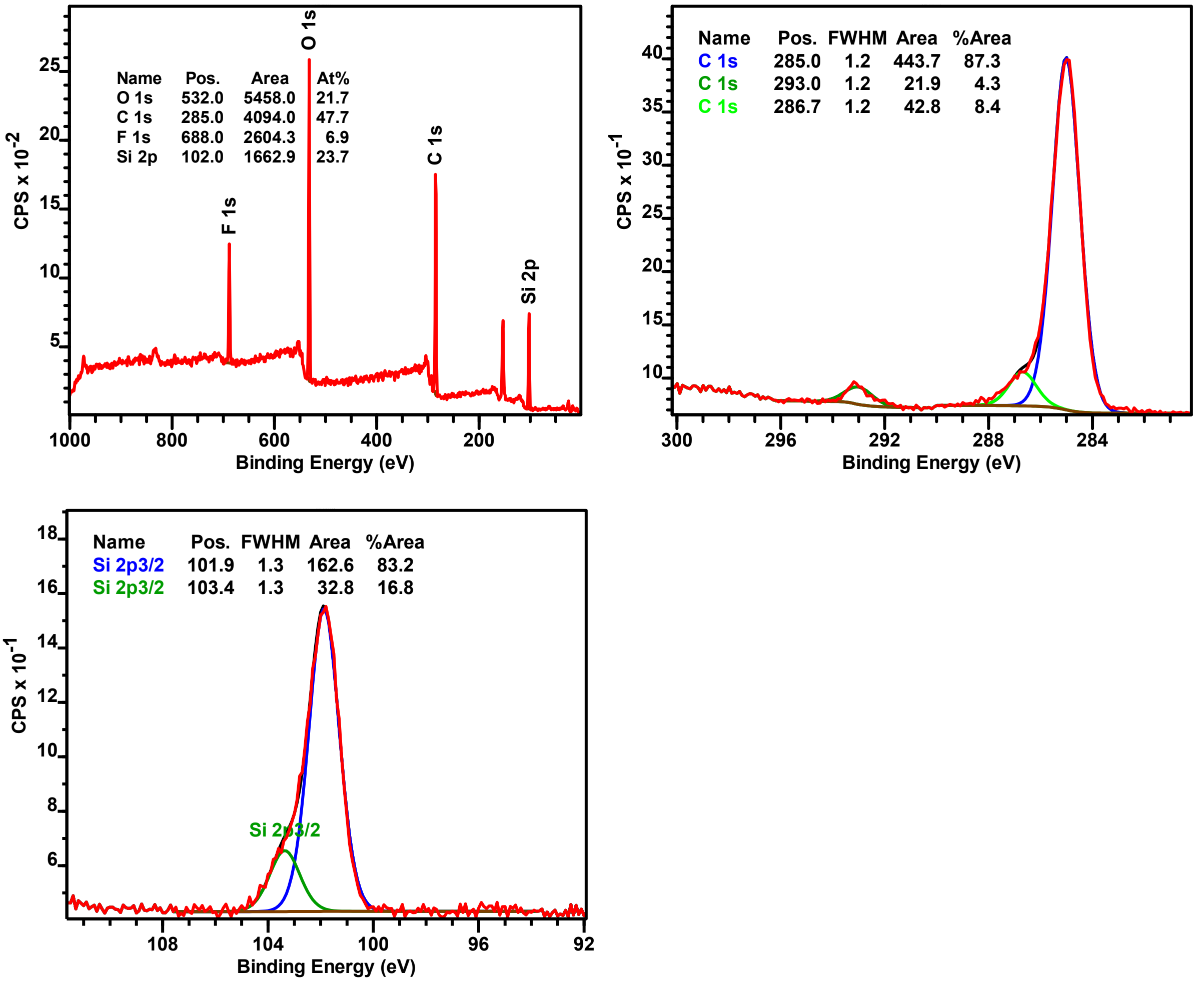


Figure S9: Left: XPS wide scan of **3**-Si NPs. Right: Carbon 1s narrow scan of the same Si NPs. Bottom: Silicon narrow scan of the same Si NPs.

S5 Optical properties

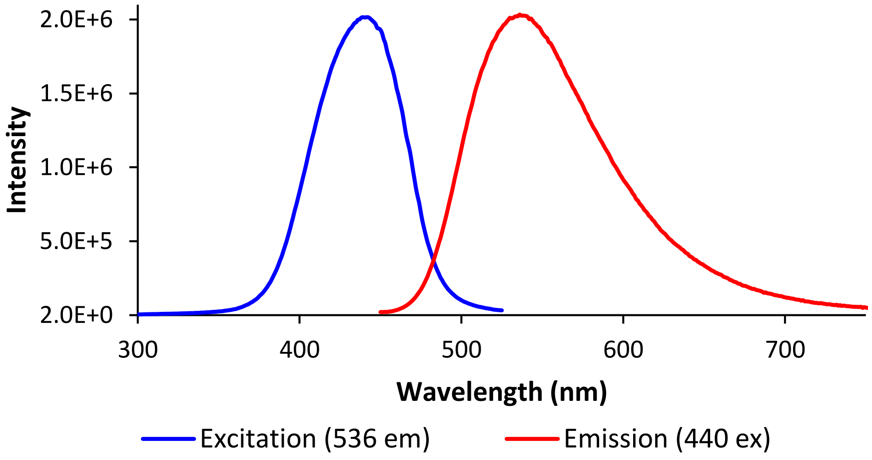


Figure S10: *Excitation and emission spectrum of Si NPs modified with **3**.*

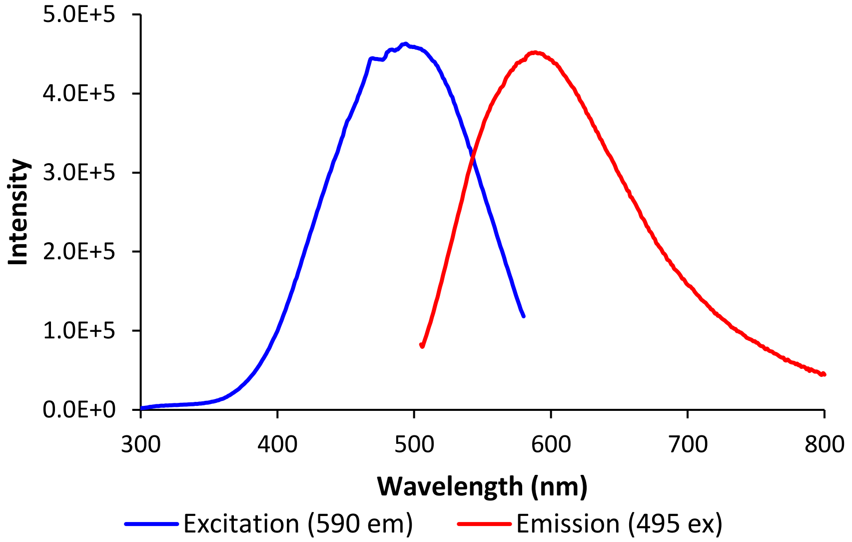


Figure S11: *Excitation and emission spectrum of Si NPs modified with* ***2****.*

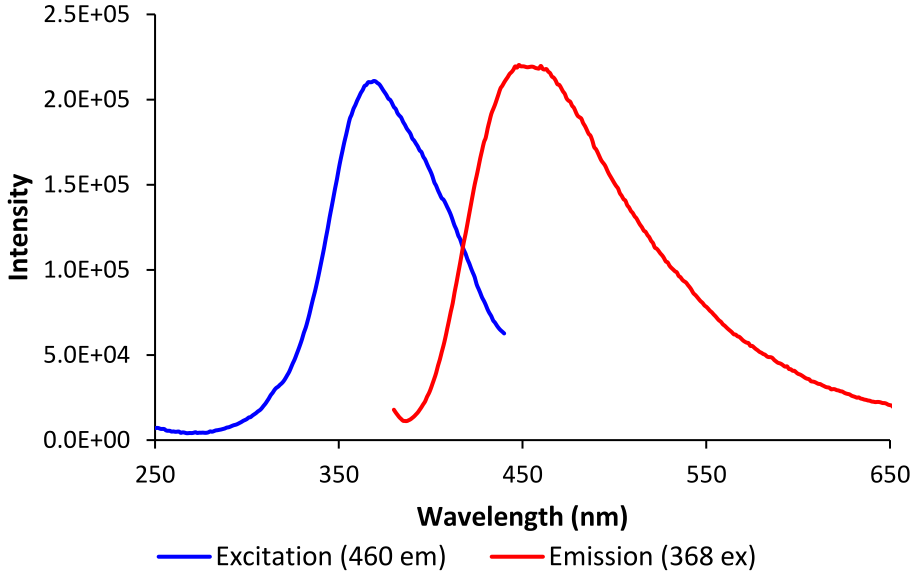


Figure S12: Excitation and emission spectrum of the water-soluble, 1-thioglucose-coated Si NPs.

S6 TEM results

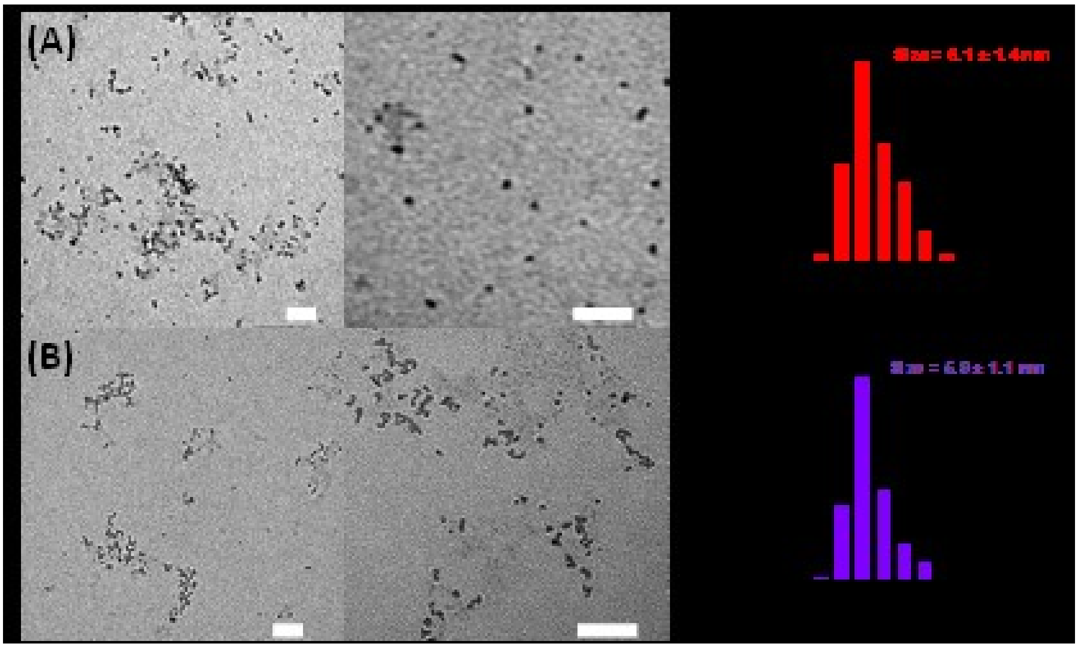


Figure S13: TEM images and size distributions of H-Si NPs (A) and **3**-Si NPs (B). The scale bar represents 50 nm, and the size distribution was determined from 300 particles.

S7 Sugar-coated Si NPs characterization

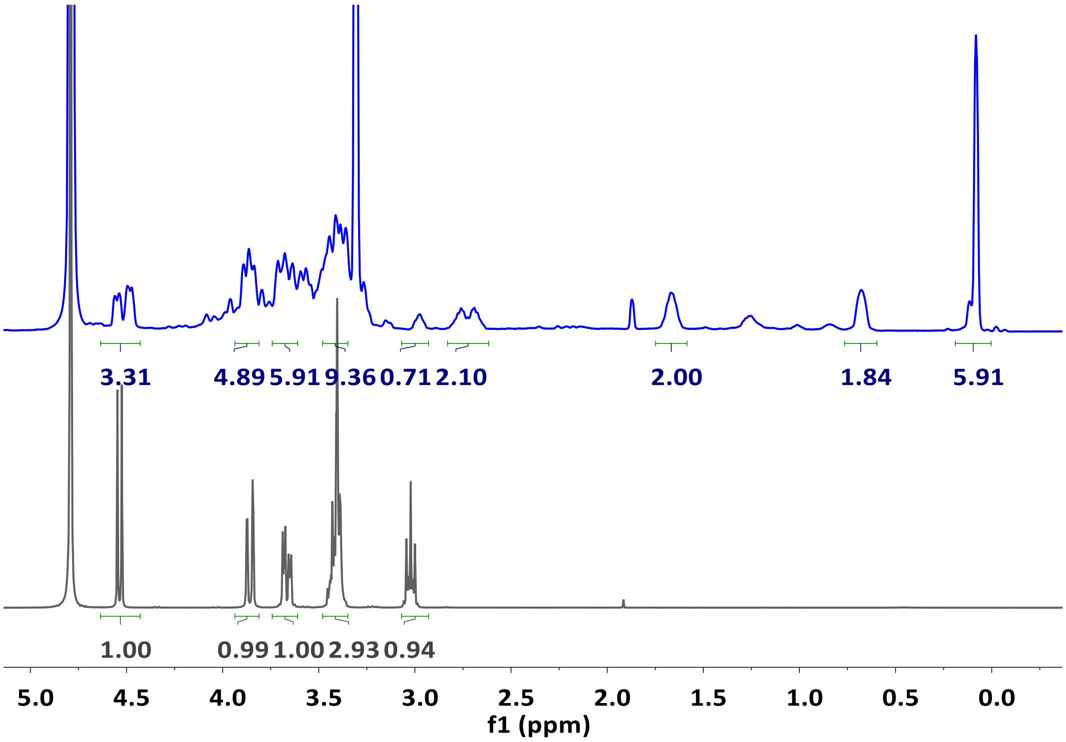


Figure S14: ^{1}H NMR spectrum of 1-thio-glucose-coated Si NPs in D_2O.

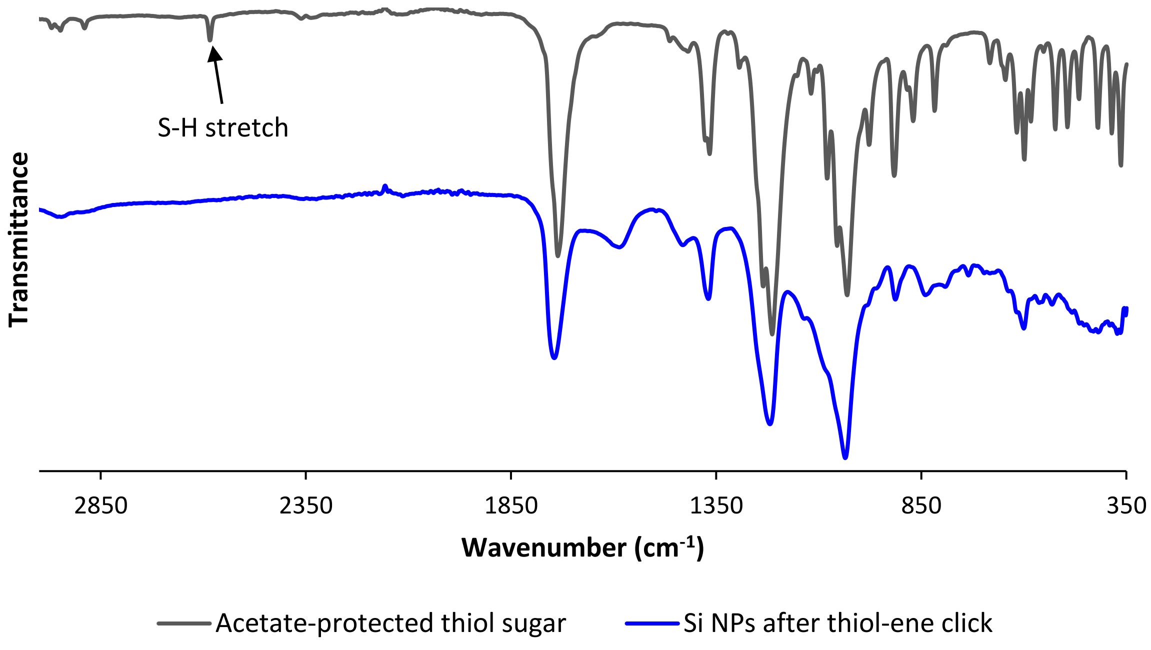


Figure S15: IR spectrum of **1**-Si NPs after a thiol-ene click reaction with 1-thio-β-D-glucose tetraacetate.

S8 Reaction enthalpy calculation

To calculate the reaction enthalpy for the functionalization of the Si NPs via wB97XD/6-311+G(d,p) calculations, the following structures were used (Figure S18): a model Si_8 compound was used to represent the hydrogen-terminated Si NP. It is assumed the use of this model compound has little effect on the enthalpy calculation. The energies of all structures were calculated under both vacuum and solvent conditions, where the dielectric SMD model was used to mimic DMSO as the solvent. The results can be found in Table S1.

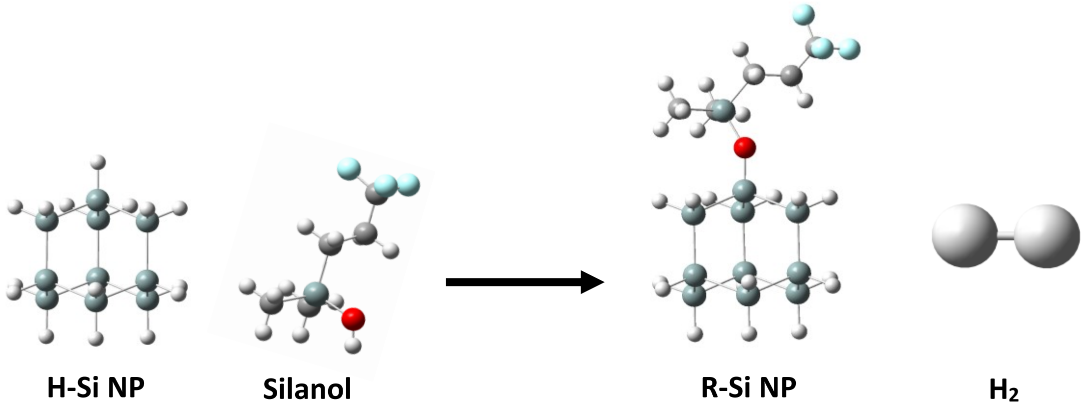


Figure S16: Chemical structures used for the calculation of the reaction enthalpy.

Table S1: Energy calculations for the structures shown in Figure S16.

	H-Si NP	Silanol	R-Si NP	H_2	ΔH
E_{vacuum} (Hartree)	-2904.507	-861.356	-3764.722	-1.163	**-0.02**
E_{vacuum} (kcal/mol)	-1822604.1	-540508.8	-2362396.8	-729.6	**-13.5**
E_{DMSO} (Hartree)	-2904.510	-861.347	-3764.720	-1.164	**-0.03**
E_{DMSO} (kcal/mol)	-1822606.2	-540502.8	-2362395.7	-730.2	**-16.9**