

Supporting Information

One-Pot Gram-scale Synthesis of Hydrogen-Terminated Silicon Nanoparticles

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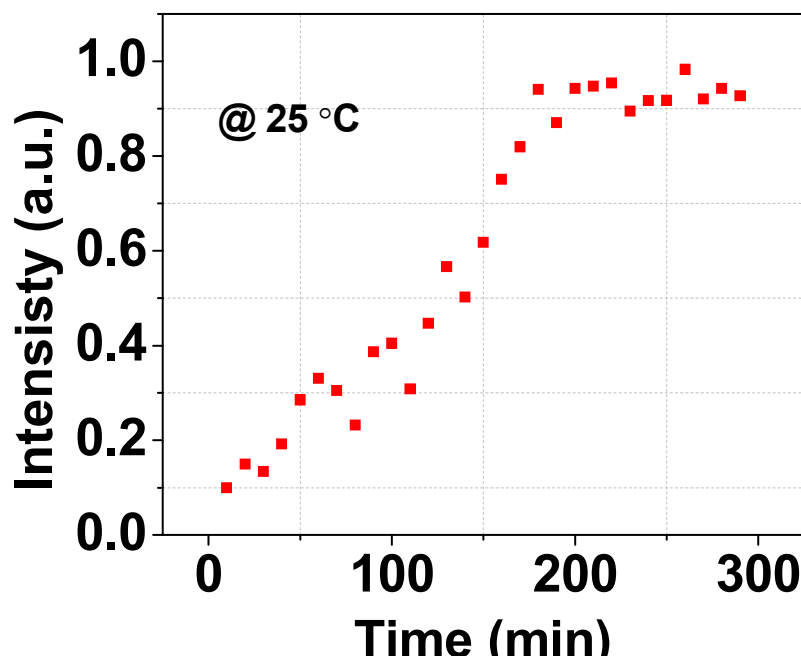


Figure S1. Development of the fluorescence intensity during the synthesis of H-Si NPs prepared at room temperature (25 °C), as measured at an emission wavelength of 450 nm.

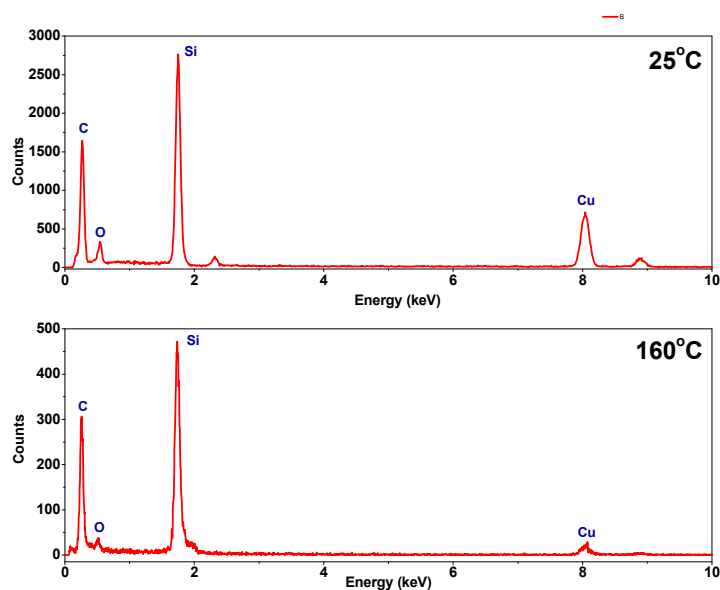


Figure S2. Energy dispersive X-ray (EDX) analysis of H-Si NPs prepared at 25°C (upper figure) prepared at 160 °C (lower figure).

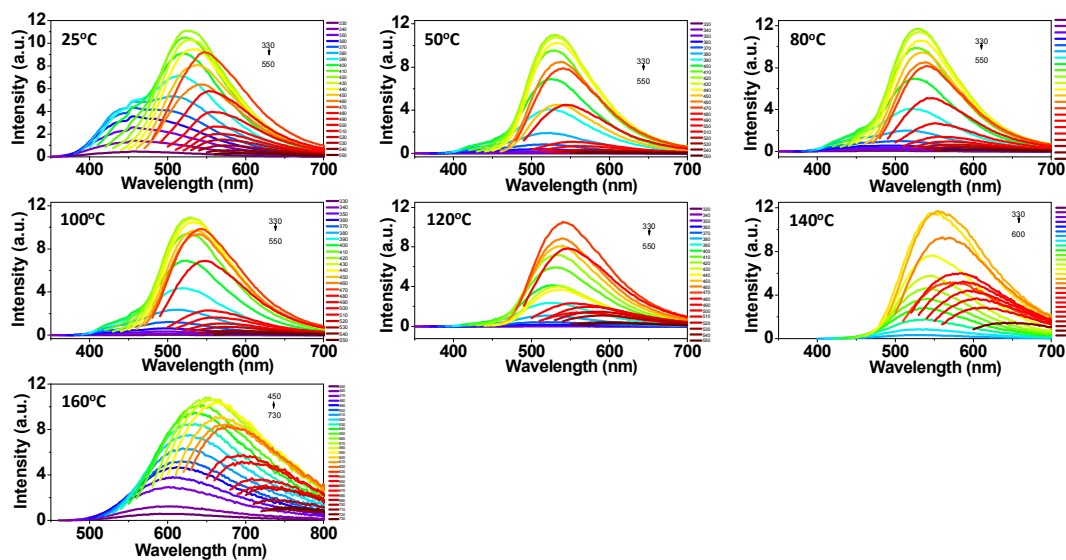


Figure S3. Excitation–emission plots of H-Si NPs as a function of the temperature of preparation.

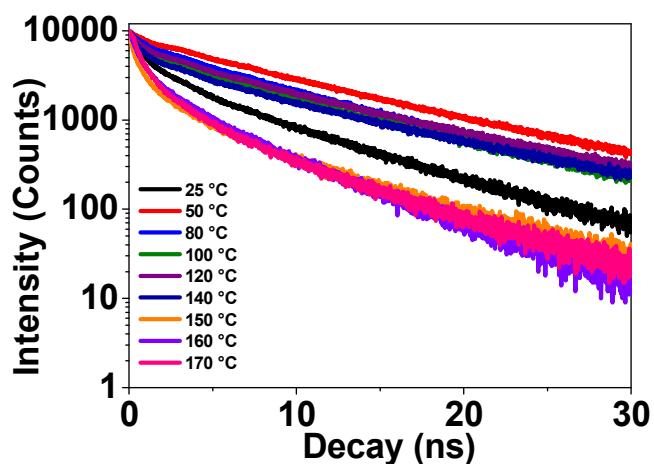


Figure S4. Photoluminescence decay curves of H-Si NPs as a function of the temperature of preparation.

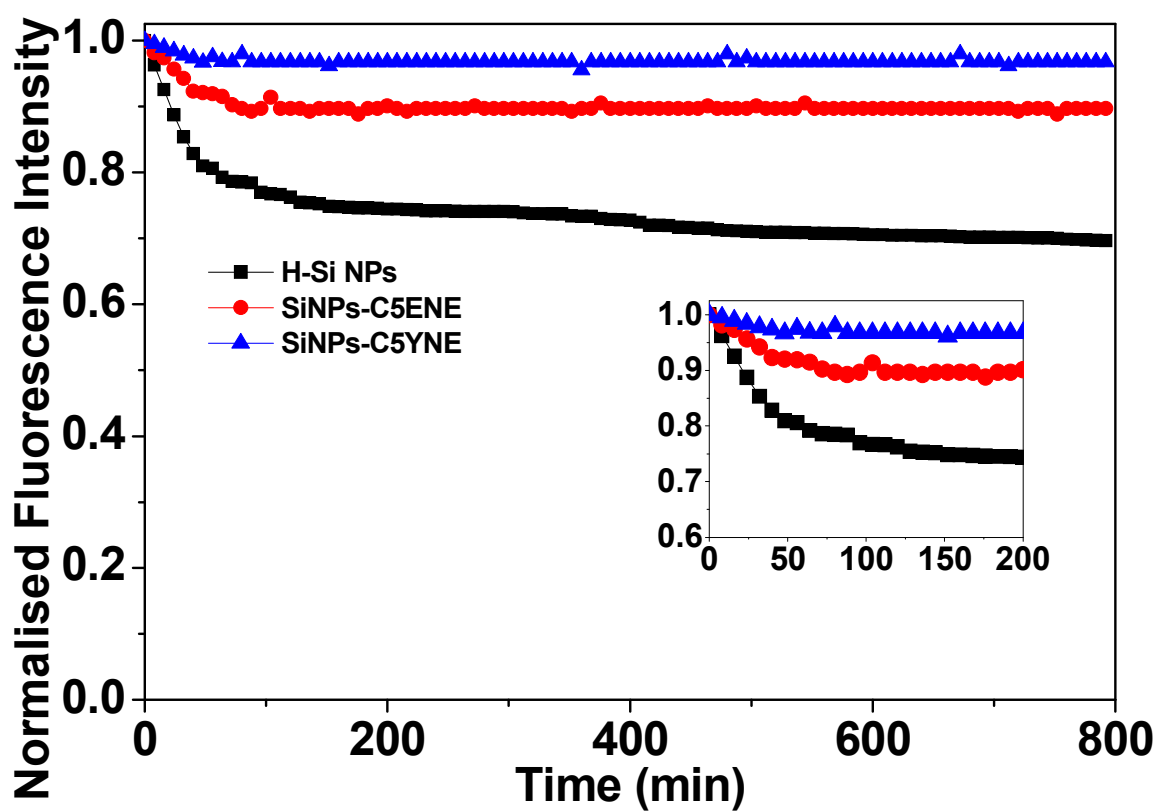


Figure S5. Stability of the fluorescence under ambient conditions of H-Si NPs, 1-pentene-modified and 1-pentyne-modified Si NPs.

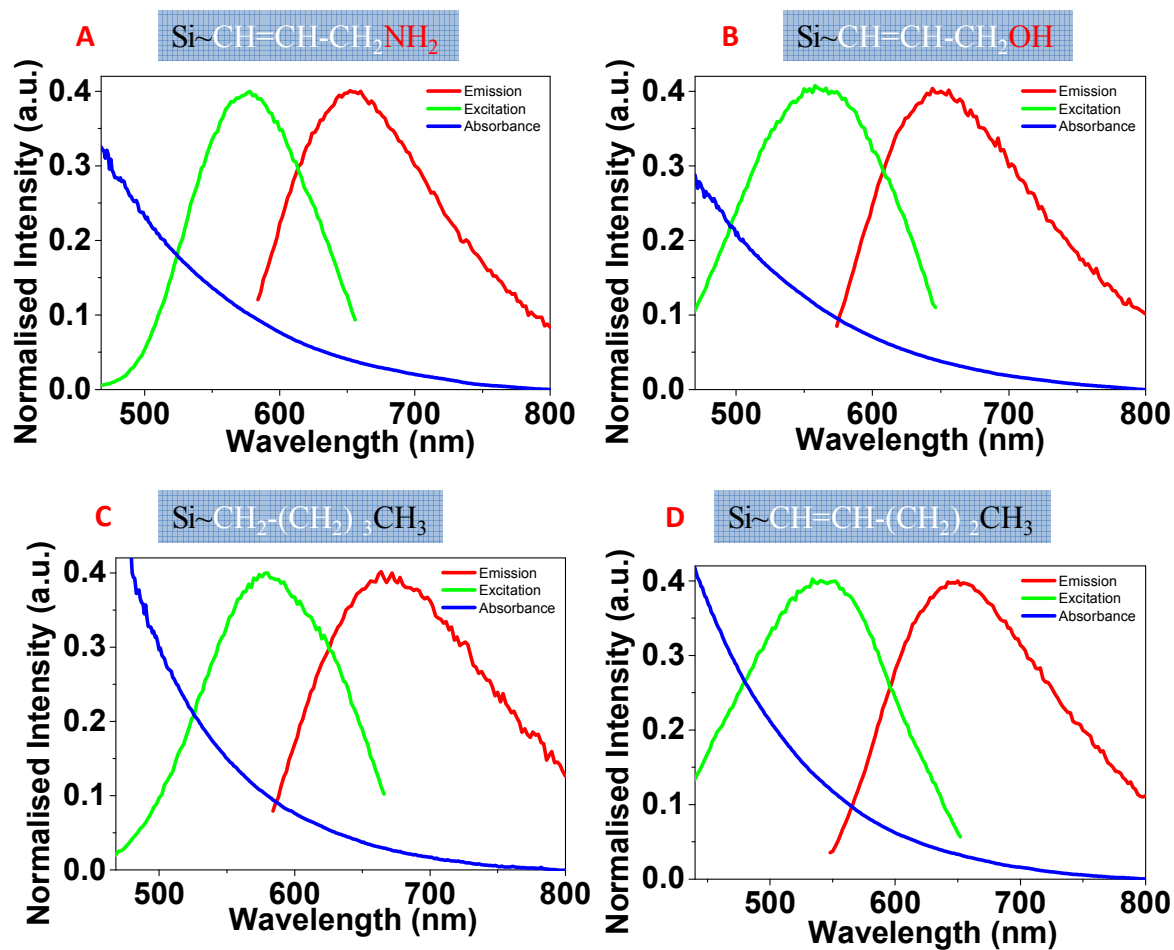


Figure S6. Excitation–emission and absorbance with excitation and emission plots for H-Si NPs as coated with propargyl amine; in water) (A), propargyl alcohol (in water) (B), 1-pentene (in dichloromethane) (C), and 1-pentyne (in dichloromethane) (D) after purifications.

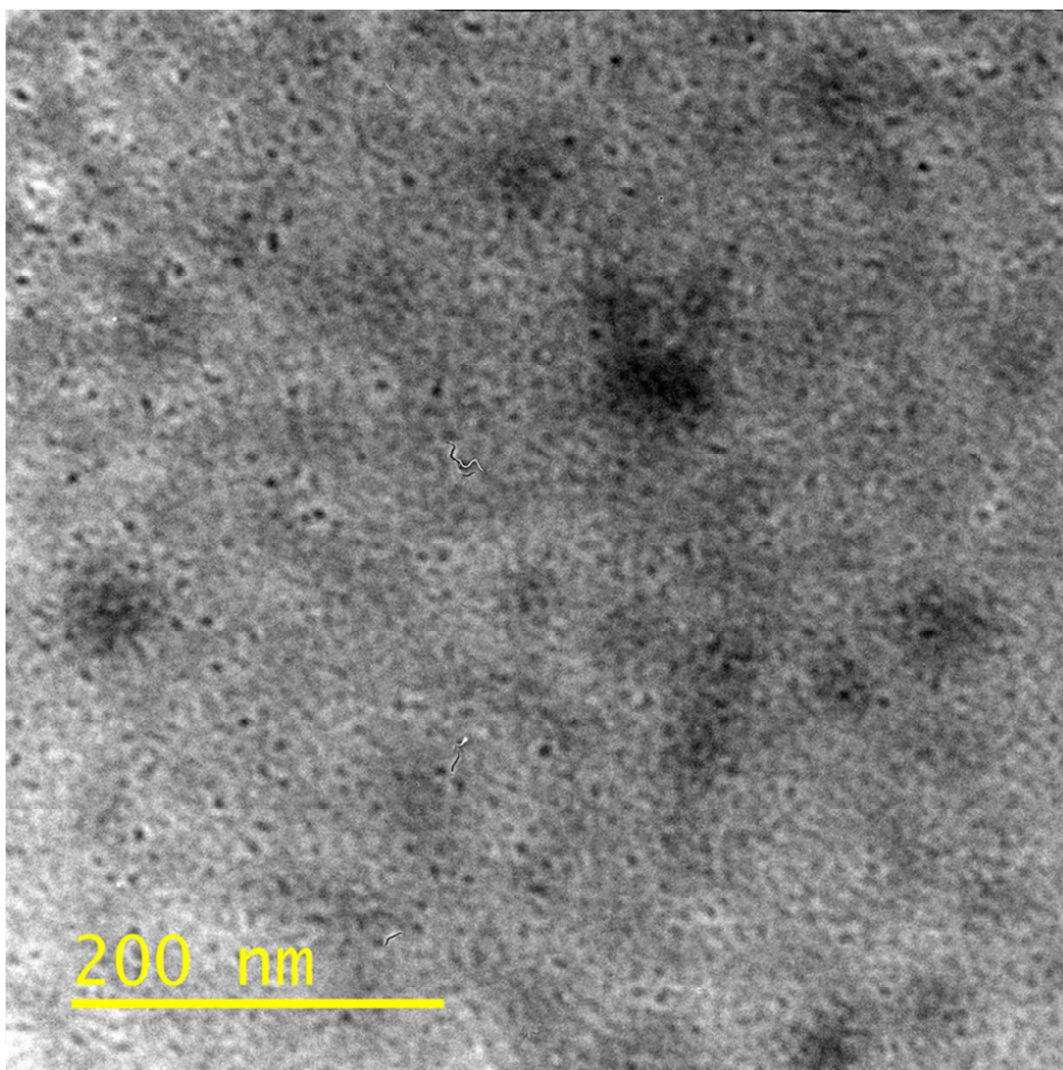


Figure S7. TEM images for 1-pentene-modified H-Si NPs.

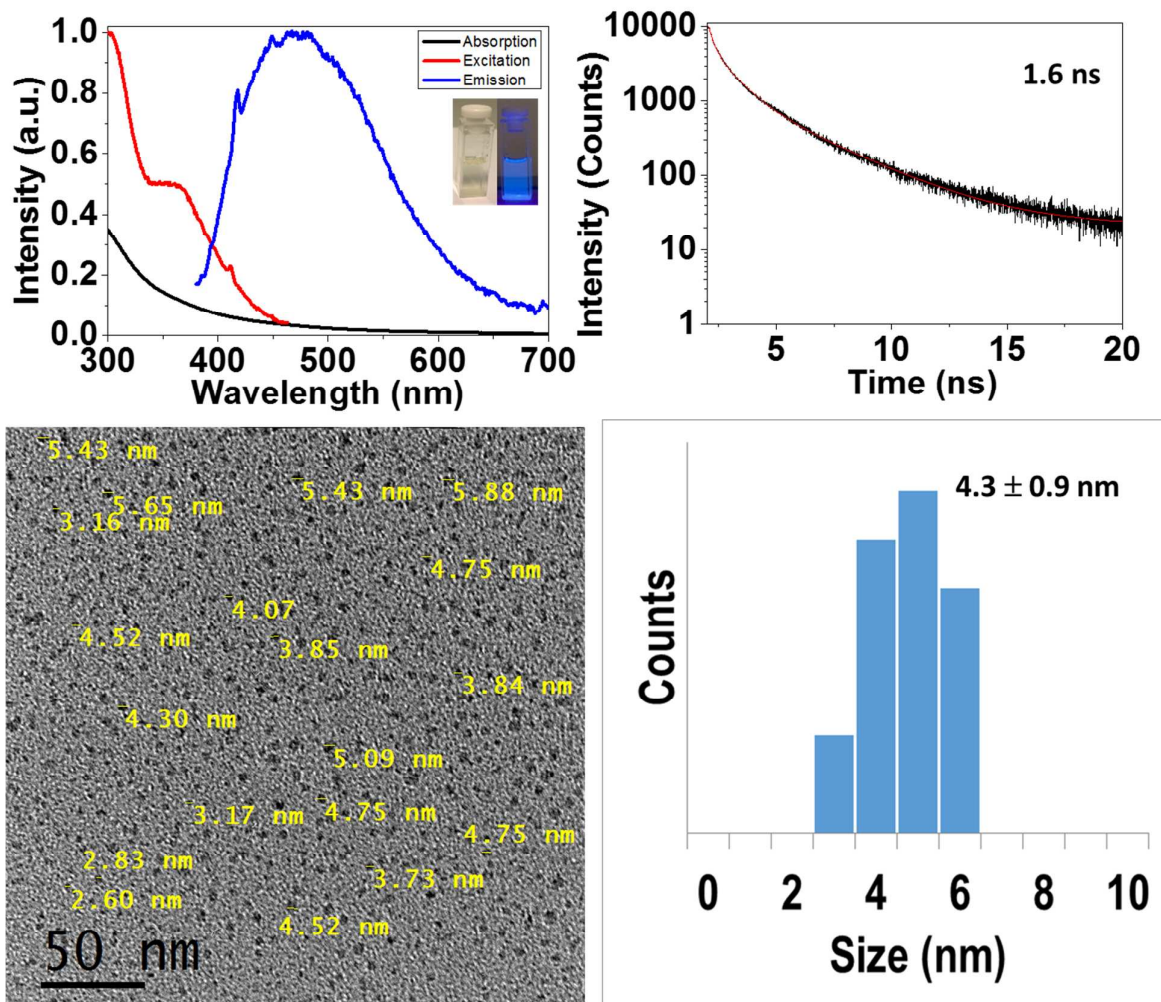


Figure S8: (Top, left) Optical properties freshly HF etched H-SiNPs in dichloromethane UV-Vis absorption (Black), florescent excitation (emission at 472 nm, red) and fluorescent emission (excitation at 372 nm, blue). (Top, right) fluorescence lifetime for freshly HF etched H-SiNPs in dichloromethane. (Bottom, left and right) TEM image of HF etched H-SiNPs and histogram for size distribution respectively.

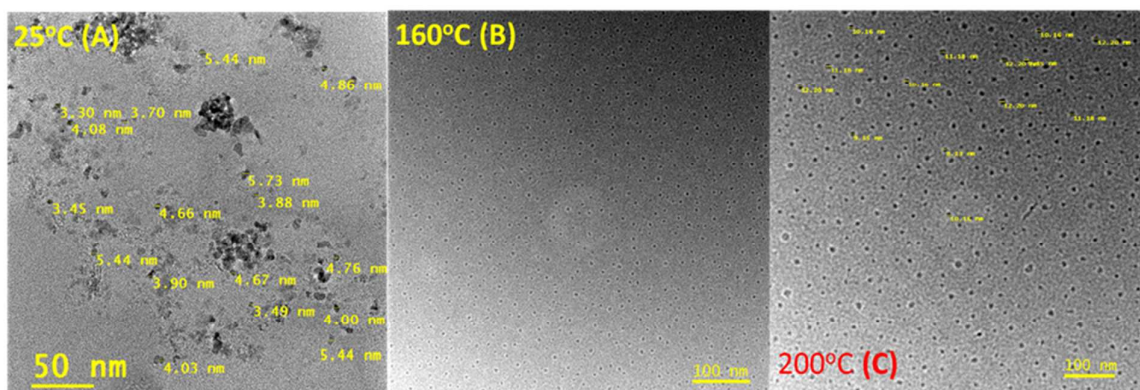


Figure S9: Transmission electron microscopy images for H-SiNPs prepared at 25°C (A), 160°C (B), and 200°C (C) in microwave.

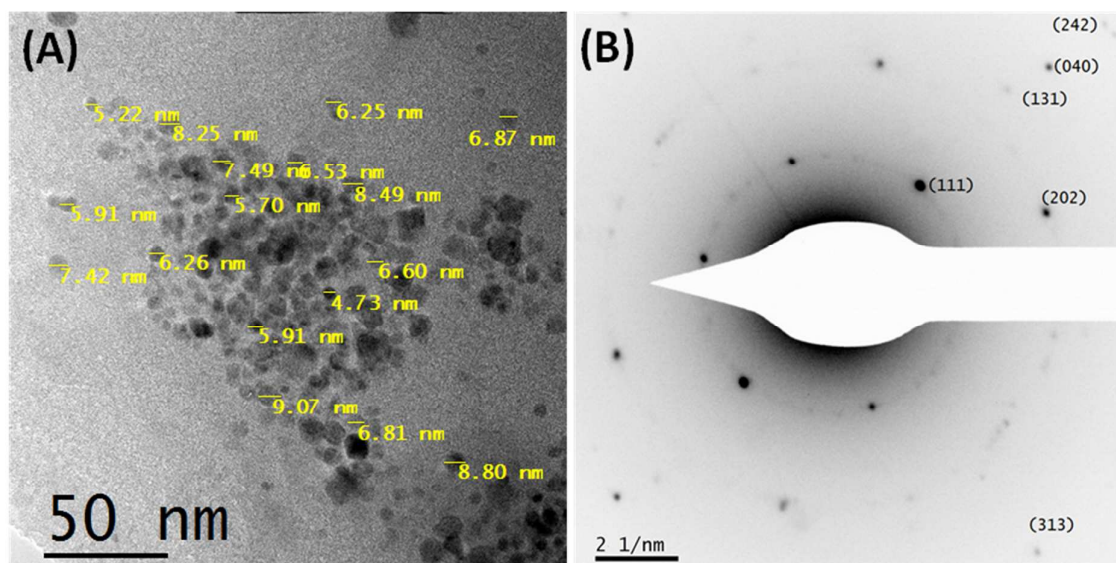


Figure S10. (A) TEM analysis of propargylamine-modified H-Si NPs (B) Electron diffraction pattern for H-SiNP modified with propargylamine.

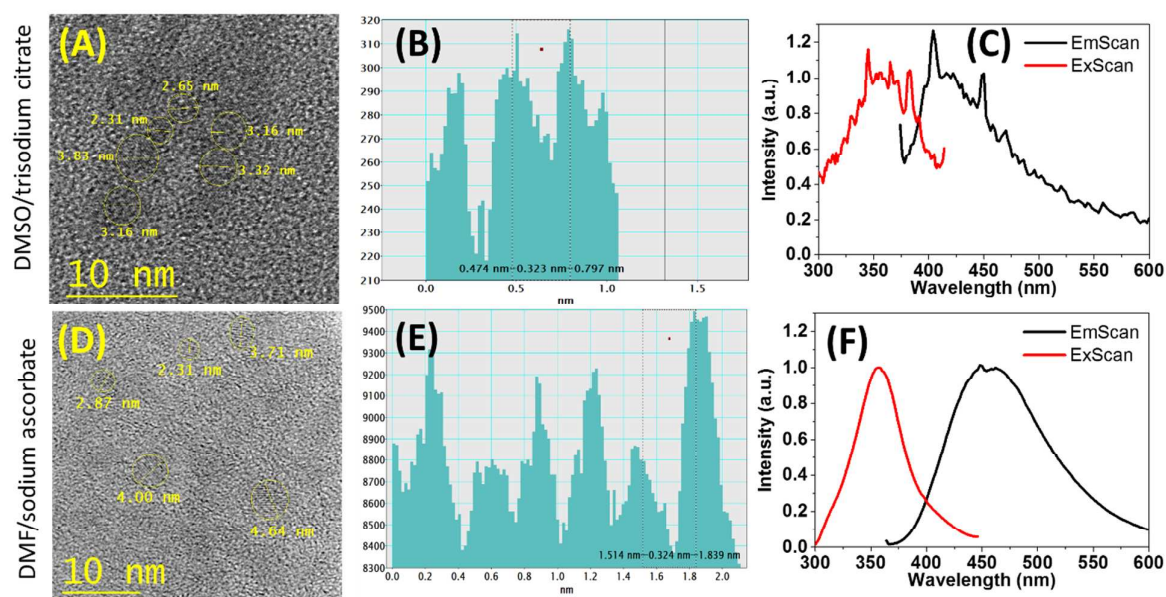


Figure S11: Characterization of H-Si NPs prepared at 160 °C for 30 min heating in microwave using DMSO as solvent with trisodium citrate: (A) Transmission electron microscopy images (B) Lattice spacing measurements from HR-TEM image, revealing a well-resolved Si(111) lattice spacing of 0.32 nm, and (C) Fluorescence emission and excitation spectra. Characterization of H-Si NPs prepared at 200 °C for 30 min heating in microwave using DMF as solvent with sodium ascorbate: (D) Transmission electron microscopy images, (E) Lattice spacing measurements from HR-TEM image, revealing crystallinity with a well-resolved Si(111) lattice spacing of 0.32 nm, and (F) Fluorescence emission and excitation spectra.

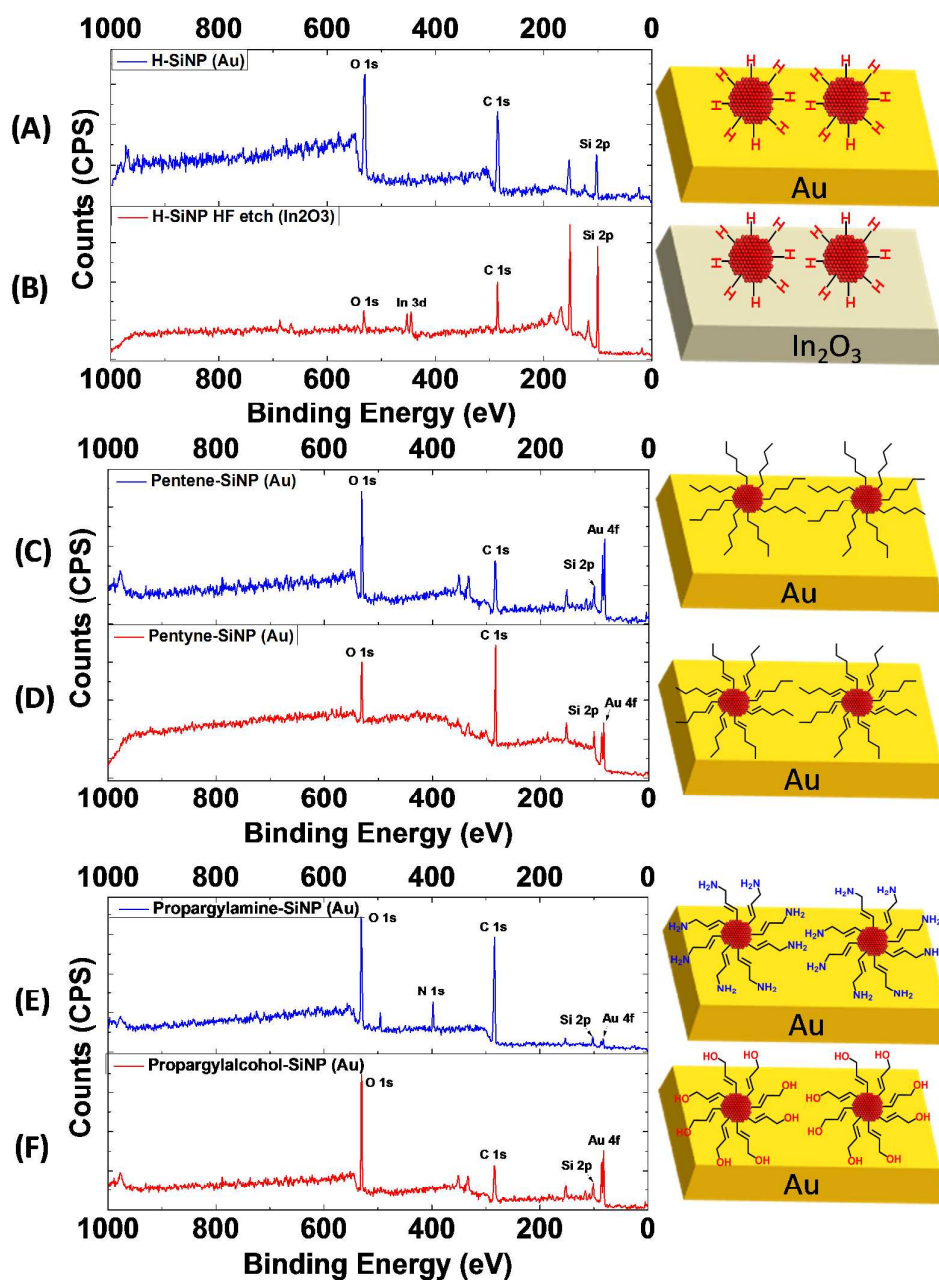


Figure S12: XPS wide scan spectra: (A) H-Si NPs obtained in DMSO at 160 °C (O = 24.4%, C = 50.8%, and Si = 24.8%). (B) H-Si NPs etched in HF (In = 1.4%, O = 5.4%, C = 30.2%, and Si = 63.0%). (C) H-Si NPs coated with 1-pentene (O = 23.0%, C = 49.9%, and Si = 27.1%). (D) H-Si NPs coated with 1-pentyne (O = 11.9%, C = 59.8%, and Si = 28.3%). (E) H-Si NPs coated with propargylamine (HC≡CCH₂NH₂) (O = 18.9%, C = 66.3%, N = 8.1%, and Si = 6.8%). (F) H-Si NPs coated with propargyl alcohol (HC≡CCH₂OH) (O = 27.0%, C = 51.1%, and Si = 21.9%). Samples A, C-F were deposited on a gold (Au) surface. Sample B was deposited on indium oxide (In₂O₃)

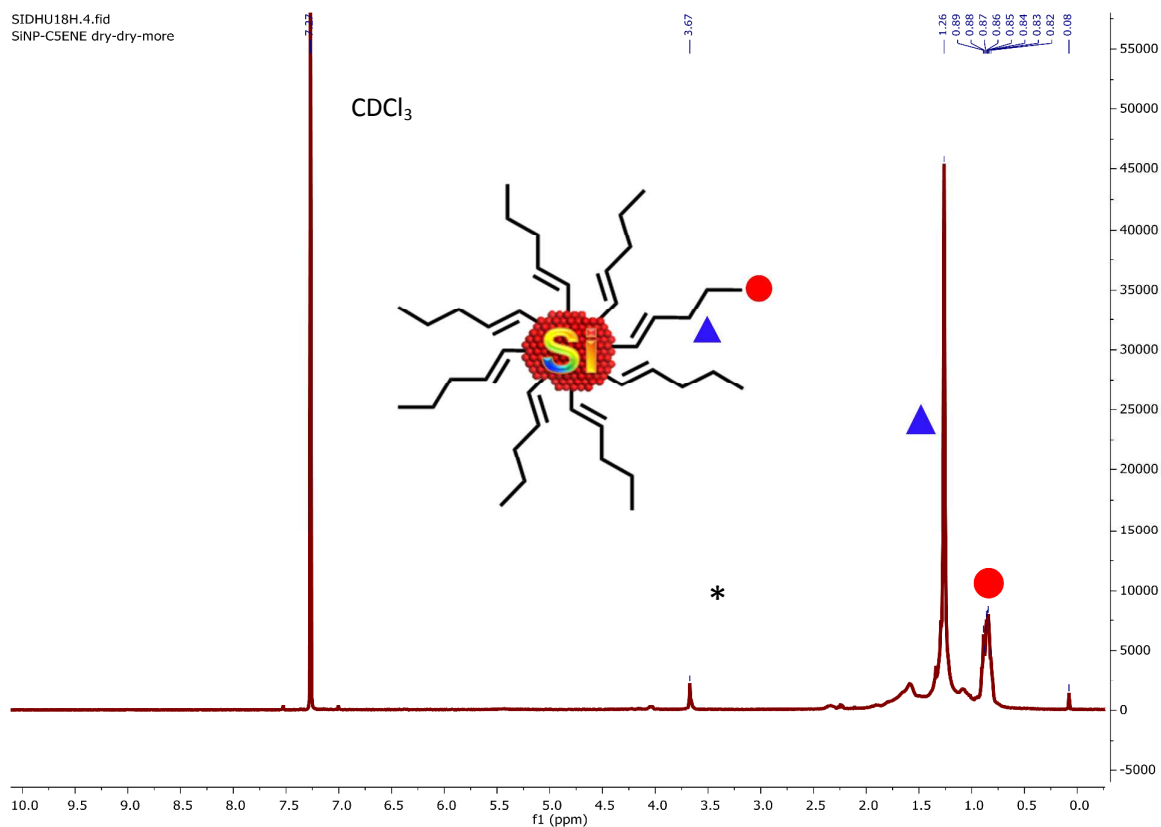


Figure S13: ^1H NMR spectrum of pentyne-grafted silicon nanoparticles in deuterated chloroform (CDCl_3).

XRD also provides a simple possibility for estimating the NP size from the broadening of the XRD reflections by means of the so-called Scherrer formula:

$$d = \frac{K\lambda}{w \cos \theta} \quad \text{.....(eq.1S)}$$

where d is average crystallite size, λ is the wavelength of the radiation, θ is the angle of the considered Bragg reflection which is 0.1789 nm ($1.79 \text{ \AA}$) for $\text{Co K}\alpha$, K is a constant close to unity for cubic crystallites is 0.94 . w is the width on a 2θ scale. Peak width = 1.05° . The TEM data in Figure 3A show that this estimate is overestimating the size slightly.

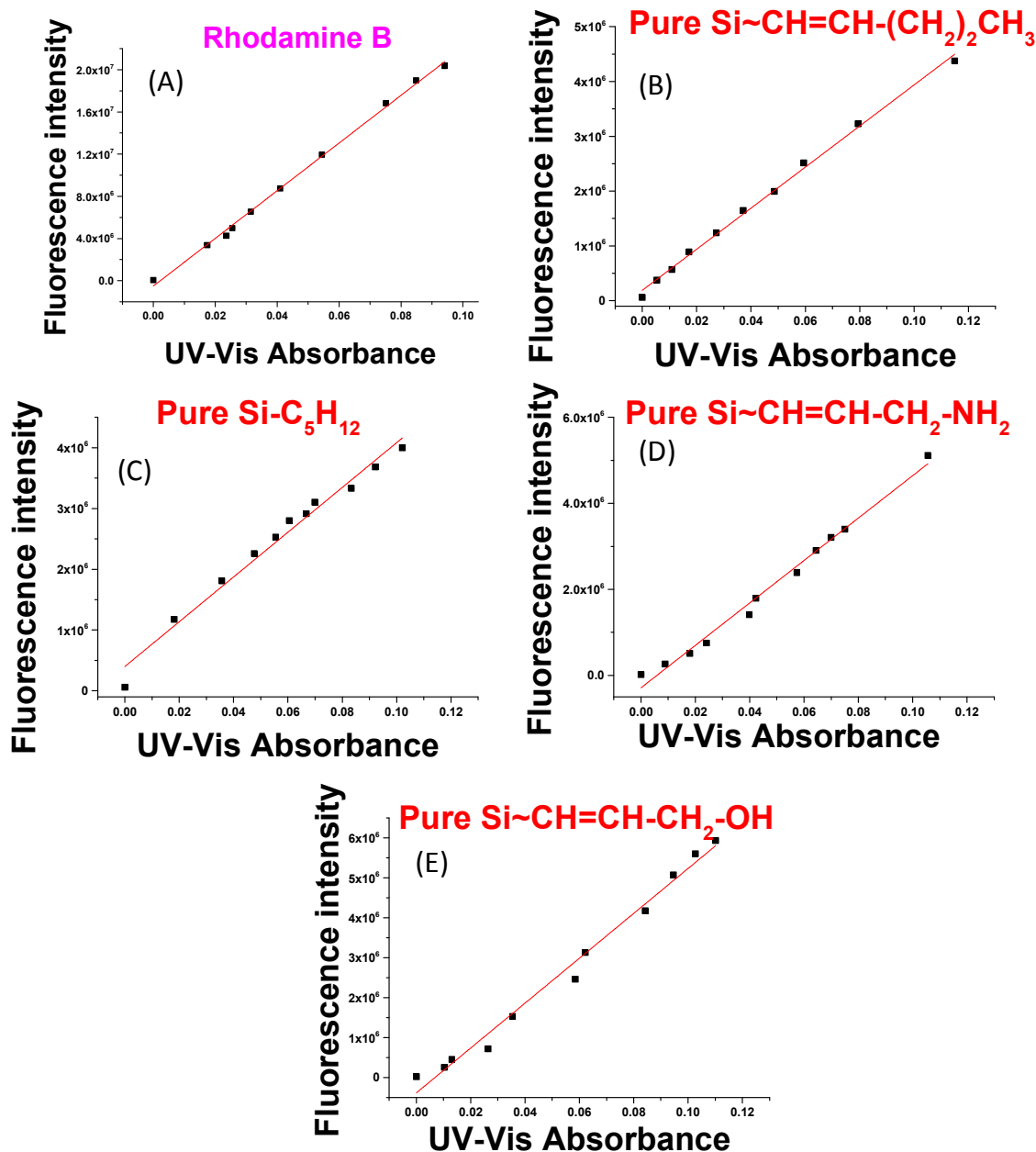


Figure S14: Measurement of fluorescence quantum yield for purified functional Si NPs using Rhodamine B (in dichloromethane) as a reference (A). Integrated fluorescence intensity dependence on the absorbance of functional Si NPs (B) Pure Si~CH=CH-(CH₂)₂CH₃, (**QY = 12.1%**) (in dichloromethane), (C) Si-C₅H₁₂, (**QY = 12.5%**) (in dichloromethane), (D) Si~CH=CH-CH₂-NH₂, (**QY = 12.7%**) (in water) and (E) Si~CH=CH-CH₂-OH (**QY = 14.3%**) (in water). The solid lines represent the fitting results for each set of data and $R^2 = 0.99$.

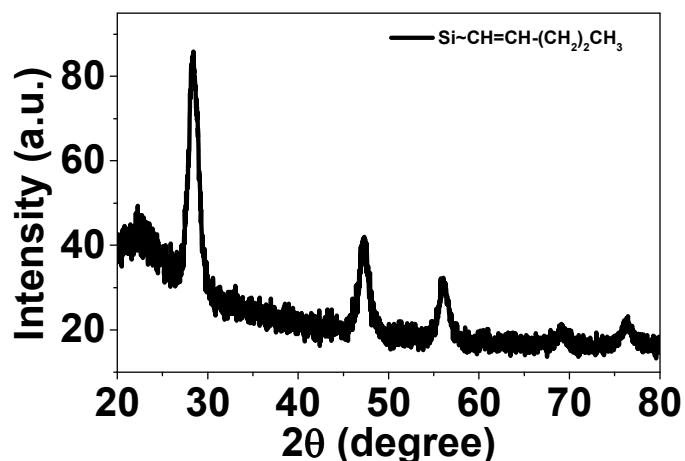


Figure S15: X-ray diffraction patterns for the H-Si NPs coated with 1-pentyne.

Calculation of Relative Photoluminescence Quantum Yield (PLQY). For the relative PLQYs we compared the integral emission spectra of the sample and the standard obtained under identical measurement conditions at various concentrations, and from the resulting linear fit interpolated to obtain for all solutions the integrated fluorescence intensity for $A = 0.1000$. **Figure S14** shows for all Si NPs such graph fitted with a linear least-square fit. The PLQYs were calculated according to the following equation 2S:^{1,2}

$$\Phi = \Phi_R * \frac{F_S}{F_R} * \frac{1 - 10^{-(Abs\lambda_{ex})_R}}{1 - 10^{-(Abs\lambda_{ex})_s}} * \frac{n_s^2}{n_R^2} \quad \text{.....(eq.2S)}$$

Where Φ is the relative fluorescence quantum yield, Φ_R is the quantum yield of the reference (in this case set at 68%), F_s is the integral of the emission spectrum for nanoparticles and F_R is the integral of the emission spectrum for reference, $Abs\lambda_{ex}$ is the light absorption at the excitation wavelength (here thus taken to be: 0.1000), and n is the refractive index of the solvent for (dichloromethane = 1.4125, water = 1.3333). The subscripts s and R refer to the sample and reference, respectively.

Yield and average mass of H-terminated and modified Silicon nanoparticles:

Method adapted from *Chem. Commun.* **2006**, 1433–1435

From the TEM result we know that the size of H-Si NPs is ~7 nm and $R_{\text{cluster-SiNp}} \approx 3.5$ nm, and $R_{\text{atomSi}} = 0.132$ nm.

The number of silicon atoms per nanoparticle was estimated as follows:

$$N_{\text{Si}} = ((R_{\text{cluster-SiNp}}) / (R_{\text{atomSi}}))^3$$

$$N_{\text{Si}} = ((3.5 * 10^{-9}) / (132 * 10^{-9}))^3$$

$$N_{\text{Si}} = 18.6 * 10^3 \text{ atoms of silicon per nanoparticle}$$

The number of surface atoms

$$N_s = 4 * N^{2/3}$$

$$N_s = 4 * (18.6 * 10^3)^{2/3}$$

$$N_s = 2.8 * 10^3 \text{ atoms of silicon on the nanoparticle surface.}$$

Average Molecular weight (M_w) of a single nanoparticle : Total Number of Silicon and Hydrogen

$$= (18.6 * 10^3 * 27.9 \text{ for Si}) + (2.8 * 10^3 * 1.0 \text{ for H})$$

$$M_w = 524 \text{ kDa for single H-Si NPs}$$

Nanoparticle	Theoretical Mw (@ 7 nm and 100 % hydrosilylation)	Expt. obtained materials (gm)	Calculated yield (%)
H-Si NPs	524 kDa	0.31	95
Si~CH=CH-(CH ₂) ₂ CH ₃	716 kDa	0.21	50
Si-C ₅ H ₁₂	721 kDa	0.18	42
Si~CH=CH-CH ₂ -NH ₂	687 kDa	0.28	70
Si~CH=CH-CH ₂ -OH	679 kDa	0.25	61

1. Brouwer, A. M., Standards for photoluminescence quantum yield measurements in solution (IUPAC technical report). *Pure Appl. Chem.* **2011**, 83, 2213-2228.
2. Grabolle, M.; Spieles, M.; Lesnyak, V.; Gaponik, N.; Eychmüller, A.; Resch-Genger, U., Determination of the Fluorescence Quantum Yield of Quantum Dots: Suitable Procedures and Achievable Uncertainties. *Anal. Chem.* **2009**, 81, 6285-6294.