

## SUPPLEMENTARY INFORMATION

## Gas-Phase Grafting for the Multifunctional Surface Modification of Silicon Quantum Dots

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## 1. Gas-Phase Synthesis Conditions

Synthesis and partial functionalization of materials were reproducibly performed in a lab at room temperature using the general conditions described in section 2.1 of the main text. Below are a list of the precise flow rates and pressures used to synthesize each of the samples used within the study. In the sample name “d” refers to the SiNC diameter as determined by the bandedge photoluminescent peak fitting described by Wheeler et al.<sup>1</sup> The alkyl chain ligands used were 1-hexene (Sigma Aldrich 95%), 1-octene (Sigma Aldrich 98%), or 1-dodecene (Sigma Aldrich 99%). As these compounds differ in length, their vapor pressures vary under standard conditions (25 °C, 1 atm), with 1-dodecene at 19.27 Pa, 1-octene at 2317.19 Pa, and 1-hexene at 24794.58 Pa, as found using the Antoine equation and constants determined by A. Forziati et. al.<sup>2</sup> The three orders of magnitude in vapor pressure variation requires the ligand vapors within the bubbler to be diluted with hydrogen attaining a higher internal bubbler pressure, while maintaining precise control of the flow balance in and out of the bubbler system. Thus, the optimized conditions for critical loading of each alkyl chain is performed at different pressures and flowrates to achieve the minimum ligand flux needed to maintain solubility as shown below in Table S1.

**Table S1** Conditions used for in-flight synthesis and partial functionalization of the SiQD described within the main text.

Sample	Ligand	Reactor Pres. (Torr)	1.38% SiH <sub>4</sub> :Ar (sccm)	Pure H <sub>2</sub> (sccm)	Bubbler H <sub>2</sub> (sccm)	Aprox. Bubbler Pres. (kPa)
Si-dodecyl (d = 2.8)	1-dodecene	0.70	60	97.5	2.5	0.1
Si-dodecyl (d = 3.0)	1-dodecene	0.80	60	97.5	2.5	0.1
Si-dodecyl aka. critical (d = 3.1 nm)	1-dodecene	0.85	60	97.5	2.5	0.1
Si-dodecyl (d = 3.3 nm)	1-dodecene	1.00	60	97.5	2.5	0.1
Si-dodecyl (High) (d = 3.1 nm)	1-dodecene	0.85	60	90	10	0.1
Pristine (d = 3.1 nm)	None	0.85	60	100	0	NA
Si-hexyl (d = 3.1 nm)	1-hexene	0.85	60	90	10	101

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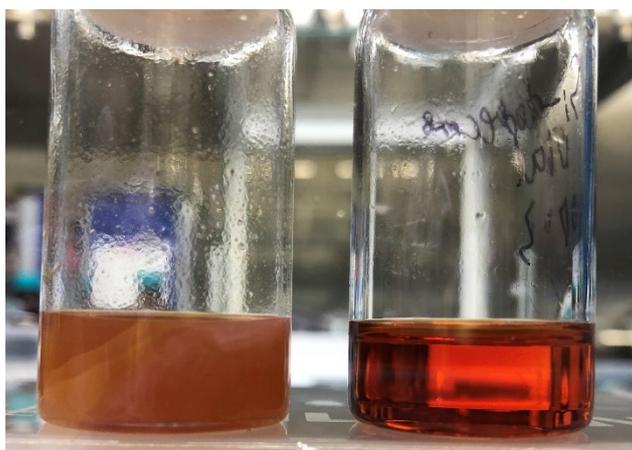
Si-octyl (d = 3.1 nm)	1-octene	0.85	60	95	5	20
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## 2. Liquid-Phase Hydrosilylation

The SiQDs partially functionalized with alkyl chains are diluted with mesitylene until the optical density at 488 nm is  $\sim 1.2$  in a 10 mm pathlength cuvette, as measured via UV-Vis absorption with an Agilent Technologies Cary 5000 spectrometer. To adjust the amount of transmitter molecules attached to SiQDs, a varying amount of 9-vinylanthracene (9VA, TCI America 97%) is added during the SiQD hydrosilylation process. The specific parameters for different components are displayed in Table S1. The small volume of solution was obtained by pipettes (3-25  $\mu\text{L}$ , 10-100  $\mu\text{L}$ , 100-1000  $\mu\text{L}$ ) and all components for each sample were added to a 20 mL vial with a Teflon cap. These samples are sealed and heated to 180  $^{\circ}\text{C}$  for 1.5 hours under constant stirring. This induces the formation of 9-ethylanthracene (9EA) onto the SiQD surface (labeled as Si:9EA). After the reaction, samples are purified by addition of methanol (methanol: mixture = 2:1 by volume) followed by centrifuging at 12000 rpm for 30 mins. The precipitated materials are then redispersed in 1.5 mL of toluene, followed by addition of 3 mL of methanol and centrifuged at 12000 rpm for 20 mins again. The cleaning procedure is repeated three times and the final 9EA grafted SiQD sample is redispersed in toluene. At this point the SiQD are fully functionalized with both the alkyl chain ligand (Si-hexyl, Si-octyl, or Si-dodecyl) to maintain solubility and the transmitter ligand (9EA), as illustrated in Figure 1b. For photon upconversion measurements, the 9EA functionalized SiQDs solution is diluted with toluene to achieve an OD value of  $\sim 0.1$  at 488 nm in a 1 cm pathlength cuvette, then 9,10-diphenylanthracene (DPA, TCI America 98%) is added for a final DPA concentration of 5.2 mM. The mixture is transferred into a 10 mm x 10 mm quartz cuvette sealed with an air-tight Teflon cap for further optical characterization.

**Table S2** Standard mixtures used for optimizing 9EA surface concentration on SiQD through in-solution reactions.

	Si NC in Mesitylene ( $\text{OD}_{488} = 1.2$ )	9VA in Mesitylene (1 mg/mL)	Mesitylene	Total volume
Sample 1	200 $\mu\text{L}$	8 $\mu\text{L}$	1792 $\mu\text{L}$	2000 $\mu\text{L}$
Sample 2	200 $\mu\text{L}$	31 $\mu\text{L}$	1769 $\mu\text{L}$	2000 $\mu\text{L}$
Sample 3	200 $\mu\text{L}$	125 $\mu\text{L}$	1675 $\mu\text{L}$	2000 $\mu\text{L}$
Sample 4	200 $\mu\text{L}$	500 $\mu\text{L}$	1300 $\mu\text{L}$	2000 $\mu\text{L}$



**Fig. S1** Subcritical (left) and critical (right) alkyl chain ligand loading of partially functionalized SiQDs in mesitylene at room temperature.

### 3. Transmitter Molecule Measurement and Luminescence Quantum Yield Calculation

#### 3.1 Transmitter Molecule Measurement

The average number of 9EA groups per quantum dot is estimated by the following procedure. First, the absorption spectra of the SiQDs with alkyl chains but without 9EA groups and then with both alkyl chains and 9EA groups are dissolved in toluene are measured separately. Then, the contribution from the SiQD with only the alkyl chain is subtracted to isolate the absorbance from the 9EA groups:

$$\langle N_{9EA} \rangle = \frac{[9EA]}{[SiQD]} = \frac{\left( abs_{F:SiQD,395nm} - abs_{SiQD,395nm} \frac{\langle abs_{F:SiQD} \rangle}{\langle abs_{SiQD} \rangle} \right) \epsilon_{SiQD,488nm}}{\epsilon_{9VA,389nm} abs_{F:SiQD,488nm}} \quad (S1)$$

Here,  $\langle abs_{F:SiQD} \rangle / \langle abs_{SiQD} \rangle$  is the ratio between the absorbance of the fully functionalized and partially functionalized quantum dots in the 550-700 nm region. The extinction coefficient of 9MA at 389 nm ( $\epsilon_{9MA,389nm}$ ) in toluene is  $8413 \text{ M}^{-1}\text{cm}^{-1}$ , while the extinction coefficient of SiQD with size approximately 3.1 nm at 488 nm is  $10000 \text{ M}^{-1}\text{cm}^{-1}$ .<sup>3-5</sup>

#### 3.2 Photon Upconversion Quantum Yield Calculation

Photon upconversion measurements were performed using a 488 nm OBIS Coherent laser as excitation sources and an Ocean Optics Maya 2000 Pro spectrometer for detection of upconverted light. Emitted photoluminescence (PL) was filtered through a ThorLabs 488 nm notch filter before being received by the spectrometer to remove scattered excitation light. For each upconversion measurement, the system was calibrated using Rhodamine 6G (R6G) dissolved in ethanol as an emission reference (PLQY = 95%). The upconversion photon quantum yield (UCQY) was determined using the following expression:

$$\phi_{UC} = 2 \times \phi_{ref} \times \frac{\text{photons absorbed by reference}}{\text{photons absorbed by upconversion solution}} \times \frac{\text{upconversion PL}}{\text{reference PL}} \quad (S2a)$$

$$= 2 \times \phi_{R6G} \times \frac{1 - 10^{-OD_{R6G}}}{1 - 10^{-OD_{SiQD}}} \times \frac{n_{DPA}^2}{n_{R6G}^2} \times \frac{[Area]_{DPA}}{[Area]_{R6G}} \quad (S2b)$$

where  $\phi_{ref}$  is the PLQY of R6G,  $n_{DPA}$  and  $n_{R6G}$  are the refractive indices of the solvents for the DPA upconversion and R6G reference solutions (toluene and ethanol, respectively),  $[Area]_{DPA}$  and  $[Area]_{R6G}$  are the integrated areas of the fluorescence peaks of DPA and R6G, respectively.  $OD_{R6G}$  and  $OD_{SiQD}$  denote the absorbance of SiQDs and R6G at the laser excitation wavelength. Note: This expression includes a factor of 2 to normalize the maximum UCQY that is achievable to a value of 100%.

#### 3.3 Si QDs Photoluminescence Quantum Yield Calculation

The SiQD PL quantum yield (PLQY) was determined using the following expression:

$$\phi_{UC} = \phi_{ref} \times \frac{\text{photons absorbed by reference}}{\text{photons absorbed by upconversion solution}} \times \frac{\text{SiQD PL}}{\text{reference PL}} \quad (S3a)$$

$$= \phi_{R6G} \times \frac{1 - 10^{-OD_{R6G}}}{1 - 10^{-OD_{SiQD}}} \times \frac{n_{DPA}^2}{n_{R6G}^2} \times \frac{[Area]_{SiQD}}{[Area]_{R6G}} \quad (S3b)$$

where  $\phi_{ref}$  is the PLQY of R6G,  $n_{DPA}$  and  $n_{R6G}$  are the refractive indices for the solvents of the DPA and R6G reference solutions (toluene and ethanol, respectively),  $[Area]_{SiQD}$  and  $[Area]_{R6G}$  are the integrated areas of the fluorescence peaks of SiQDs and R6G, respectively.  $OD_{R6G}$  and  $OD_{SiQD}$  denote the absorbance of SiQDs and R6G at the laser excitation wavelength.

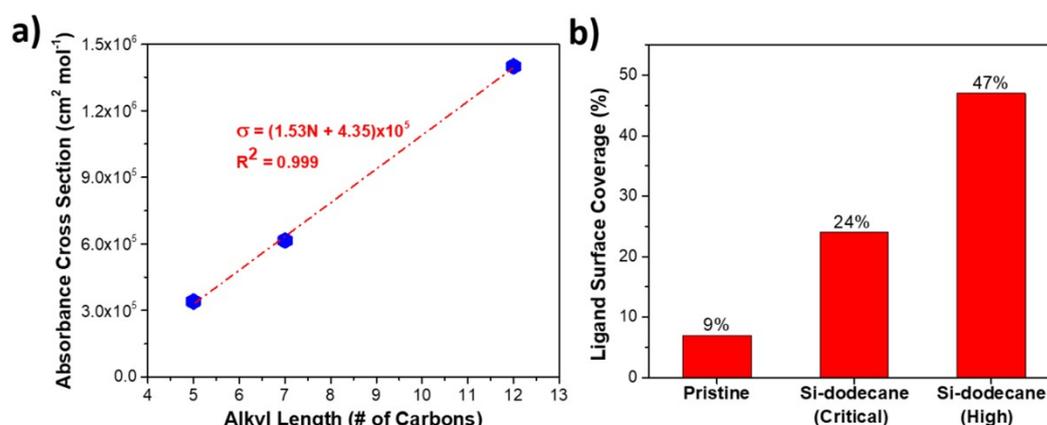
#### 4. Surface Coverage Calculation

Using the peak absorption cross sections of the C-H bond ( $2922\text{ cm}^{-1}$ ) from Klingbeil et. al. for unbound alkyl groups pentane, heptane, and dodecane a fitting was made to interpolate the values for hexane and octane as shown in Fig. S2a and Table S3.<sup>6</sup> The silyldiyne molecule (Si-H) absorption cross section at  $2130\text{ cm}^{-1}$  was then used as a proxy for all remaining surface bonds on the SiNC. A ratio of absorption amplitudes at the  $2922\text{ cm}^{-1}$  and  $2130\text{ cm}^{-1}$  peak positions is then taken and sensitivity compensation via absorption cross section values are applied as shown in Equation S2. This estimates the surface coverage ratio between the alkyl and Si-H compounds and a ligand surface coverage estimate is then determined through Equation S3 and plotted.

$$R = \left( \frac{A_{SiH}}{A_{CH}} \right) \left( \frac{\sigma_{CH}}{\sigma_{SiH}} \right) \quad (S4)$$

$$\text{Surface Coverage \%} = 100 \left( \frac{R}{R + 1} \right) \quad (S5)$$

In these equations  $R$  is the surface coverage ratio,  $A_{SiH}$  and  $A_{CH}$  are the experimental absorptions at  $2130\text{ cm}^{-1}$  and  $2922\text{ cm}^{-1}$  respectively, while  $\sigma_{SiH}$  and  $\sigma_{CH}$  are the absorption cross sections of the silyldiyne and ligand chain at  $2130\text{ cm}^{-1}$  and  $2922\text{ cm}^{-1}$  respectively. It is worth noting that the literature sources for the absorption cross sections used for all species in this analysis were performed on unbound molecules. The resulting ligand surface coverages are plotted in Fig. 5a and Fig. S2b where the coverage for the "Pristine" sample used the dodecane absorption cross section.



**Fig. S2** a) Fitting of the absorption cross section at  $2922\text{ cm}^{-1}$  for alkyl groups with respect to carbon chain length and b) predicted ligand surface coverage using the silyldiyne and dodecane absorption cross sections for samples produced with differing amounts of 1-dodecene flow.

**Table S3** Absorption cross sections at a given wavenumber.

Molecule	Wavenumber (cm <sup>-1</sup> )	Absorbance Cross Section (cm <sup>2</sup> /molecule)	Source
Silyldiyne (SiH)	2130	6.35E-19	7
Hexane (C <sub>6</sub> H <sub>12</sub> )	2922	7.95E-19	Interpolated from (S2a)
Octane (C <sub>8</sub> H <sub>16</sub> )	2922	1.30E-18	Interpolated from (S2a)
Dodecane (C <sub>12</sub> H <sub>24</sub> )	2922	2.31E-18	Interpolated from (S2a)

## 5. Surface Atom Calculation

There are multiple commonly used methods for approximating the total number of atoms or number of surface atoms on a spherical nanoparticle. As crystal structures deform significantly when dealing with nanomaterials all methods can only be used as an approximation, so for accuracy two methods were employed in this study. Both of which required the SiNC diameter ( $d = 3.1 \text{ nm}$ ) as well as its associated surface area ( $S = 30.6 \text{ nm}^2$ ) and volume ( $V = 15.9 \text{ nm}^3$ ) as determined through basic geometry.

### 5.1 Density Method

The first method appears to be the most common and utilizes readily available information such as silicon's atomic mass (

$A_{\Gamma} = 28.085 \frac{\text{g}}{\text{mol}}$ ), density ( $\sigma = 2.329 \frac{\text{g}}{\text{cm}^3}$ ), and covalent bond length ( $r_A = 0.111 \text{ nm}$ ). From there the total number of atoms is determined by dividing the volume of the nanoparticle by an approximate atomic volume as found through the density and atomic mass, where  $N_A$  is Avogadro's constant.

$$\text{Atoms}_{\text{Total}} = V \frac{\sigma}{A_{\Gamma}} N_A = 779.4 \text{ atoms} \quad (\text{S6})$$

To determine the number of surface atoms the approach is simply to reduce the radius of the particle by 1 fully bonded atomic layer or 2 covalent bond lengths. Repeat the process with the reduced particle diameter and subtract the number of atoms in this reduced particle from the original diameter.

$$d_{\text{core}} = d - 4r_A = 2.656 \text{ nm} \quad (\text{S7})$$

$$\text{Atoms}_{\text{Surface}} = \text{Atoms}_{\text{Total}} - \left( \frac{1}{6} \pi d_{\text{core}}^3 \right) \frac{\sigma}{A_{\Gamma}} N_A = 289.1 \text{ atoms} \quad (\text{S8})$$

### 5.2 Unit Cell Method

The second method is based on the silicon unit cell and its key features. Silicon has a diamond structure which means that it contains  $N_V = 8$  atoms per cell with  $N_S = 2$  bisected atoms on each cell face, which is  $a = 0.0543 \text{ nm}$  in length.

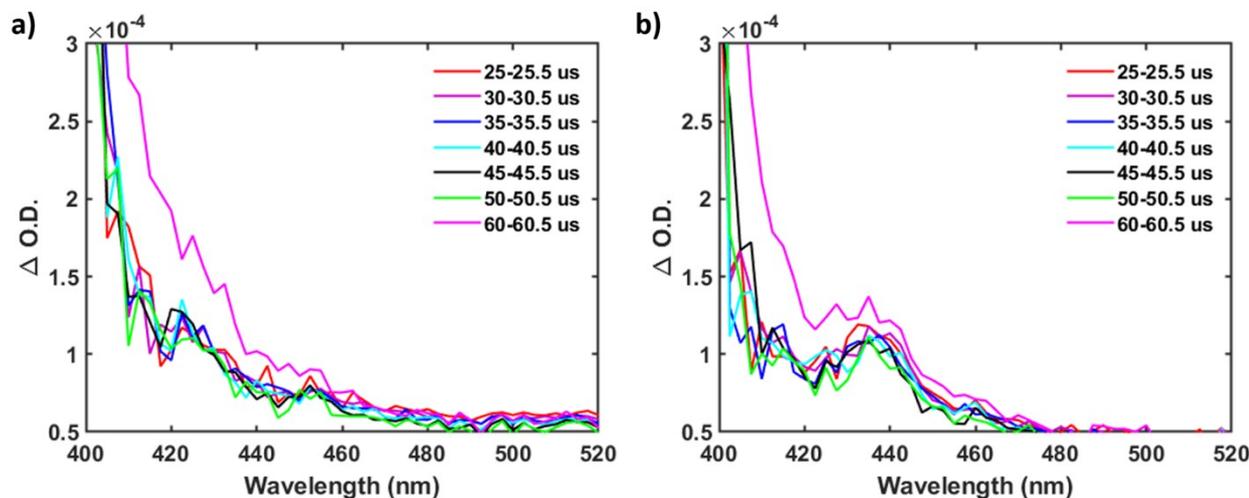
$$\text{Atoms}_{\text{Total}} = \frac{V}{a^3} N_V = 779.4 \text{ atoms} \quad (\text{S9})$$

$$\text{Atoms}_{\text{Surface}} = \frac{S}{a^2} N_S = 204.8 \text{ atoms} \quad (\text{S10})$$

As can be seen, both methods give approximately the same number of atoms within the nanoparticle total volume  $\sim 795$  atoms but differ in the number of surface bound atoms leaving the possible range for the 3.1 nm silicon nanoparticle as likely being between 207 and 294 atoms.

## 6. Transient Absorption (TA) Data

Using transient absorption with excitation at 532 nm, triplet energy transfer from SiQD to attached 9EA was tested on critically loaded Si-dodecyl ( $d = 3.1$  nm) samples both with and without 9EA attachment as shown in Figure S3. For SiQD functionalized with 9EA there is a peak resonance at 435 nm that corresponds to the triplet excited states absorption of the surface-bound 9EA, while no such peak was observed for SiQD without 9EA. Since laser light at 532 nm is unable to excite 9EA directly and can only excite SiQD, this triplet signal of 9EA must be a result of the triplet transfer from SiQD, demonstrating the energy transfer between the SiQD sensitizer and the 9EA transmitter molecule.



**Fig. S3** TA spectra of (a) Si-dodecyl without 9EA and (b) Si-dodecyl with 9EA ( $d = 3.1$  nm, 3 9EA molecules per SiQD) in toluene excited at 532 nm. (TA measurements were conducted using an enVISION spectrometer from Magnitude Instruments that employed a 532 nm excitation laser with a 10 kHz repetition rate and a pump fluence of  $150 \mu\text{J}/\text{cm}^2$ . The instrument response function for these measurements was found to give a time resolution of 4.2 ns.)

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