One-pot synthesis of colloidal silicon quantum dots and surface functionalization via thiol-ene click chemistry

Supporting Information

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S1.Experimental

Chemicals and Materials

All chemicals used were purchased from Sigma-Aldrich and were used as received unless otherwise stated. All dry solvents were obtained after passing through PURE-SOLV (Innovative Technology) solvent purification system with oxygen and water content below 15 ppm.

Synthesis of silicon quantum dots coated with allyl group

All experiments were conducted using standard Schlenk techniques. In a typical experiment, silicon tetrachloride ($SiCl_4$, 100 μL) and allyl trichlorosilane ($SiCl_3$-$CH_2CH=CH_2$, 175 μL) were mixed in 100 mL dry toluene (shown above) and sonicated for 20 min. An excess amount of $LiAlH_4$ in dry THF was then added, and the mixture further sonicated for another 30 min. The reaction was quenched by adding dry ethanol (~30 mL). All solvents were then evaporated under reduced pressure, and 10 mL hexane was added to disperse the particles. The mixture was washed with 30 mL MilliQ water, and the organic layer extracted and passed through PVDF membrane with 0.45µm pore size. If further functionalization was performed, the hexane solvent was evaporated under reduced pressure.

Surface functionalization of silicon quantum dots via thiol-ene click reactions.

The allyl terminated silicon quantum dots were dissolved in 10 mL DMF, and thiol molecules were added to the mixture in 1:5 ratio. The reaction was left in a UV chamber (254 nm) for 5 hours. After the reaction, all of the solvent were removed by evaporation under reduced pressure. For purification, the particle mixtures were either dialyzed in semi-permeable membrane with 4kDa cut off against MilliQ water for 24 hrs, or heated under reduced pressure in the case of thiol-butane. Purified quantum dots were dispersed in 5 mL of water or hexane depending on the surface groups.

Characterization methods

All TEM images were recorded on a Philip CM200 microscope operated at 200 kV. For typical sample preparation, ~ 5µL of concentrated quantum dots solution was dropped on a copper grid covered with carbon film and solvent evaporated in room temperature. All TEM images were visualized without staining. For IR spectroscopy of surface groups attached to silicon quantum dots, 5 µL of concentrated quantum dots solution was dropped on a KBr plate. Transmittance spectra were measured on a AVARTAR-320 FT-IR Spectrometer. ^{1}H-NMR experiments were run on a Bruker DPX 300MHz spectrometer equipped with an autosampler. NMR spectra of silicon quantum dots were prepared by adding ~ 5 mg silicon quantum dots in deuterated solvents (i.e. $CDCl_3$ or D_2O depending on surface groups).

S.2 TEM images of SiQDs with various functional groups

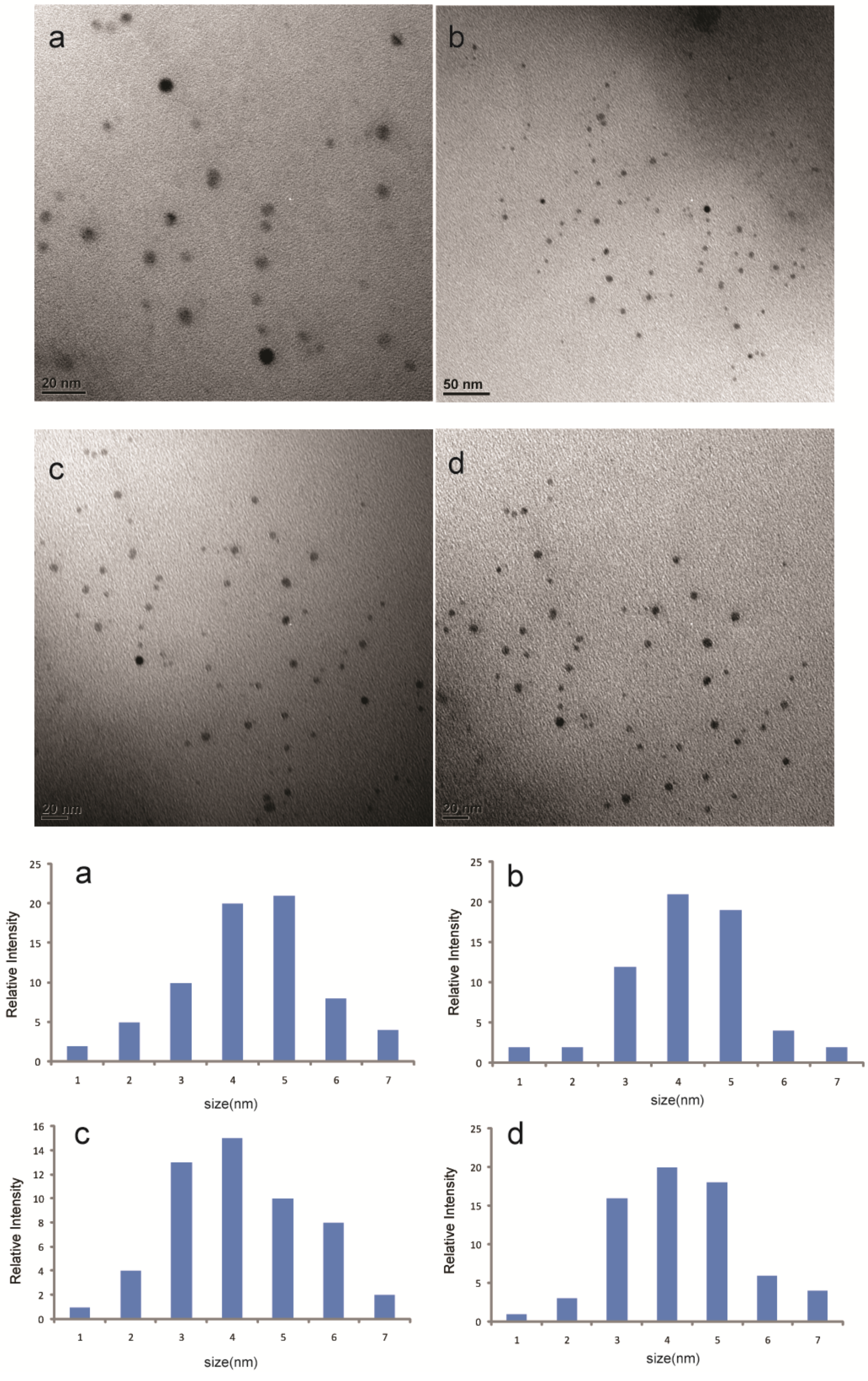

Figure S1. Representative TEM images of SiQDs with different surface groups. From a-d showing terminal groups as: a) SiQD-NH$_2$ (4.3±1.4 nm), , b) SiQD-COOH (4.2 ±1.1 nm), c) SiQD-SO$_3^-$ (4.1±1.3 nm), d) SiQD-butane (4.2±1.3 nm).

S.2 ^{1}H-NMR spectra of surface functionalized SiQDs

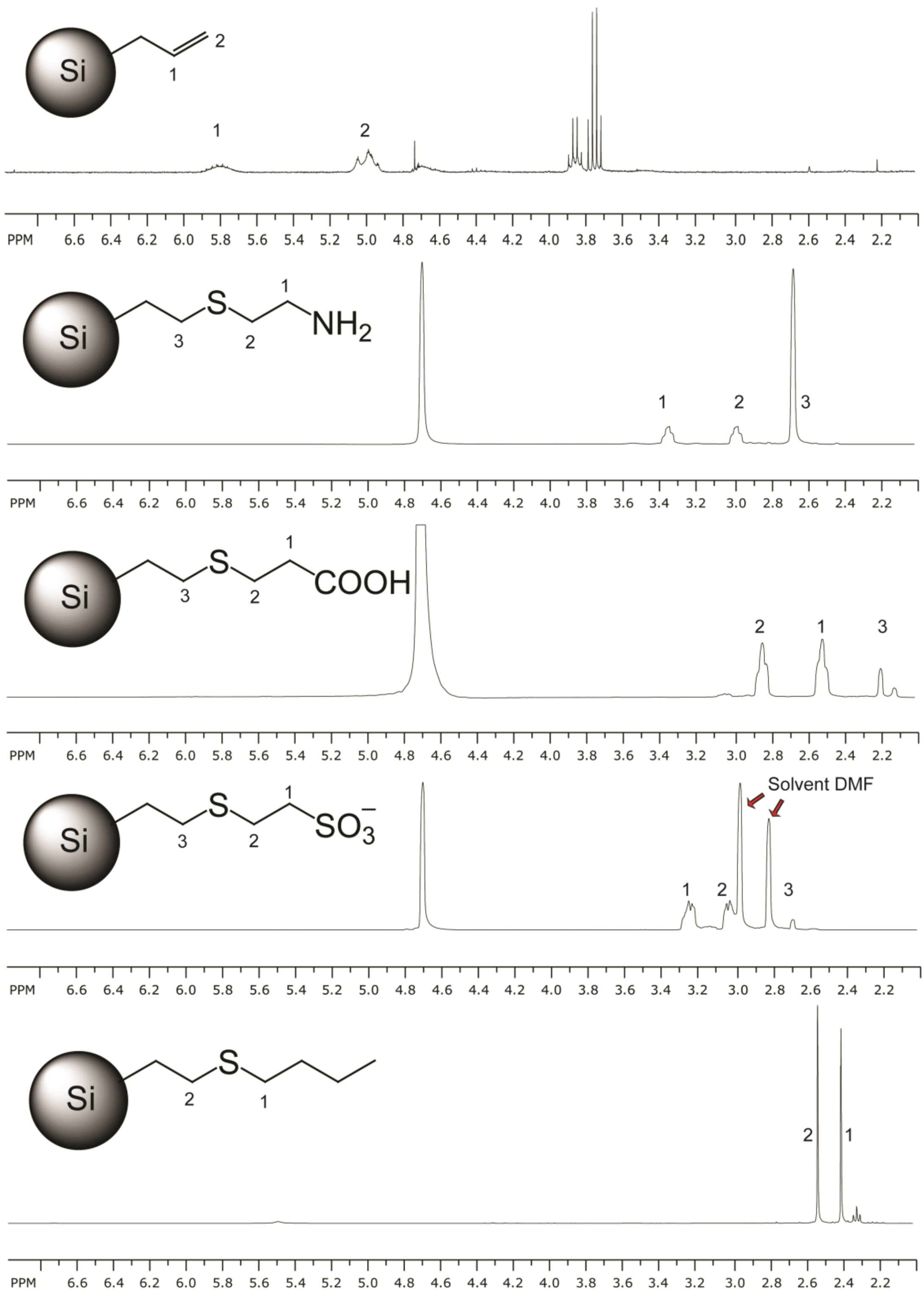

Figure S2. ^{1}H-NMR spectra showing different surface groups on SiQDs. Peaks from the surface groups of SiQDs are significantly broadened, which is likely due to the slow tumbling of the particles in solvents, causing difficulties in resolving some of the splitting patterns. For allyl terminated SiQDs, two peaks at 5.8 ppm (singlet) and 5.0 ppm (doublet) are typical for terminal alkene groups. These two peaks disappear after performing the click reaction, indicating reaction of the alkene with the SH group. In addition, for thiol-amine terminated quantum dots, the two peaks at 2.97 ppm (triplet) and 3.34 ppm (triplet) are due to the CH_2 protons on the attached thiol-amine molecules. Similarly, For thiol-carboxyl terminated quantum dots, the two peaks at 2.85 ppm (triplet) and 2.51 ppm (triplet) are due to the CH_2 protons on the attached thiol-carboxyl molecules. For thiol-sulfonate terminated quantum dots, the two peaks at 3.25 ppm (multiplet) and 3.05 ppm (multiplet) are due to the CH_2 protons on the attached thiol-sulfonate molecules. For thiol-butane terminated quantum dots, the two peaks at 2.55 ppm and 2.42 ppm are due to the CH_2 protons next to the thiol groups.

S.3 UV absorption and Photoluminescence (PL) spectra

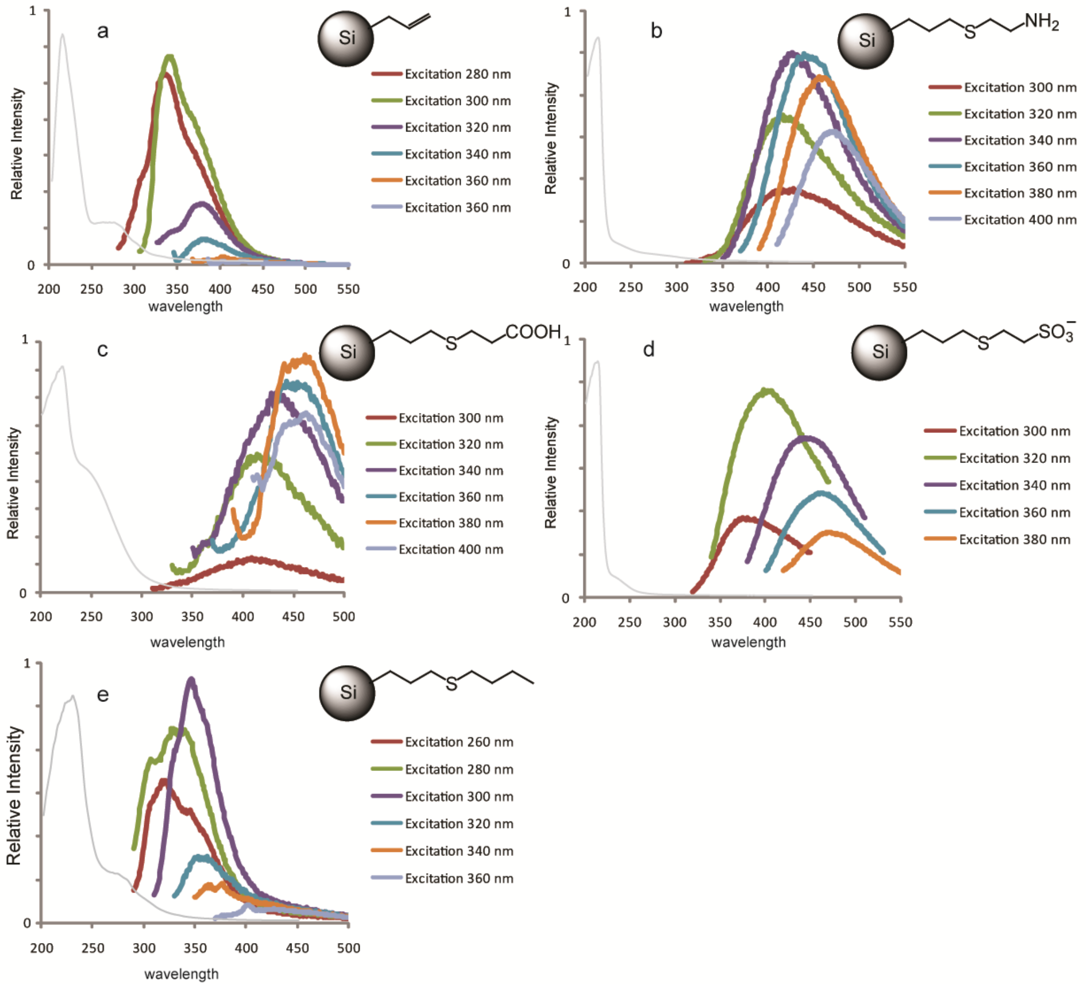

Figure S3. Absorption (grey) and emission profiles of SiQDs functionalized with different surface groups. From a-e with terminal groups as: a) SiQD-allyl, b) SiQD-NH_2, c) SiQD-COOH, d) SiQD-SO_3^-, e) SiQD-butane. The strong variation of size and shape of the fluorescence peak is probably due to the fact that a different proportion of the silicon quantum dots are being excited by the excitation source, giving fluorescence in different shape/position, as seen elsewhere[1-3].

S.4 Determination of Quantum Yields

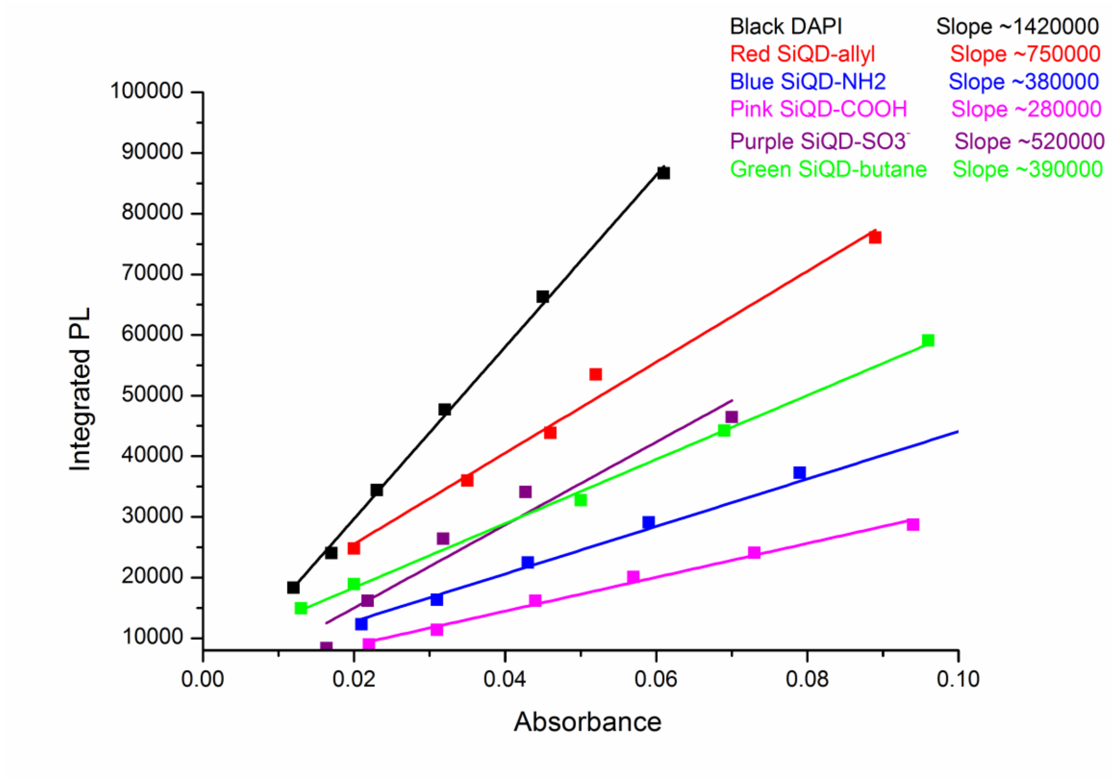

Figure S4. Quantum yields (Φ) of SiQDs with different surface groups are measured using a published method[4] in reference with 4',6-diamidino-2-phenylindole (DAPI)[5]. The dye has comparable absorption and emission profiles with the dots, with a reported quantum yield of 4.5% in water[5]. Specifically, Φ is determined as the ratio of integrated PL intensity vs. absorbance with a range of diluted samples in each case.

$$\text{i.e.}\quad \Phi_{\mathrm{SiQD}} = \Phi_{\mathrm{DAPI}} \frac{\mathrm{Em\_QDs/Em\_DAPI}}{\mathrm{Abs\_QDs/Abs\_DAPI}}$$

Table S1 Quantum Yield of SiQDs with Different Surface Groups

Fluorophores	Quantum Yield (Φ)
DAPI	4.5 %
SiQD-Allyl	2.5 %
SiQD-NH2	1.2 %
SiQD-COOH	0.9 %
SiQD-SO_3^-	1.6 %
SiQD-butane	1.2 %

References

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