

The Effects of Electronic Coupling between Capping Molecular and Quantum Dot on the Light Absorption and Emission in Octyl, Styryl, and 4-Ethynylstyryl Terminated Silicon Quantum Dots

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Experimental.

Hydrogen-terminated silicon quantum dots (H-Si QDs) were synthesized using the mini-emulsion method reported by Tilley et al.,¹ with the modification that the remaining reducing agent LiAlH_4 was quenched by CuSO_4 instead of methanol.² A mixture of SiCl_4 (1.33 g, 7.8 mmol) and tetraoctylammonium bromide (TOAB, 13.5 g) in anhydrous toluene (900 ml) was sonicated for 90 minutes. 13.5 of a LiAlH_4 solution (2 M in THF, 27 mmol) were added to reduce the SiCl_4 to H-Si QD and the reaction was kept under sonication for 3 hours. The excess LiAlH_4 was quenched by dried CuSO_4 (21 g, 84.6 mmol). Then, the mixture solution was divided to 3 flasks. The first flask, 10 ml of 1-octene and 0.3 ml of a 0.05 M H_2PtCl_6 solution in methanol were added. The second flask, 10 ml of phenylacetylene and 0.3 ml of a 0.05 M H_2PtCl_6 solution in methanol were added. The third flask, 0.5 g of 1,4-diethynylbenzene in anhydrous toluene and 0.3 ml of a 0.05 M H_2PtCl_6 solution in methanol were added. These functionalization steps were carried out for 2 days at room temperature under Ar atmosphere.

For purification of octyl Si QD, all solvent were removed at about 40°C under reduced pressure to obtain dried solid. The octyl Si QD was collected by hexane and the hexane solution were extracted with N-methylformamide (3 times), water (3 times), brine (2 times) and dried over anhydrous MgSO_4 . Finally, we obtained octyl Si QD as white resin.

For purification of styryl Si QD, all solvent were removed at about 40°C under reduced pressure to obtain dried solid. The styryl Si QD was collected by hexane and the hexane solution was extracted with N-methylformamide (3 times), AgNO₃ in NH₃ (3 times), water (3 times), and brine (2 times) and dried over anhydrous MgSO₄. Finally, we obtained styryl Si QD as yellow resin.

For purification of 4-ethynylstyryl Si QD, all solvent were removed at about 40°C under reduced pressure to obtain dried solid. The 4-ethynylstyryl Si QD was collected by hexane and the hexane solvent was removed at about 40°C under reduced pressure to obtain dried solid. The remaining capping molecules and surfactant were separated by the column chromatography of silica-gel (40-63 μm) using system solvent (hexane: dichloromethane). Finally, the product was obtained as yellow solid.

Results and Discussion.

The chemical structure of octyl Si QD was confirmed by FT-IR and ¹H NMR spectroscopy in Figure S1a and Figure S2a. Alkyl group on surface octyl Si QD including the asymmetric stretching, symmetric stretching, and in plane bending or scissoring of the C-CH₂- asymmetric, C-CH₃ symmetric, respectively were obtained at 2917.1 cm⁻¹, 2851.8cm⁻¹.³ The peak at 1460.7 cm⁻¹ is broadened by the inclusion of the C-CH₂. The peaks between 1000-1100 cm⁻¹ corresponded to Si-OR stretching vibrations and indicated that the oxidation of Si QD had occurred. In the ¹H-NMR spectrum of

octyl Si QD (Figure S2b), two groups proton, $-\text{CH}_2$ and CH_3 were assigned at ~ 1.3 and 0.9 ppm, respectively.² The relative proton integral ratio of $(-\text{CH}_2)$ and $(-\text{CH}_3)$ (1:0.21) shows that the majority of the product is the octyl terminated Si QDs.

For styryl Si QD sample, the styryl group (C_8H_6-) was confirmed by FT-IR and ^1H NMR spectroscopy in Figure S1b and Figure S2b. The peaks at 2917.1 cm^{-1} , 2851.8 cm^{-1} in Figure S1b were due to the sp^3-CH_2 , or sp^3-CH_3 from remaining hexane solvent. We observed peak at 3027 cm^{-1} attributed to vibration sp^2 -hybridized C-H stretching modes. The peaks at 1605.4 cm^{-1} are attributed to the C=C vibration.⁴ The peaks at $1600\text{-}1700\text{ cm}^{-1}$ were attributed to the overtone of aromatic ring of capping. The in-plane C-H bending of the phenyl ring were obtained at about 1024 and 1074 cm^{-1} . The structure of styryl Si QD was further confirmed by ^1H -NMR spectrum, as shown in Figure S2b. Chemical shift of proton in the phenyl ring were in the range from 6.8 to 8 ppm. Two protons, $\text{Si}-\text{CH}=\text{C}$ and $-\text{CH}=\text{C}-$, were in the range from 5.5 to 6.2 ppm.⁵ Two peaks, marked by (*) in Figure S2b, whose chemical shifts were 0.89 , 1.25 ppm may be arisen from remaining hexane.

For 4-ethynylstyryl Si QD sample, the 4-ethynylstyryl group was confirmed by FT-IR and ^1H NMR spectroscopy in Figure S1c and Figure S2c. The peak at 3284.9 cm^{-1} was attributed to the $\equiv\text{C}-\text{H}$ stretching band. The vibration at 2104 cm^{-1} indicated the presence of $\text{C}\equiv\text{C}$ stretching band. The peaks at $1600\text{-}1700\text{ cm}^{-1}$ were attributed to the overtone of aromatic ring of capping. The key peak at 1605.4 cm^{-1} (4-ethynylstyryl Si

QD or Styryl Si QD) were assigned to the C=C bond in conjugation with Si atoms on the QD surface (Si-C=C-, see the chemical structures shown in Scheme 1). This peak was red-shifted by 40 cm⁻¹ from 1640 cm⁻¹ in typical alkenes to about 1605.4 cm⁻¹ due to σ - π conjugation between the σ orbital of the Si atom and the π orbital of vinyl group.⁴ The ¹H-NMR spectrum (Fig. S2c) of 4-ethynylstyryl Si QD, we observe multiple signals characteristic for proton of phenyl group in the range 6.7-8 ppm. Two protons, Si-CH=C (1) and -CH=C- (2), were obtained at ~5.0 and 5.8 ppm, respectively. The free functional group (-C≡C-H) of 4-ethynylstyryl Si QD can also get signal with centre at 3.1 ppm. Four peaks, marked by (*) of 4-ethynylstyryl Si QD in Figure S2, whose chemical shifts were 0.89, 1.25, 1.56, and 2 ppm may be arisen from remaining hexane or toluene solvent.

The Time-resolved photoluminescent results were best fitted by a three component exponential equation: $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$, where $A_{1,2,3}$ and $\tau_{1,2,3}$ are the amplitude and lifetime of each component, respectively.

- Average lifetime was calculated from equation:

$$\tau_{aver} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3}$$

- Radiative transition rate is calculated from equation:

$$\square \quad k_f = \frac{\Phi}{\tau_{aver}}$$

Where Φ is the average quantum yield of Si QDs measured at 325 excitation by comparison with quinine sulfate whose quantum yield is 55 %.

The fitting parameter, calculated average lifetime are summarized in below.

Si QD	A ₁	τ_1 (ns)	A ₂	τ_2 (ns)	A ₃	τ_3 (ns)	τ_{aver}
octyl-	0.23	8.41	0.89	2.19	0.92	0.84	4.59
styryl-	0.49	4.92	8.37	1.72	4.29	0.53	1.99
4-ethynylstyryl-	0.12	3.73	3.38	1.15	13.31	0.55	0.88

In order to correlate the change in optical gaps of Si QD with extending conjugated capping molecules compared with UV-vis absorption and PL results, we first model the Si QD as a typical core-shell structure and then calculate the carrier's probability at capping layer of octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD. The structures of the Si QD core (regarded as H-Si QD) and the shelling molecule are shown in Figure S5. To calculate the probability of carriers at the capping layer, we used a very simple particle in a box model, as illustrated in Figure S5, in which r is the radius of the Si QD core, set to 0.9 nm, t is the barrier thickness assumed to be the length of the shelling molecules, as inserted in Figure S5; V_{Se} and V_{Sh} are the barrier heights for the electron and hole, respectively. DFT-B3LYP calculations were conducted to calculate the orbital energies of the Si QD core (regarded as H-Si QD) and the shelling molecule, hence V_{Se} , V_{Sh} , and t values, as presented in Figure 5. The one-dimensional (x axis) Schrödinger equation for the particle in a box is:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m^*}{h^2}(V_{(x)} - E)\psi = 0 \quad \text{where} \quad \begin{cases} V_{(x)} = \infty (|x| \geq t+r) \\ V_{(x)} = V_s (r \leq |x| \leq t+r) \\ V_{(x)} = 0 (|x| \leq r) \end{cases}$$

The probability densities ($|\Psi|^2$) finding the electron and the hole along x axis were solved numerically, using the Numerov method. The probability percentage of the electron or the hole in the shelling layer is obtained by integrating the $|\Psi|^2$ function in the shelling regions.

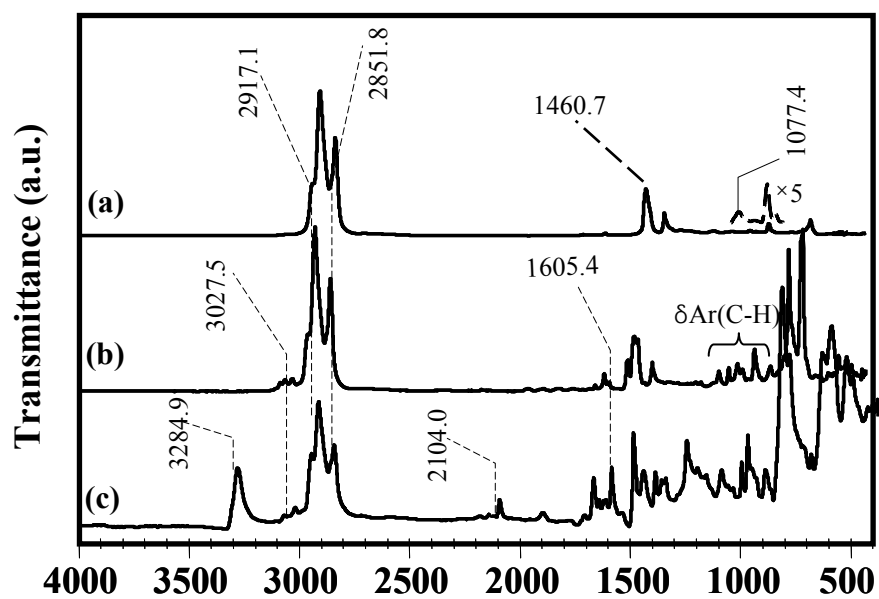


Figure S1. FT-IR spectra of the octyl Si QDs (a), styryl Si QDs (b), and 4-ethynylstyryl Si QDs (c).

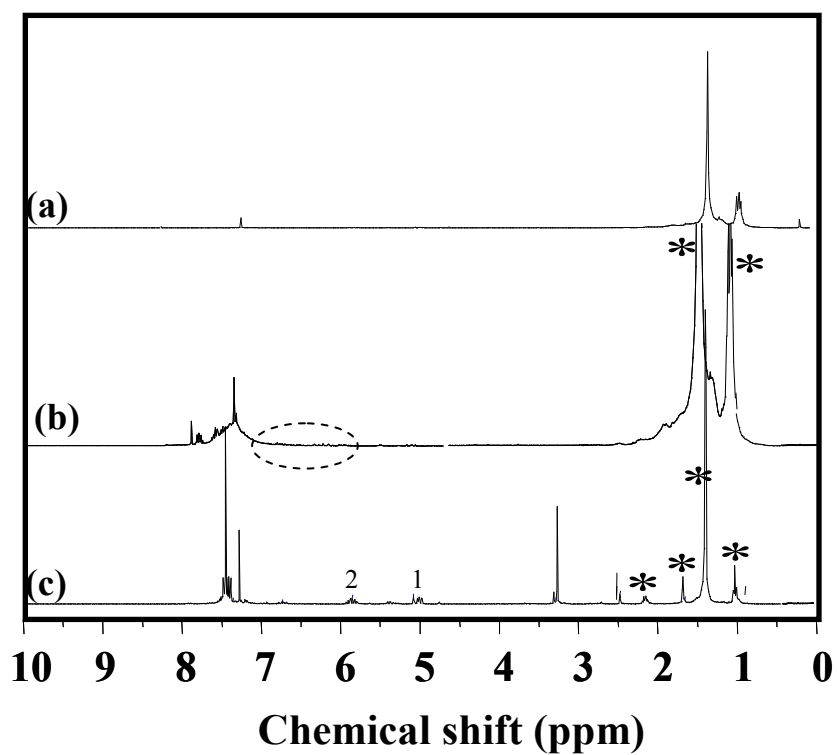


Figure S2. ¹H-NMR spectra of the octyl Si QDs (a), styryl Si QDs (b), and 4-ethynylstyryl Si QDs (c).

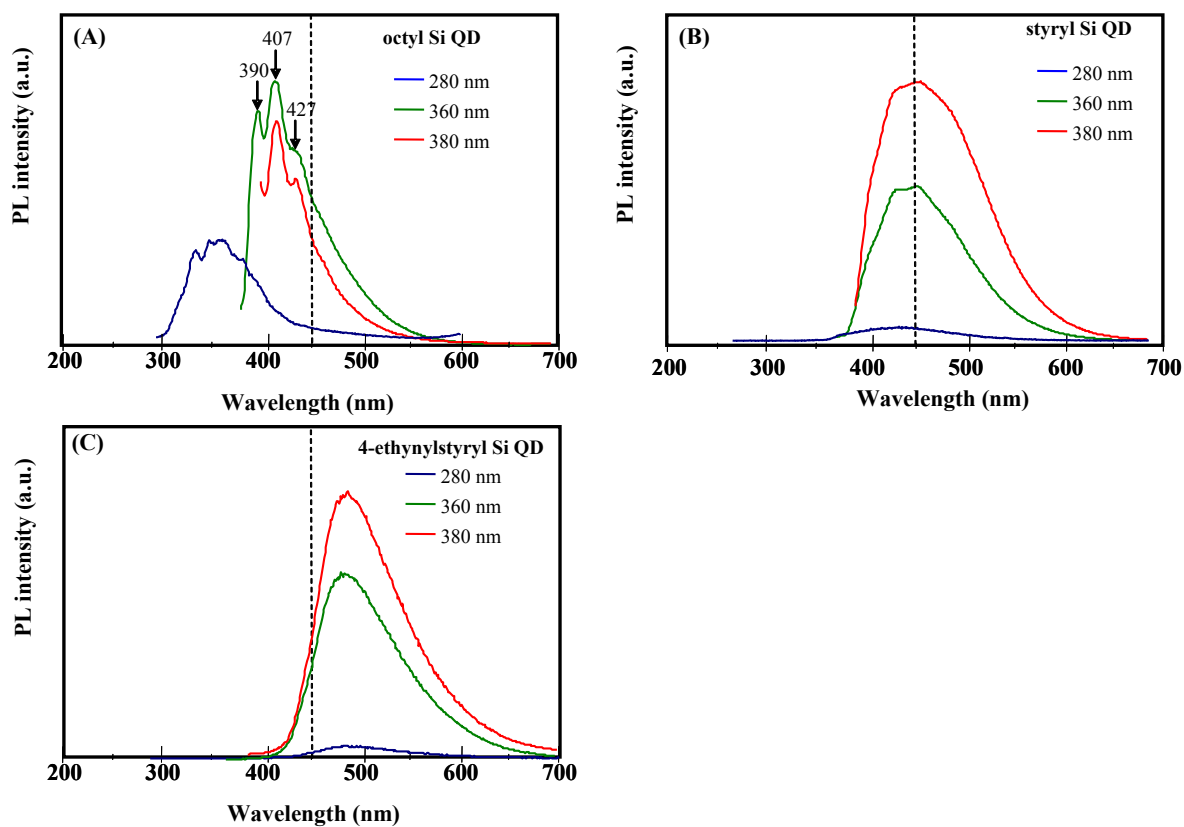


Figure S3. PL spectra of the as-prepared Si QD samples: A) octyl Si QD, B) styryl Si QDs, and C) 4-ethynylstyryl Si QDs recorded under excitation at different wavelengths.

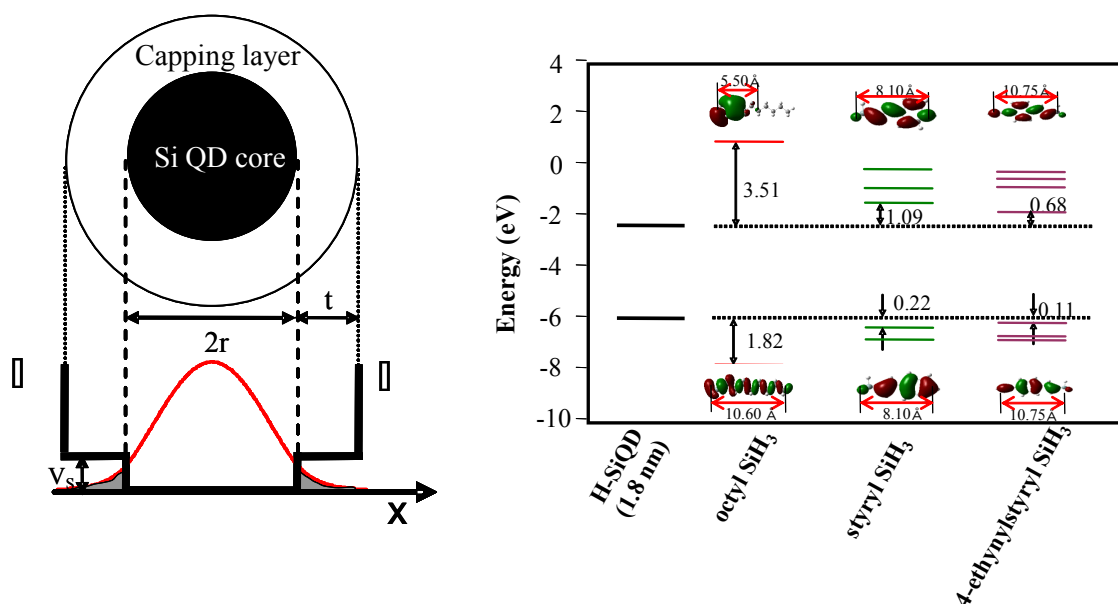


Figure S5. The “particle in a box” model for Si QDs with different capping molecules in which the Si QD core, assumed to be H-Si QD of the same size, is the well and the well barrier is composed of shelling molecules as inserted structures.

References

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