

Supporting Information

Influence of Halides on the Optical Properties of Silicon Quantum Dots.

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1 Experimental

1.1 Materials

Hydrogen silsesquioxane (HSQ) was purchased from Dow Corning Corporation as FOx-17 as a solution in methyl isobutyl ketone. Hydrofluoric acid (HF, 49% solution) was purchased from J. T. Baker. Phosphorus pentachloride (PCl_5 , 98%), bromine (Br_2 , 99%), iodine (I_2 , 99%), n-hexylmagnesium bromide ($\text{C}_6\text{H}_{13}\text{MgBr}$, 2.0 M in THF), n-hexylmagnesium chloride ($\text{C}_6\text{H}_{13}\text{MgCl}$, 2.0 M in THF), methylmagnesium bromide (CH_3MgBr , 3.0 M in ether), n-butylmagnesium chloride ($\text{C}_4\text{H}_9\text{MgCl}$, 2.0 M in THF), n-dodecylmagnesium ($\text{C}_{12}\text{H}_{25}\text{MgBr}$, 1.0 M in ether), anhydrous toluene, methanol (ACS grade), and ethanol (ACS grade) were all purchased from Sigma-Aldrich. All the chemicals were used as received.

1.2 Syntheses

Hydride terminated silicon nanocrystals (Si-NCs). Oxide-embedded Si-NCs were prepared using a previous well-developed procedure by our group. Solid HSQ (~ 4 g) was transferred to a quartz boat and heated in a Lindenberg Blue tube furnace from ambient temperature to peak processing temperature of 1100 °C at 18 °C/min under reducing atmosphere (5% H_2 /95% Ar). The sample was maintained at 1100 °C for an hour and allowed to cool to the room temperature. The resulting brown solid was ground using an agate mortar and pestle. This yields oxide-embedded Si-NCs with an average diameter of ca. 3 nm. To obtain larger Si-NCs, the 3 nm Si-NC composite was transferred to a carbon boat and heated to 1300 °C at 10 °C/min in a high temperature furnace (Sentro Tech Corp.) and maintained at that temperature for an hour under Ar atmosphere. The composite was allowed to cool to room temperature to yield Si-NCs with average diameters of ca. 9 nm embedded in silica matrix.

Freestanding hydride terminated Si-NCs were obtained by treating 1.00 g of the composite with 5 mL each of water, ethanol, and 49% HF for an hour. The hydrophobic hydride terminated Si-NCs were extracted using 50 mL toluene. The Si-NC/toluene mixture were centrifuged at 4000 rpm for 15 minutes and the toluene supernatant was decanted leaving

a precipitate of hydride terminated Si-NCs. The particles were washed with toluene twice and used for further reaction immediately.

Chloride terminated Si-NCs. The hydride terminated Si-NCs were transferred to a Schlenk flask with 20 mL anhydrous toluene. 1.00 g of PCl_5 was added to the above reaction mixture and heated to 45 °C for 90 minutes under Ar atmosphere. Toluene and byproducts were removed *in vacuo* to yield orange precipitate which was kept under vacuum until further functionalization.

Bromide terminated Si-NCs. The hydride terminated Si-NCs were transferred to a Schlenk flask with 20 mL anhydrous toluene. 0.5 mL Br_2 solution was transferred to the flask and reacted together for 5 minutes under Ar atmosphere. Excess Br_2 , solvent and reaction byproducts were removed *in vacuo* to yield light orange precipitate that was kept under vacuum until further use.

Iodide terminated Si-NCs. The hydride terminated Si-NCs (obtained from composite containing ca. 3 nm Si-NCs) were transferred to a Schlenk flask with 20 mL anhydrous toluene. 0.5 g of I_2 was added to the flask and reacted for 6 hours at 50°C under Ar atmosphere. Excess I_2 , toluene and reaction byproducts were removed *in vacuo* and the precipitate was stored under vacuum until further use.

Alkylation of halide terminated Si-NCs. The halide terminated Si-NCs were redispersed in 20 mL anhydrous THF. The solution was cooled using dry ice/acetone mixture and 5.0 mL hexylmagnesium chloride or hexylmagnesium bromide was added to the reaction mixture slowly and was allowed to warm to room temperature. It was then heated to 80 °C for 120 hours. The reaction was cooled to room temperature and was quenched with addition of 10 mL methanol. The solvent was removed *in vacuo* and the particles were redispersed in 20 mL of toluene. The mixture was transferred to a separatory funnel and washed with water (50 mL) thrice. The toluene layer was collected and filtered through a hydrophobic 2 μm PTFE filter to yield orange colored solution.

1.3 Characterization

Fourier Transformed Infrared Spectroscopy (FTIR). FTIR spectra were collected using a Nicolet Magna 750 IR spectrometer.

X-ray Photoelectron Spectroscopy (XPS). XPS analyses were performed using a Kratos Axis Ultra instrument operating in energy spectrum mode at 210 W. The base pressure and operating chamber pressure were maintained at 10^{-7} Pa. A monochromatic Al K_{α} source ($\lambda = 8.34 \text{ \AA}$) was used to irradiate samples, and spectra were obtained with an electron takeoff angle of 90° . To minimize sample charging the charge neutralizer filament was used as appropriate. Survey spectra were collected using an elliptical spot with major and minor axis lengths of 2 and 1 mm, respectively, and 160 eV pass energy with a step of 0.33 eV. CasaXPS software (VAMAS) was used to interpret high-resolution (HR) XP spectra. All spectra were internally calibrated to the C 1s emission (284.8 eV). After calibration, the background was subtracted using a Shirley-type background to remove most of the extrinsic loss structure. The full width at half maximum (FWHM) for all the fitted peaks was maintained below 1.2 eV.

Transmission Electron Spectroscopy (TEM). Transmission Electron Microscopy (TEM) images were obtained using a Hitachi-9500 and FEI Tecnai F30ST electron microscope with an accelerating voltage of 200 kV. TEM samples were prepared by drop coating the Si-NC suspension onto a carbon coated copper grid with a 400 μm diameter hole. The NC size was averaged over 100 particles determined using Image J software (version 1.45).

Photoluminescence Spectroscopy (PL). Photoluminescence (PL) spectra of the solution phase samples were acquired using a Varian Cary Eclipse Fluorescence Spectrometer.

Raman Spectroscopy. Raman spectra were recorded on Renishaw inVia Raman Microscope.

Lifetime Measurements. Lifetime measurements were performed using an excitation pulse of a 400-nm second harmonic signal from a BBO crystal pumped by 800-nm pulses from a Ti:Sapphire laser (Coherent RegA900 with 65 fs pulse width and 250 kHz repetition rate) with average excitation power of 1.88 mW. A fast silicon photodiode (Thorlabs, PDA36A, rise time 20.6 ns) coupled to a 300 MHz oscilloscope (Tektronix) was used to measure the carrier recombination. The photodiode was placed at a path perpendicular to the excitation beam and 10-nm bandpass filters (Edmund Optics) were used to select a particular emission wavelength.

Quantum Yield Measurements. Photoluminescence quantum yields were determined using methods adapted from the work of Williams *et al.*¹ 9,10-biphenylanthracene in cyclohexane, Coumarin 1 in absolute ethanol, fluorescein in methanol, rhodamine B in ethanol, and rhodamine 6G in methanol were used as reference dyes. Si-NCs were dissolved in toluene. All organic solvents were passed through a column of anhydrous magnesium sulfate to remove trace moisture prior to preparing the solutions. Stock solutions were prepared by dissolving 10 mg of organic dye in the appropriate solvent with stirring until the solid was completely dissolved. Solutions were filtered through a 200 µm PTFE membrane filter to remove suspended impurities and a series of diluted solution were made with absorbances ranging from 0.1 and 0.01. PL spectra were acquired for the identical solutions and the slit width was maintained from 5 – 10 depending on the species. The slopes of plots of the integrated fluorescence intensity *versus* UV-Vis absorbance curves were determined and compared to ensure the highest quality reference curves. In all cases, experimentally determined photoluminescence quantum yields of the organic dyes were in good agreement with literature values. Slopes of plots of the integrated PL intensity *versus* absorbance were determined for all Si-NC samples and the quantum yields were calculated using the following equation:

$$\varphi_x = \varphi_{st} \left(\frac{m_x}{m_{st}} \right) \left(\frac{\eta_x^2}{\eta_{st}^2} \right)$$

where, ‘ ϕ ’ is the photoluminescence quantum yield, ‘ m ’ is the slope of the integrated PL intensity vs. absorbance curve, and ‘ η ’ is the refractive index of the solvent. The subscript ‘st’

refers to the standard organic dye and ‘x’ indicates the unknown species being evaluated. The excitation wavelength, slit widths and reference for Si-NC evaluations are listed below.

Sample	Excitation wavelength (nm)	Slit width	Reference
Red emitting Si-NCs	350	5	Rhodamine 6G Rhodamine B
Yellow emitting Si-NCs	300	5	Coumarin 1 9,10-biphenylanthracene
Blue emitting Si-NCs	300	5	Coumarin 1 9,10-biphenylanthracene

¹ Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067–1071.

2 Figures

Figure S1. FTIR spectra of (A) hydride, (B) chloride, (C) bromide, and (D) iodide terminated Si-NCs.

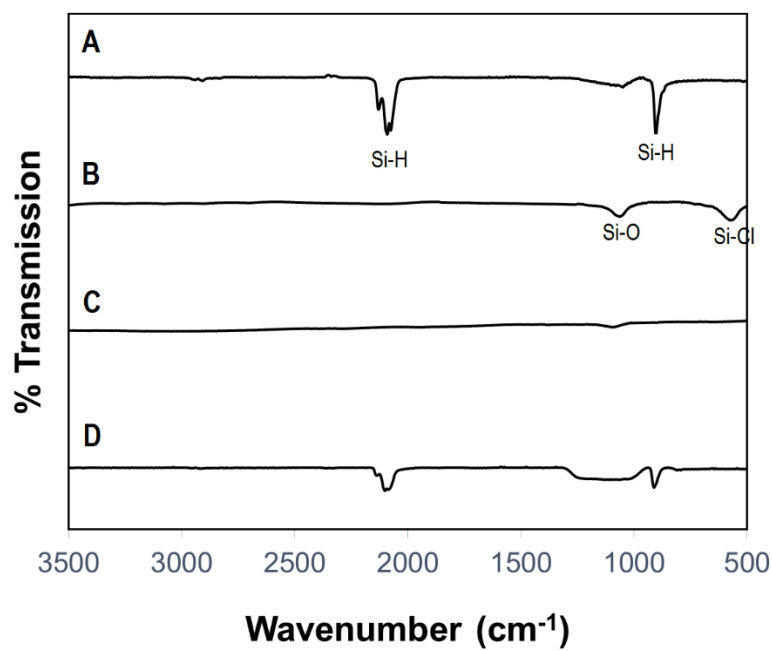


Figure S2. Raman spectra of (A) chloride, (B) bromide, and (C) iodide terminated Si-NCs.

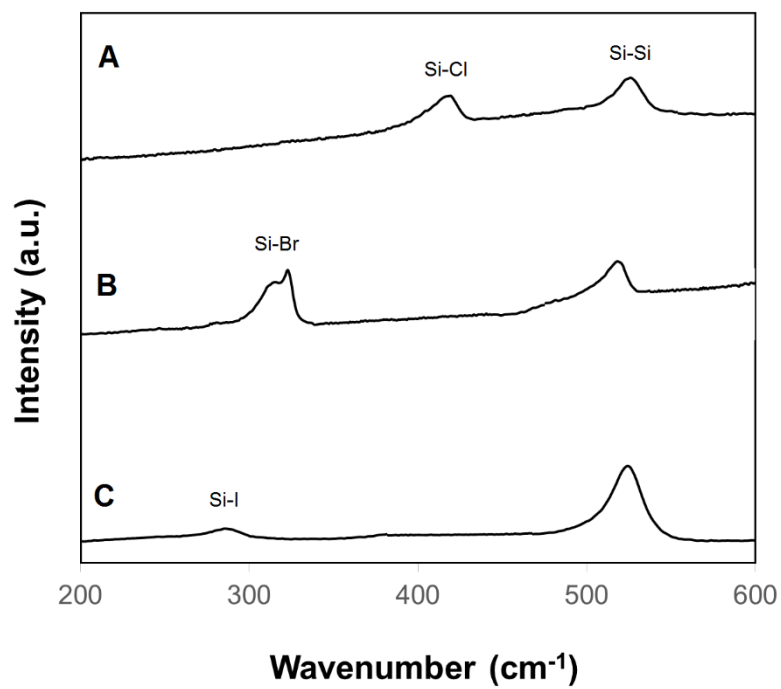


Figure S3. High resolution X-ray photoelectron spectra of (A) chloride, (B) bromide, and (C) iodide terminated Si-NCs.

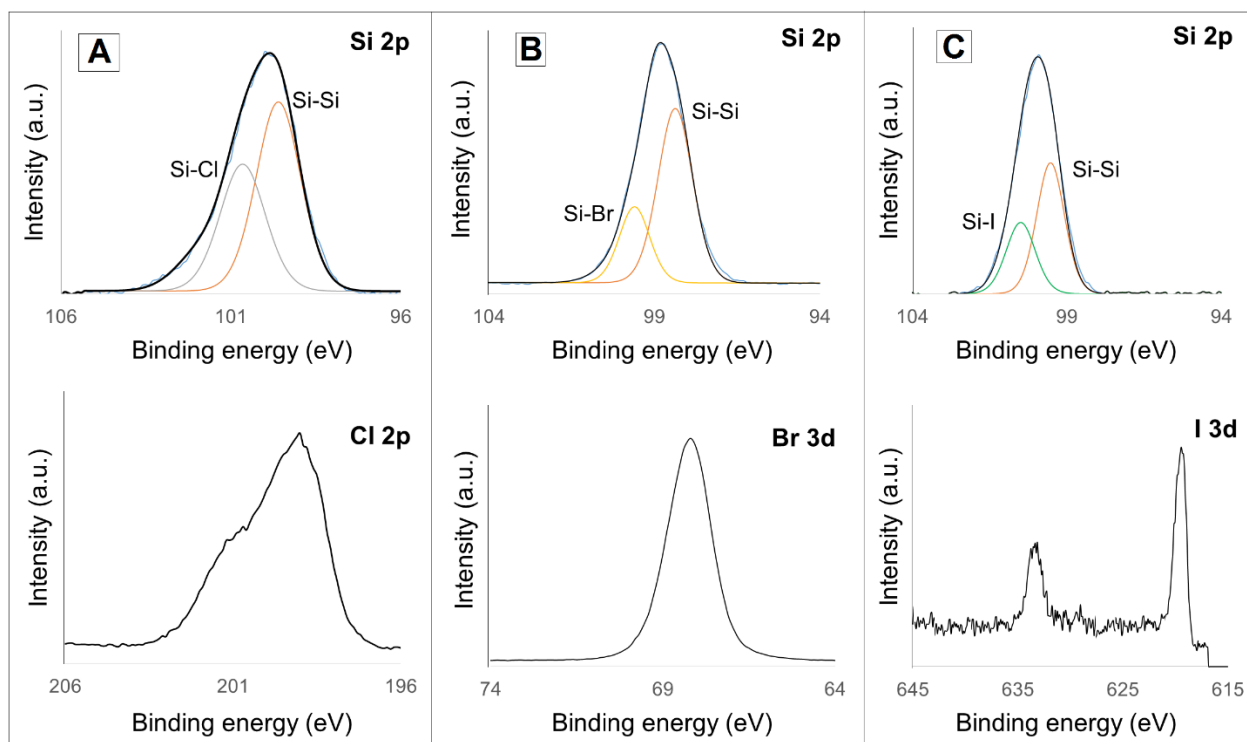


Figure S4. PL spectra of partially oxidized (A) chloride, (B) bromide, and (C) iodide terminated Si-NCs.

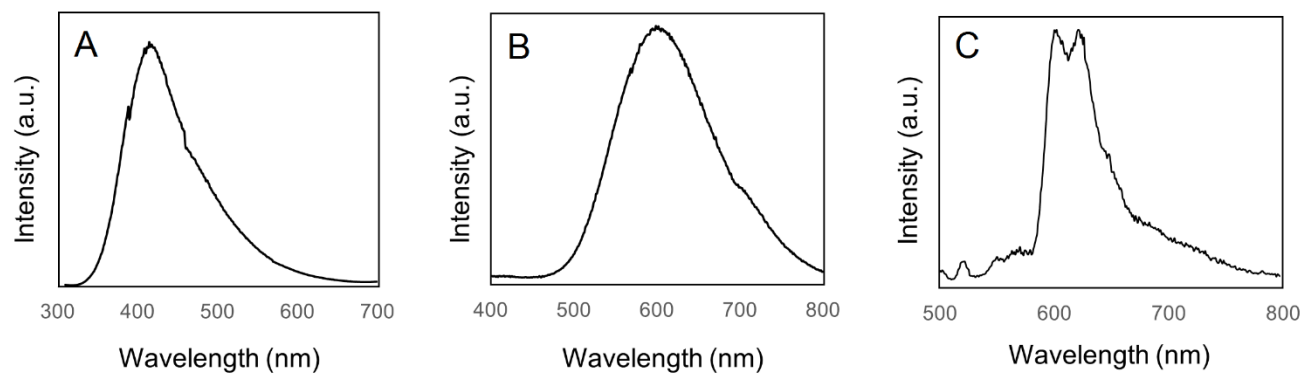


Figure S5. FTIR spectra of hexyl functionalized Si-NCs derived from (A) chloride, (B) bromide, and (C) iodide surfaces.

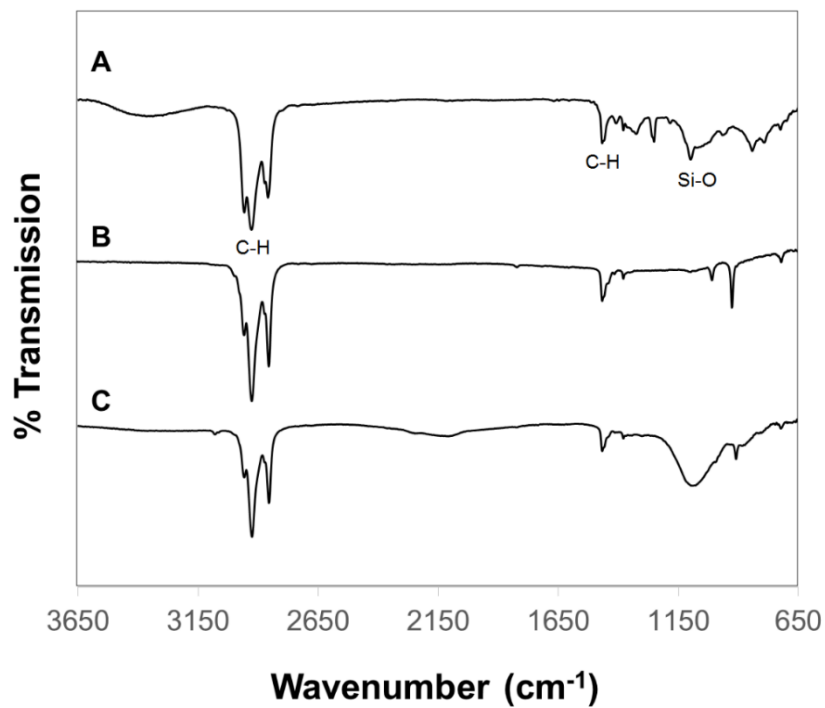


Figure S6. Excited state lifetimes of n-hexyl functionalized Si-NCs derived from iodide surface. Black line corresponds to collected data and red line is the fitted data.

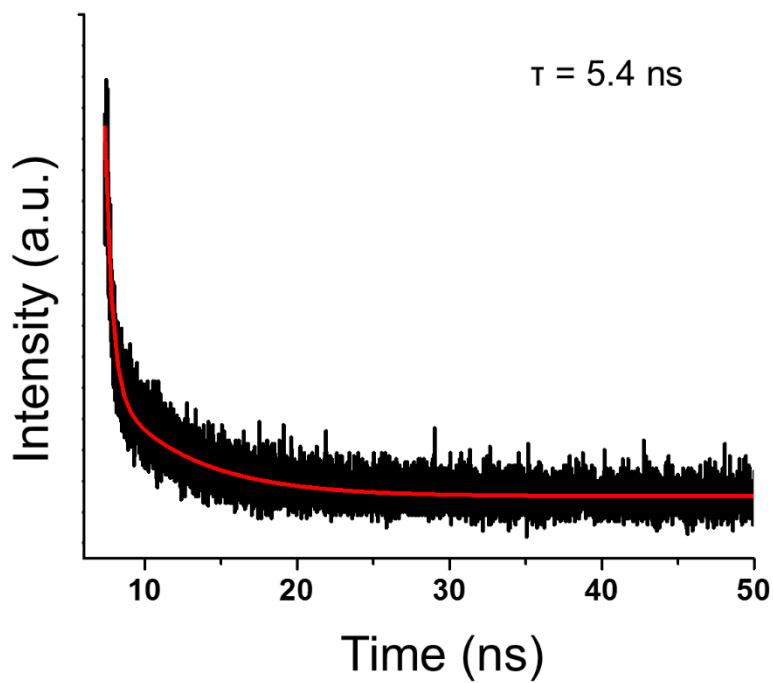


Figure S7. PL spectra of alkyl functionalized Si-NCs derived from chloride surface etched for various times. The zero minutes etched spectra was obtained from hydride terminated Si-NCs.

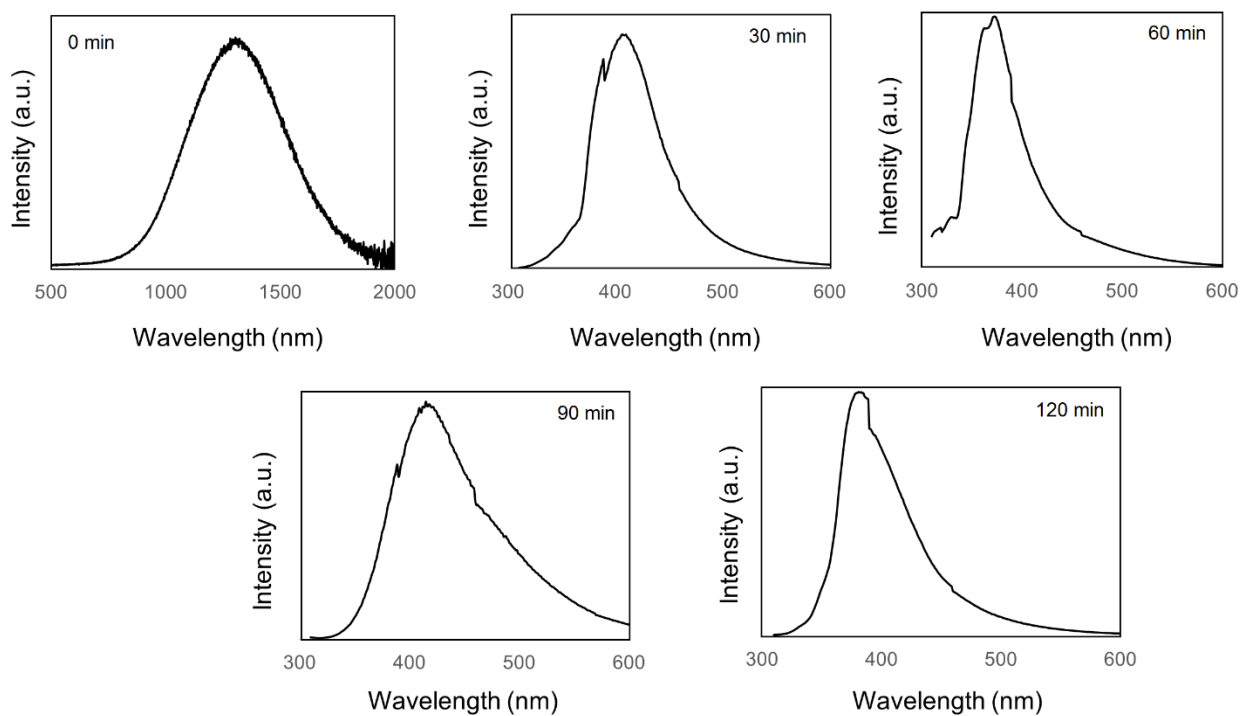


Figure S8. PL spectra of alkyl functionalized Si-NCs derived from bromide surface etched for various times. The zero minutes etched spectra was obtained from hydride terminated Si-NCs.

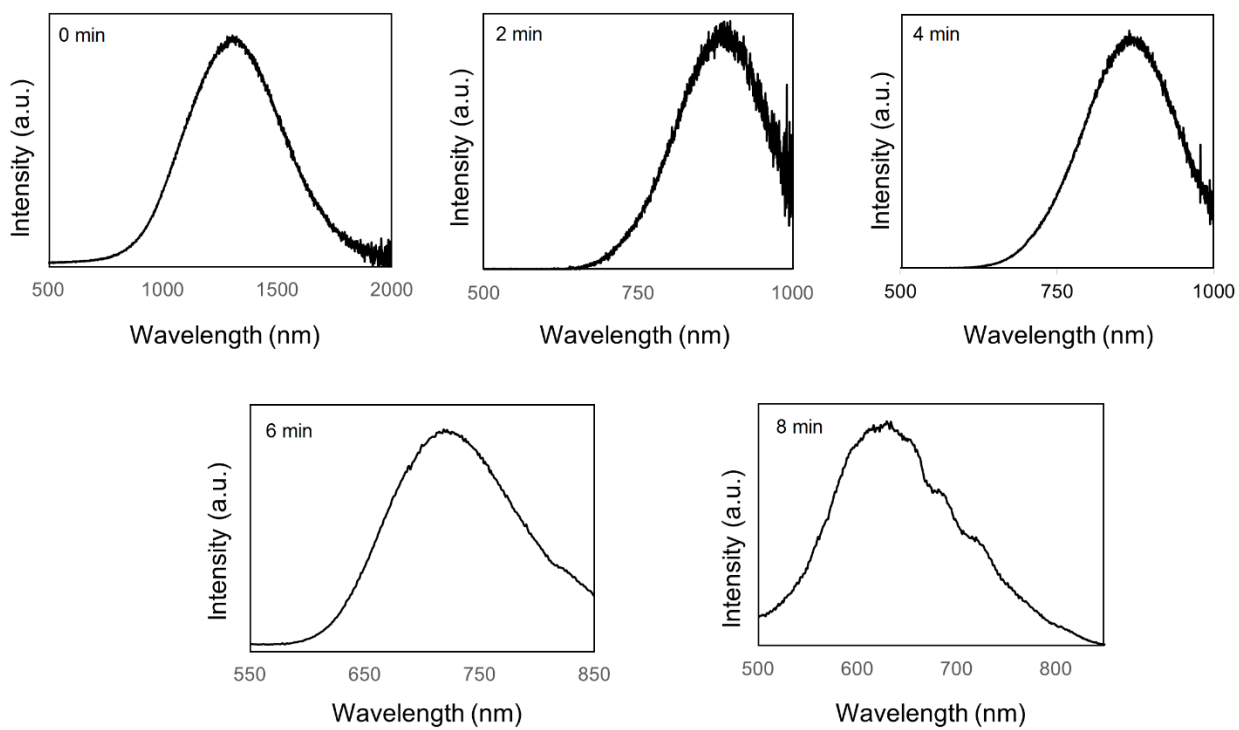


Figure S9. Excited state lifetimes of n-hexyl functionalized Si-NCs derived from chloride surface. Black line corresponds to collected data and red line is the fitted data.

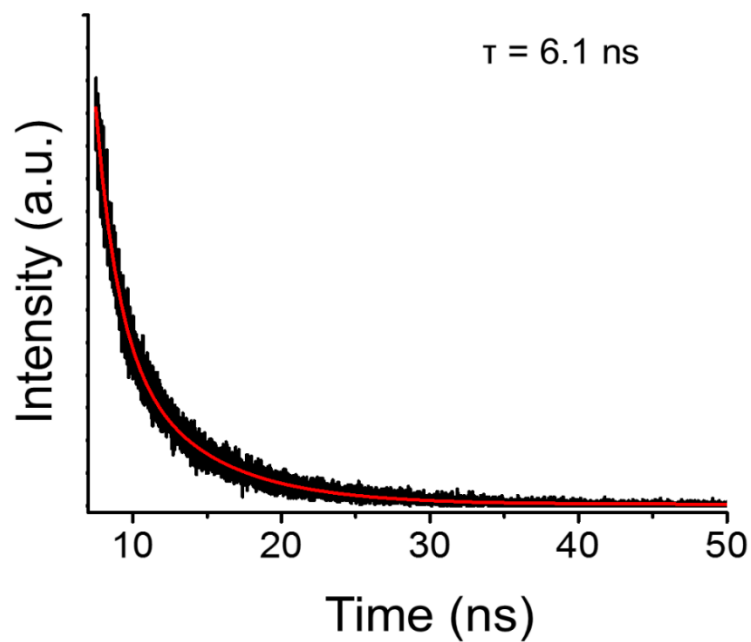


Figure S10. Excited state lifetimes of n-hexyl functionalized Si-NCs derived from bromide surface. Black line corresponds to collected data and red line is the fitted data.

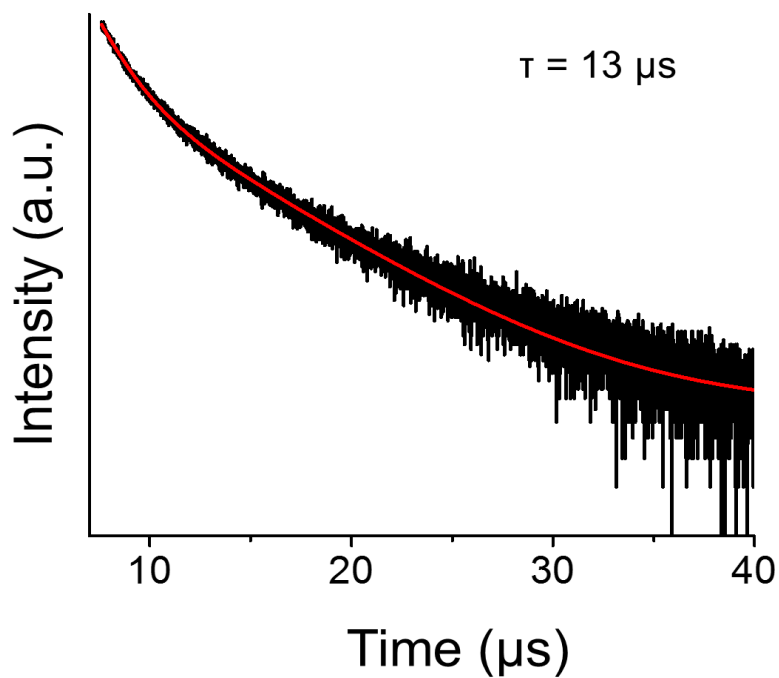


Figure S11. Excitation wavelength dependent emission spectra of n-hexyl functionalized Si-QDs derived from chloride surface.

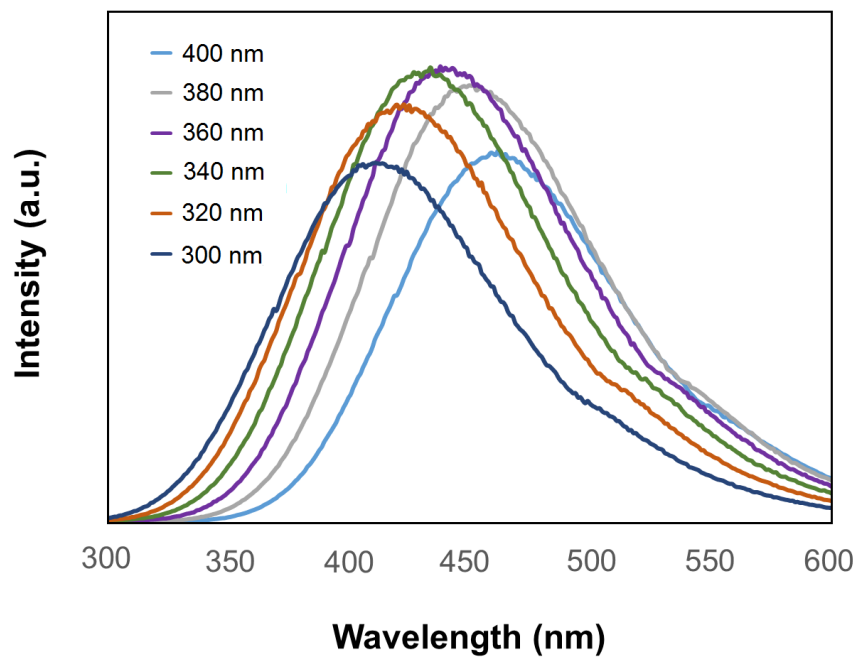


Figure S12. Excitation wavelength dependent emission spectra of n-hexyl functionalized Si-QDs derived from bromide surface.

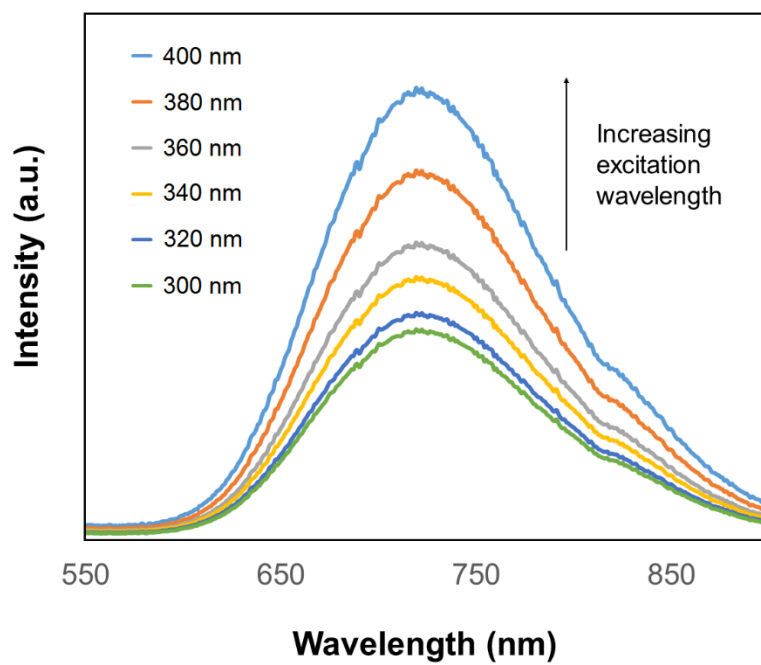


Figure S13. Excitation wavelength dependent emission spectra of n-hexyl functionalized Si-QDs derived from iodide surface.

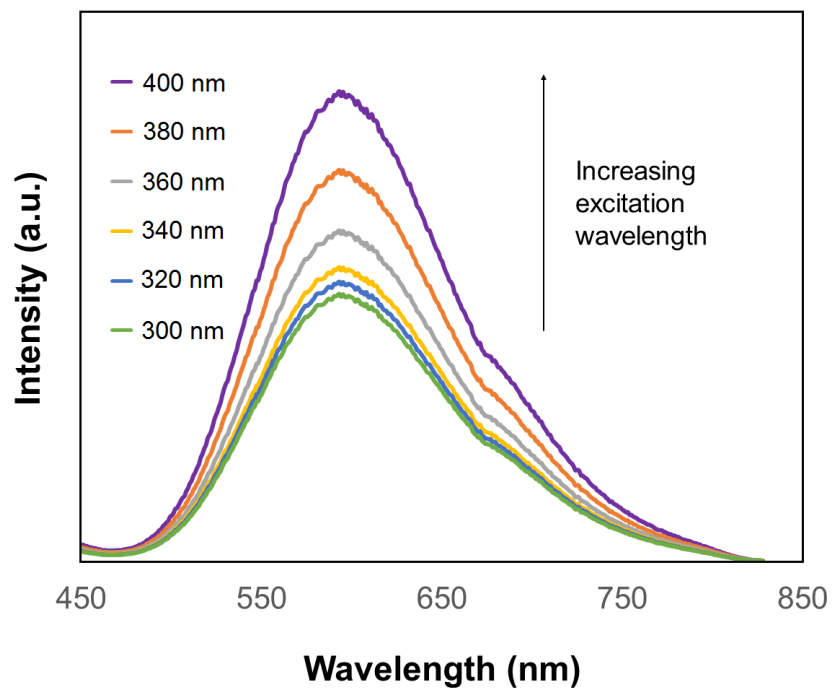


Figure S14. PL spectrum of Si-QDs obtained from reaction bromide terminated Si-QDs with n-hexylmagnesium chloride.

