

## Silicon Quantum Dots Sensors for Explosive Taggant, 2,3-dimethyl-2,3-dinitrobutane (DMNB)

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*-Supplementary Information -*

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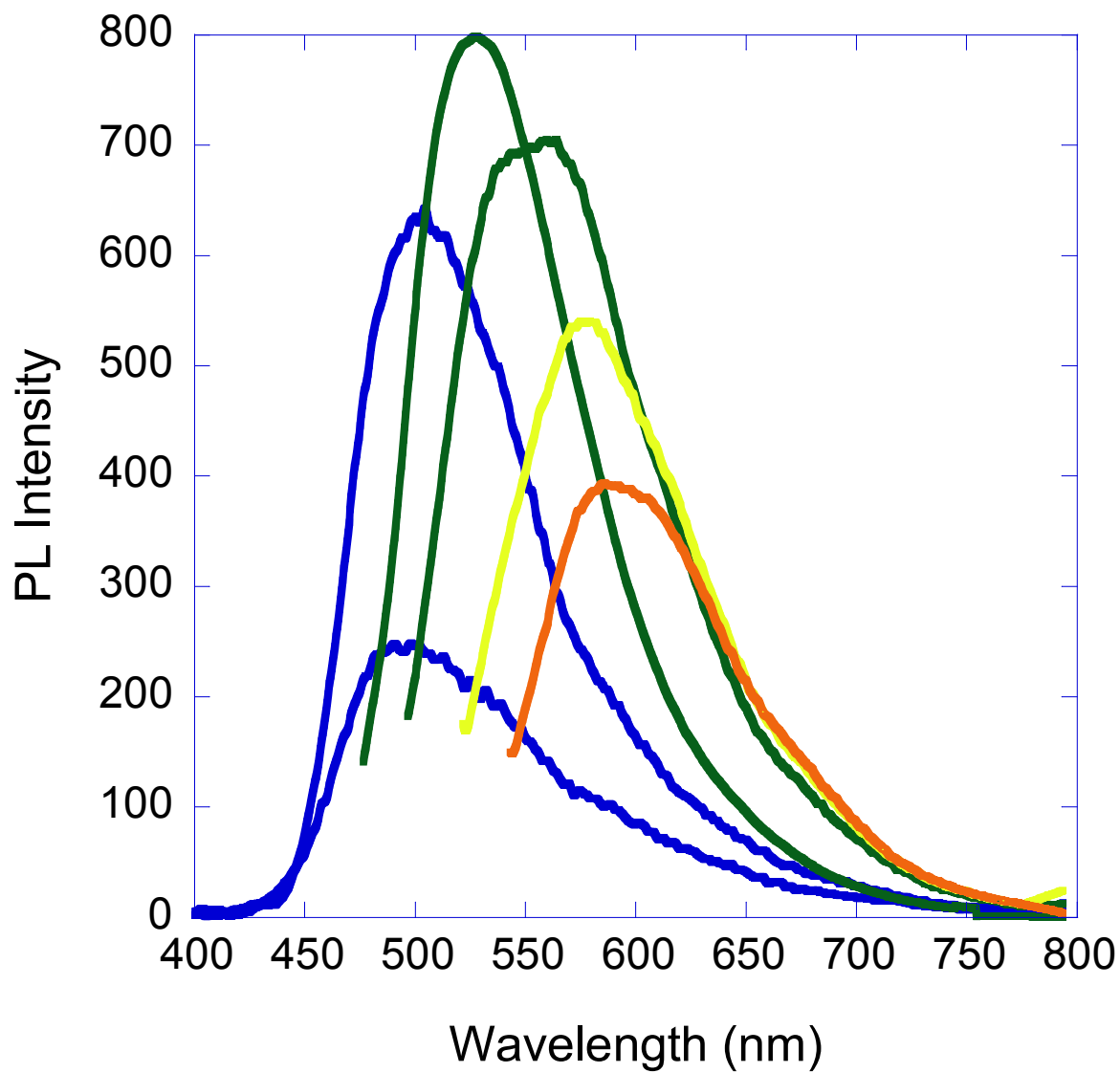
## 1. Experimental

**Materials.** Magnesium silicide (99%) and ethylenediamine (99.5%) were purchased from Aldrich and used without further purification. Dimethylformamide (Aldrich, 99.8%) was dried and distilled from calcium chloride (Aldrich, anhydrous) under argon gas. Manipulations of these chemicals were handled via standard Schlenk line techniques. DMNB was purchased from Sigma-Aldrich and used without further purification.

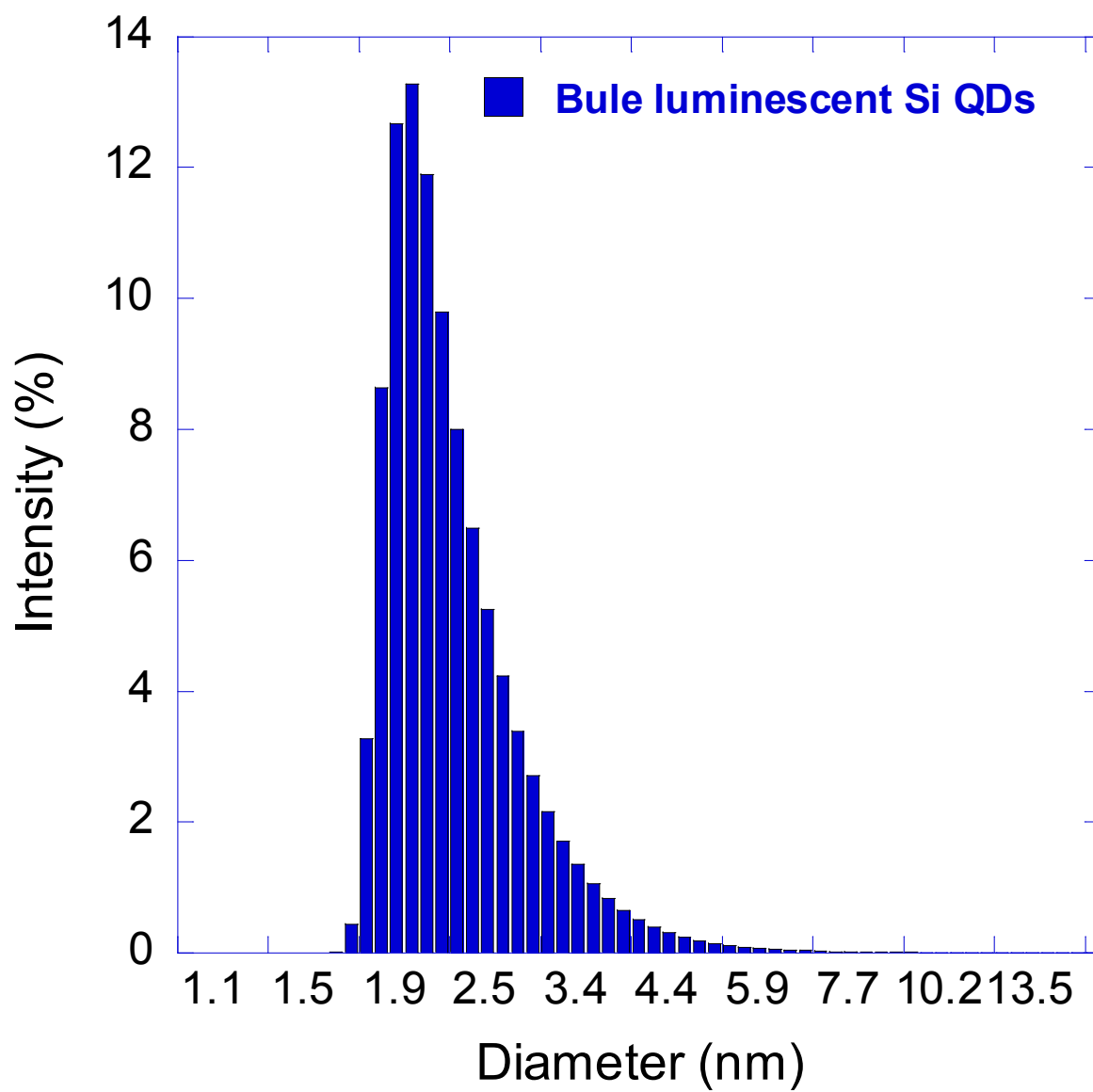
**Synthesis of Si QDs.** To obtain Si QDs, ethylenediamine dihydrochloride was obtained by adding HCl (83 mmol) slowly to 5 g (83 mmol) of ethylenediamine in 40 mL of THF in a flask at room temperature with rapid stirring under ice-water bath and the resulted white solid was filtered and dried under the reduced pressure. To obtain H-terminated Si QDs, 0.3 g (4 mmol) of Mg<sub>2</sub>Si was added to corresponding equivalents of ethylenediamine dihydrochloride in 40 mL of DMF in a Schlenk flask at room temperature under argon atmosphere. The color of solution changed to a purple suspension. The suspension mixture was refluxed at 150 °C under argon atmosphere for two days for blue luminescent Si QDs and three days for green luminescent Si QDs with continuous stirring. After the reaction, 15 mL of hexane was added to the reaction mixture, stirred for 24 hours, and settled down for 72 hours. Hexane layer containing Si QDs was decanted and centrifuged.

**Fluorescence Quenching Studies.** The detection method involves measurement of the quenching of photoluminescence of the blue luminescent Si QD ( $\lambda_{\text{max}} = 460$  nm) and green luminescent Si QD ( $\lambda_{\text{max}} = 520$  nm) by the analyte using 340 nm excitation wavelength. Fluorescence spectra of toluene solutions of the blue and green luminescent Si QDs were obtained by successive addition of aliquots of DMNB. Photoluminescence quenching of the blue and green luminescent Si QDs in toluene solutions were measured.

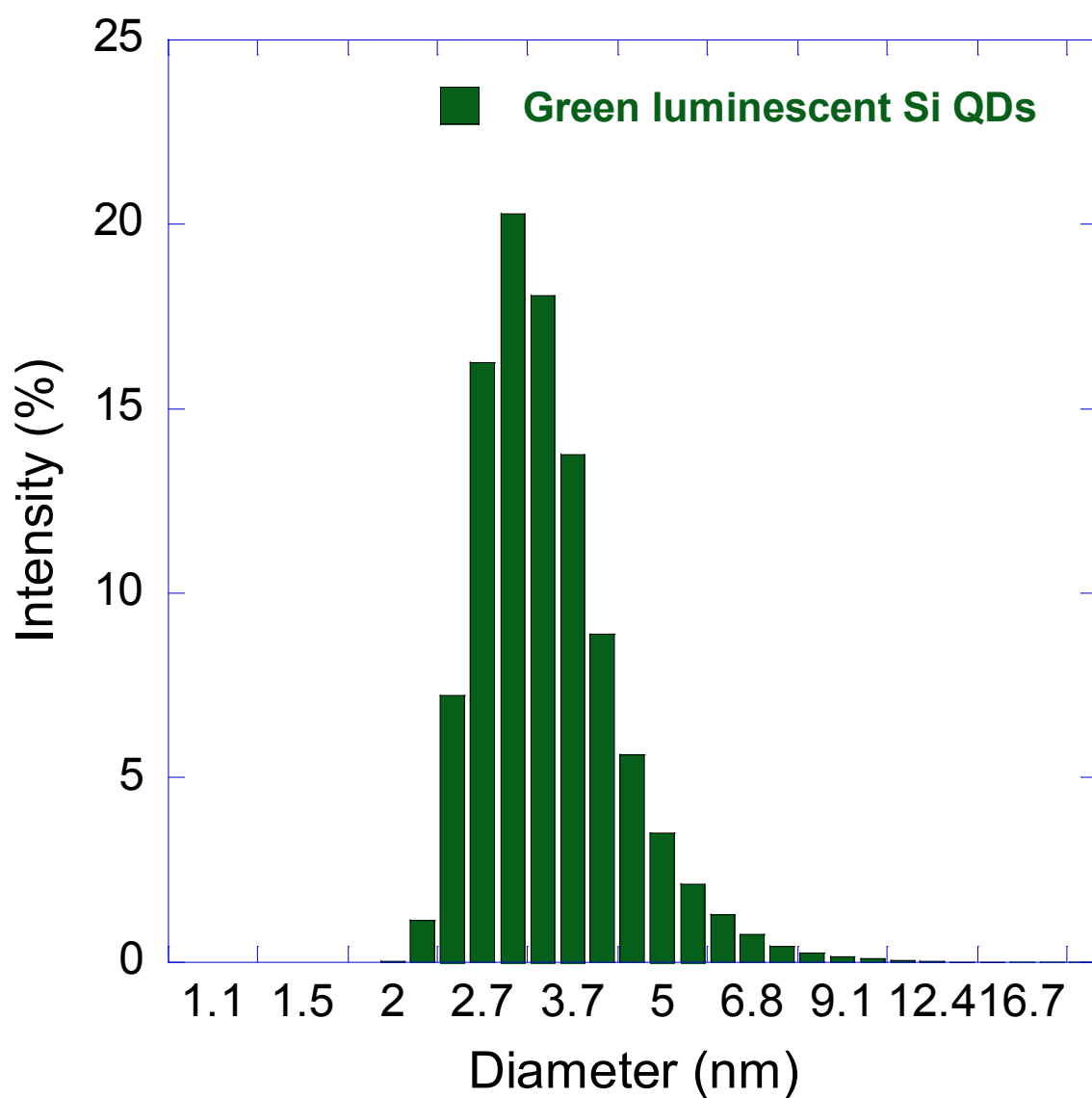
**Instrumentations.** Fourier transform infrared (FTIR) spectra were measured on Nicolet 5700 using KBr disks. Ultra violet-visible (UV-vis) absorption and PL spectra were recorded Shimadzu UV-2401 absorption spectrometer and Perkin-Elmer LS 55 fluorescence spectrometer, respectively. The high-resolution transmission electron microscopy (HR-TEM) employed in this work is a Philips TECNAI F20 microscope operating at 200 keV. The TEM specimen were prepared by dipping carbon micro-grids (Ted Pella Inc., 200 Mesh Copper Grid) into well-dispersed samples in NMP or ethanol. Absolute quantum yield measurements were carried out using a Hamamatsu C11347 system equipped with 150 W xenon lamp, PL measurement wavelength range from 400 nm to 110 nm. Fluorescence lifetime was measured using a time-resolved fluorescence spectrophotometer (MicroTime-200, Picoquant, Germany; KBSI Daegu Center). A single-mode pulsed diode laser (375 nm with a pulse width of ~240 ps and an average power of ~5  $\mu$ W) was used as an excitation source. Time-correlated single-photon counting (TCSPC) technique was used to count emission photons to enable decay curve. Exponential fittings for the measured fluorescence decay curves were performed by the iterative least-squares deconvolution fitting method using the Symphotime software (version 5.3). Dynamic light scattering (DLS) were measured using an OTSUKA Electronics CO., Ltd ELSZ-2000 Particle Size & Zeta potential Analysis system equipped with Max power 709 mW laser (scattering angle was 165.5°) and an Avalanche photodiode detector (APD).



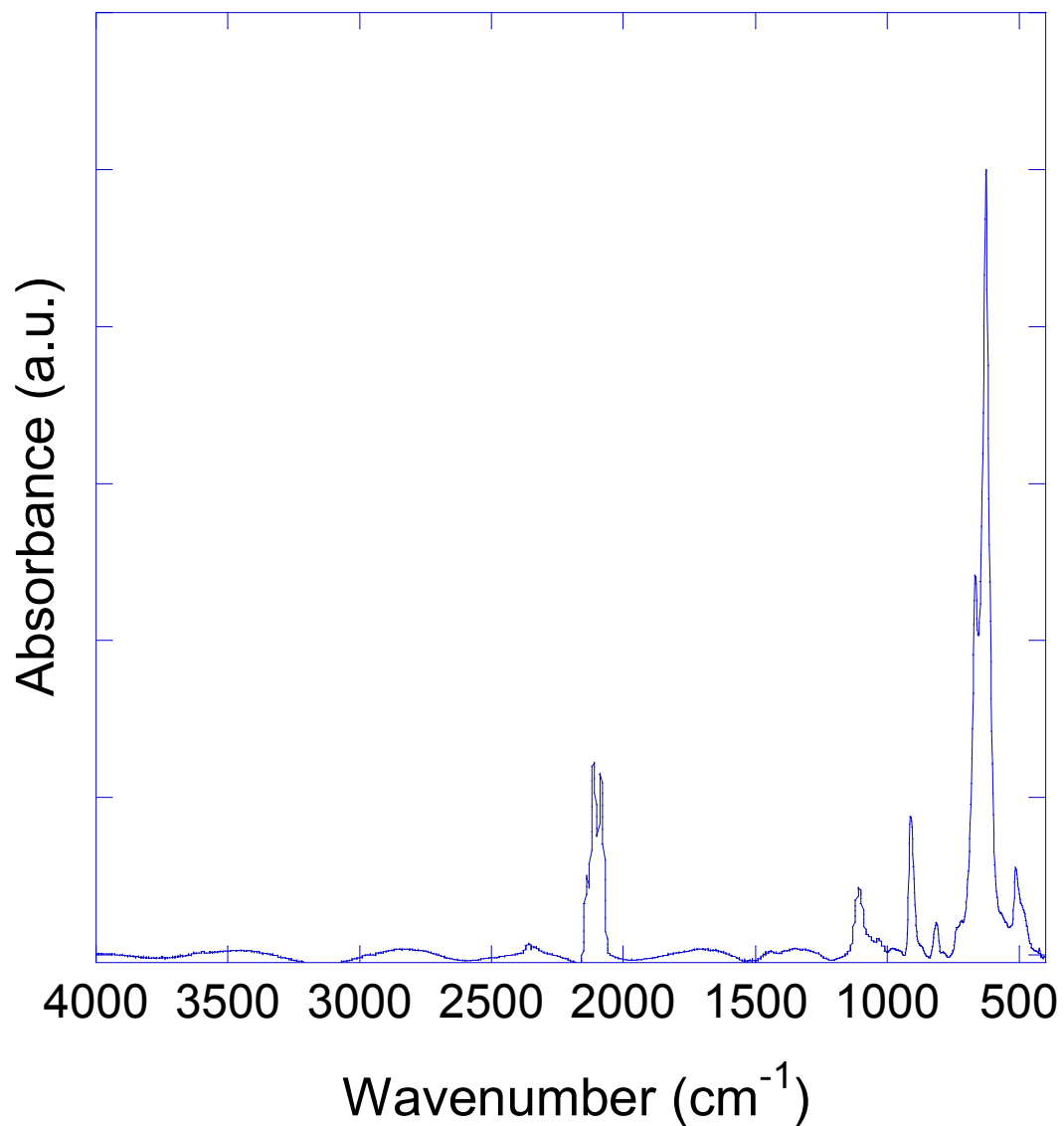
**Figure S1.** Evolution of photoluminescence of Si QDs at the excitation of 440 nm, 450 nm, 460 nm, 470 nm, 480 nm, and 490 nm having emissions at 490 nm, 500 nm, 525 nm, 560 nm, 585 nm, and 600 nm, respectively from left to right.



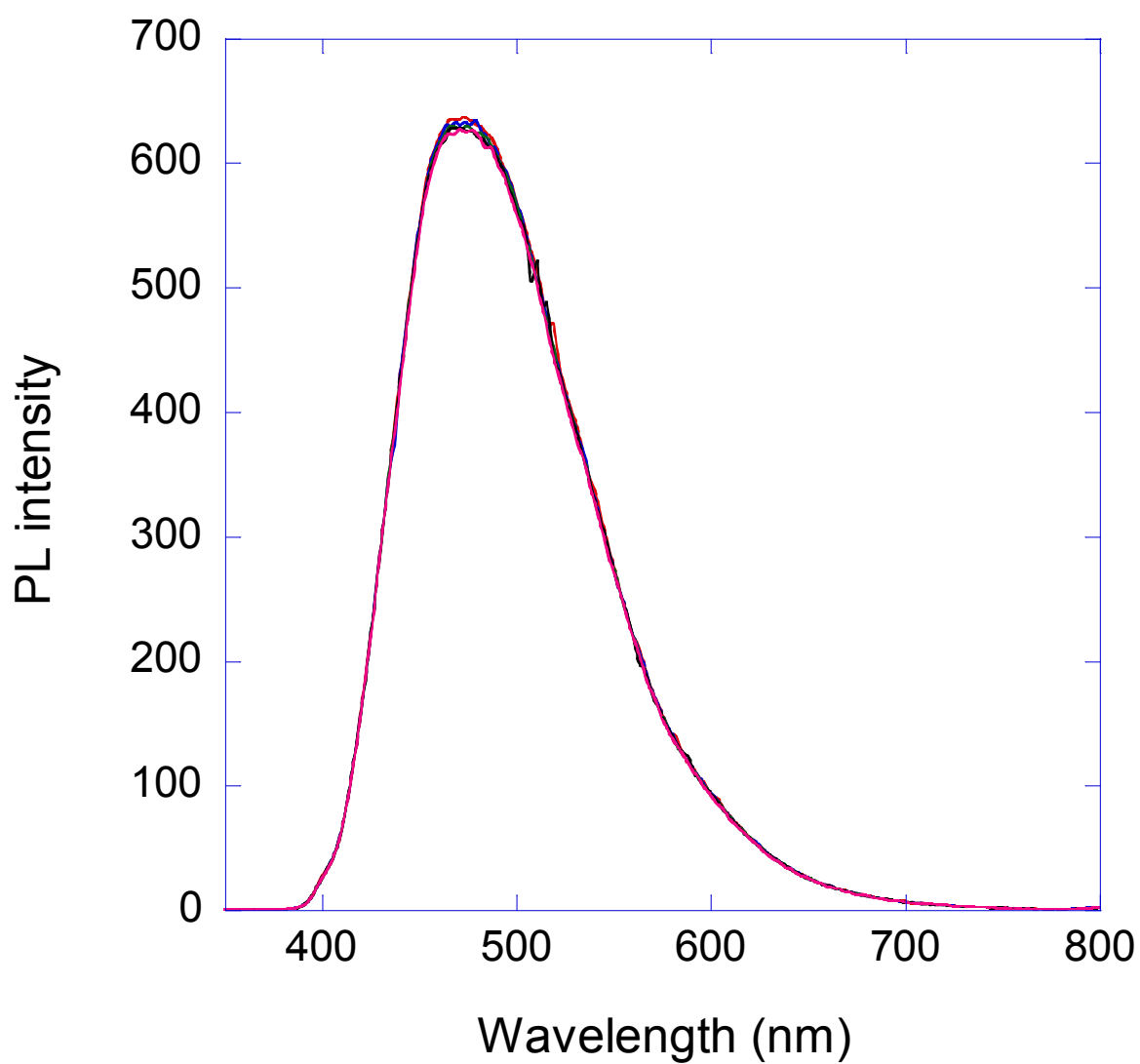
**Figure S2.** DLS data showing that the average size distribution of blue luminescent Si QDs of 2 nm.



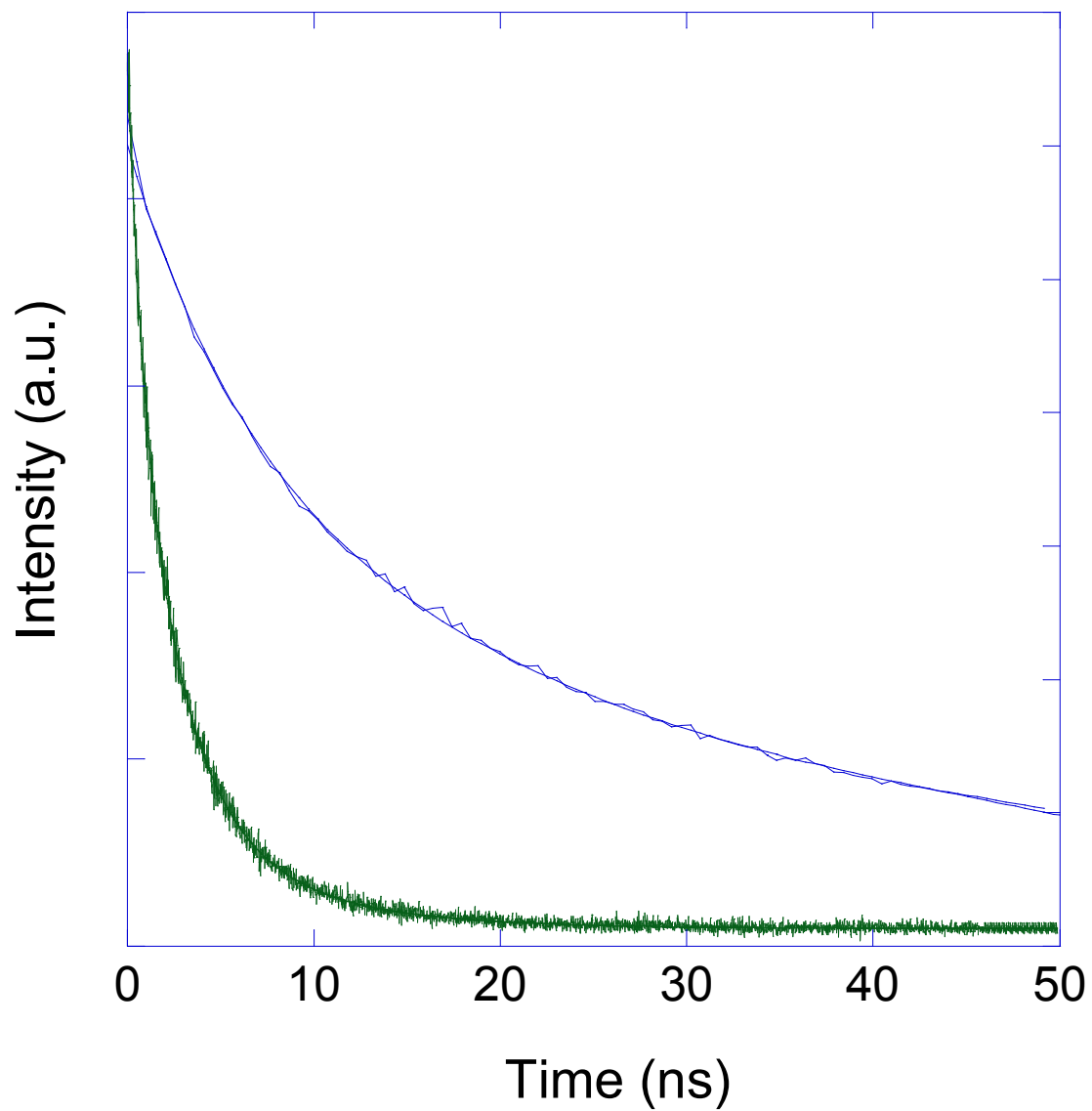
**Figure S3.** DLS data showing that the average size distribution of green luminescent Si QDs of 3 nm.



**Figure S4.** FT-IR spectrum of Si QDs shows 2150 and 914  $\text{cm}^{-1}$  for the  $\nu(\text{Si-H})$  stretching vibration and  $\delta(\text{Si-H})$  bending vibration. Strong  $\nu(\text{Si-Si})$  stretching vibration appeared at 611  $\text{cm}^{-1}$



**Figure S5.** 4 additions of 300  $\mu\text{mL}$  of ethylenediamine to the blue luminescent Si QDs in solution showed no significant changes to the PL spectra. Ethylenediamine was the only possible impurity that could have survived from the synthesis and purification processes. Thus, we tested if it could have interfered with the quenching experiment.



**Figure S6.** Blue luminescence decay dynamics of excited states of CdSe (blue) and silicon (green) quantum dots at fluorescence wavelength of both  $\lambda_{\text{max}} = 460$  nm. Lifetimes of CdSe and silicon quantum dots were 36.81 and 3.76 ns, respectively.