SUPPORTING INFORMATION :

Bioconjugation of Luminescent Silicon Quantum Dots to Gadolinium Ions for Bioimaging Applications

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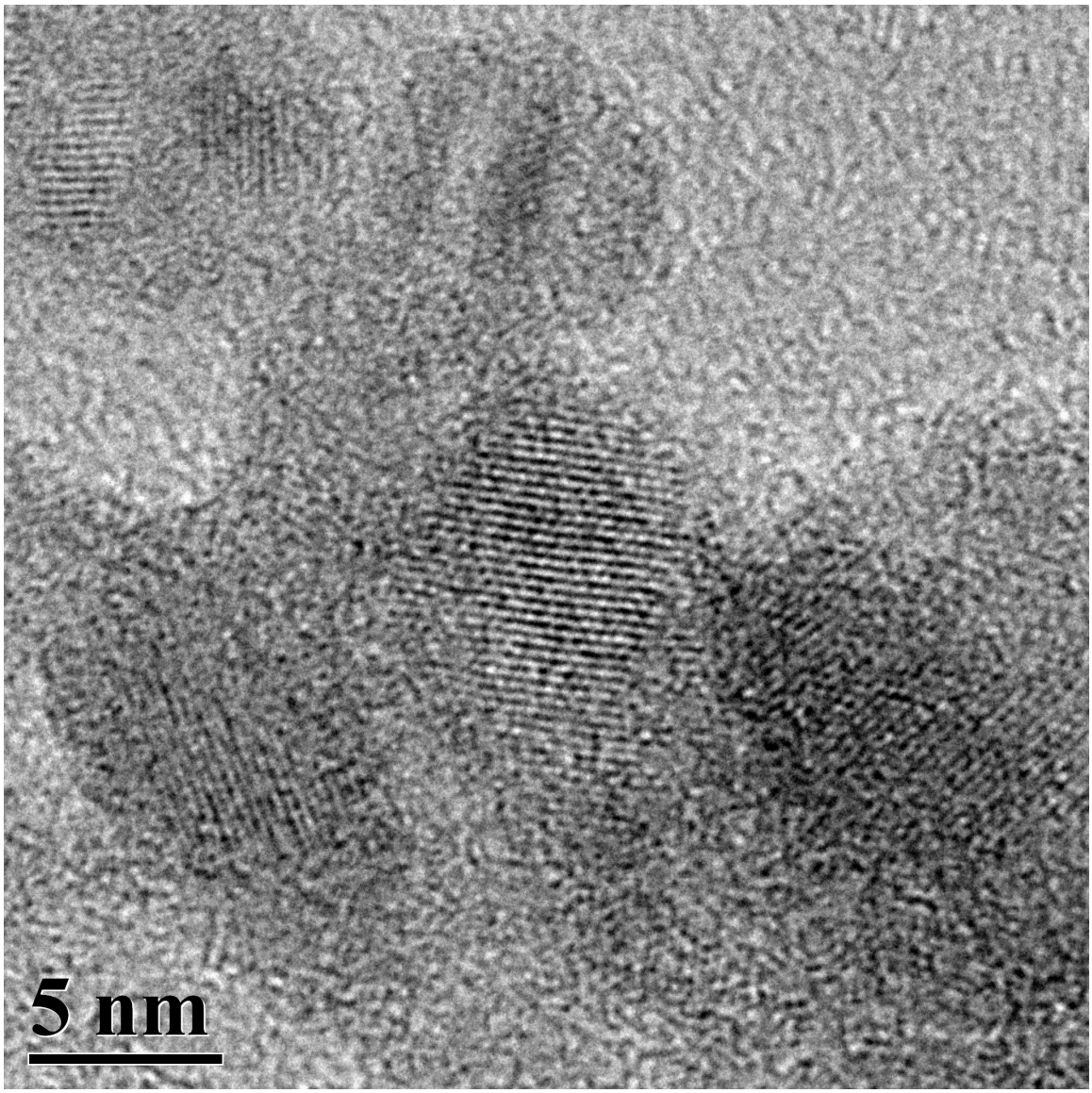


Figure S1. Transmission Electron Microscopic images of functionalized Si QDs

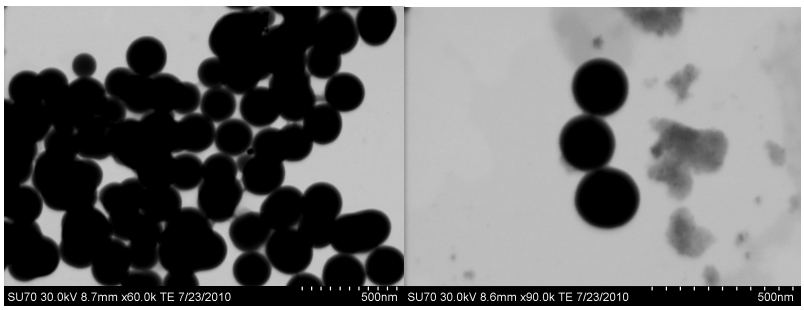


Figure S2. Scanning Electron Microscopy images of MSiQD-Gd^{3+}, with diameters between 150 nm to 170nm.

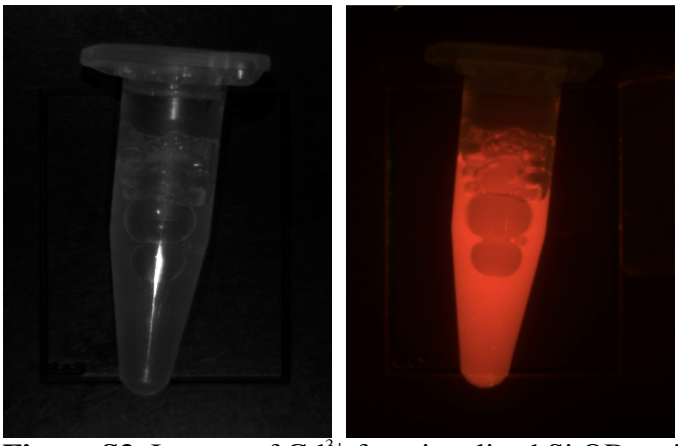


Figure S3. Images of Gd^{3+}-functionalized Si QDs micelles in water after 80 days.

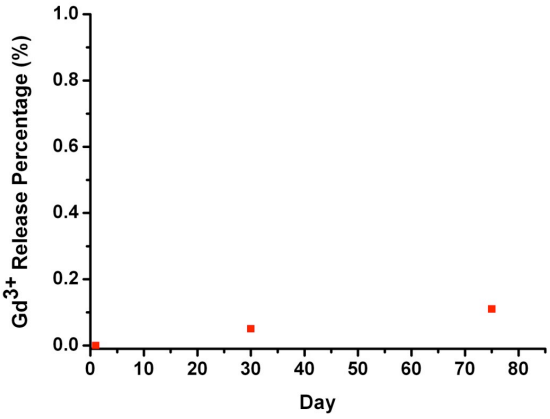


Figure S4. Percentages of Gd^{3+} leaked from original sample at the first day, 30th day, and 75th day.

Determination of free Gd^{3+} in solutions of Gd chelates

EXPERIMENTAL SECTION

Preparation of Arsenazo solution. Fifty mg of arsenazo iii was dissolved in 10ml HPLC water, then 1 mL of this stock solution was diluted with HPLC water to a total volume of 11ml, producing a 0.58 mM solution of arsenazo iii.

Preparation of Gd^{3+} solution. 0.006mM, 0.001mM, 0.0015mM, 0.002mM, 0.0025mM, 0.003mM, 0.004mM, 0.005mM, 0.006mM, 0.02mM, 0.06mM, 0.1mM, and 0.4mM Gd^{3+}

solutions were made from $GdCl_3$ and HPLC water. 1N NaOH was added to adjust pH to 5.5-6.5.

DISCUSSION

Spectrophotometric determination of free Gd^{3+} in the solution of a Gd chelate

Figure S4 shows a color photograph of arsenazo solutions with different amount of free Gd^{3+}. Visual detection is not accurate for calculating the concentration of free Gd^{3+}. However, for preliminary determination of free Gd^{3+} in the solution, it is very helpful to use it as color chart to compare.

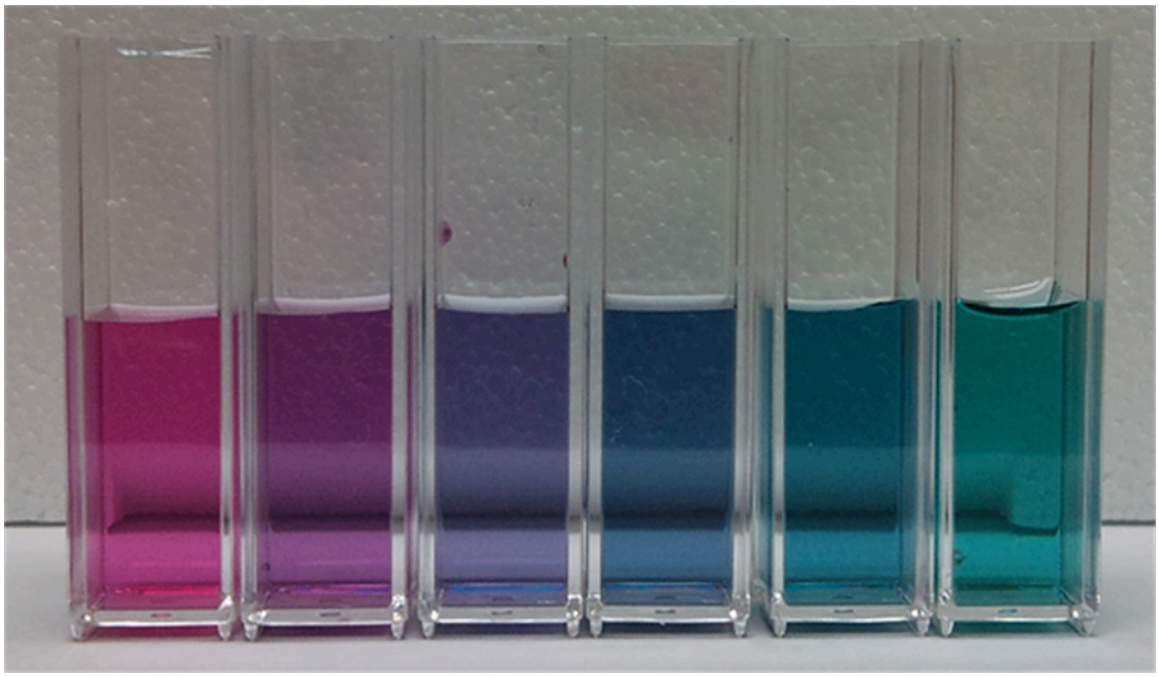


Figure S5. Color photograph of arsenazo solution (a); arsenazo solution in the presence of Gd (III) ion 0.00006mM (b), 0.001mM (c), 0.0015mM (d), 0.002mM (e), 0.006mM (f)

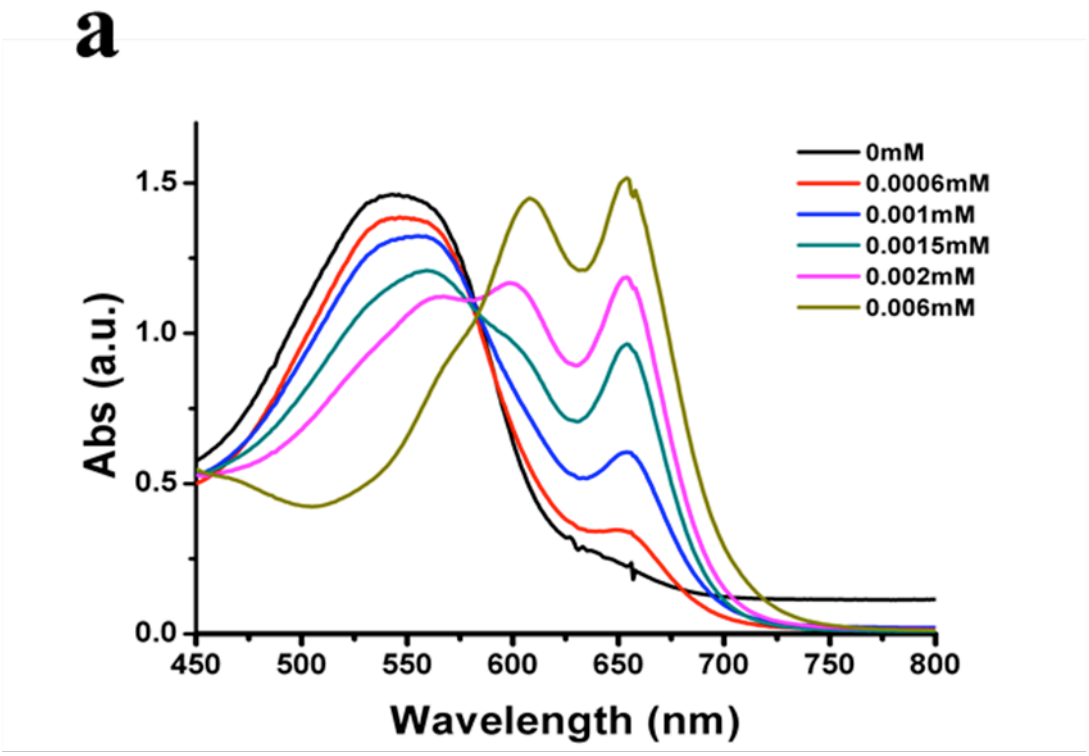
The spectrophotometric quantitation method is based on the differences in visible spectra of free and complexed arsenazo. The absorbance of arsenazo solution shows a

maximum peak at 550 nm whereas arsenazo with Gd^{3+} complex has two absorption maxima at 550nm and 658nm. In the presence of free Gd^{3+} ions, absorption at 550nm decreases and the peak at 658nm becomes significant, as shown in figure S5a. Therefore, the relative intensities of these two absorption bands change when more Gd^{3+} is added to the solution. The free Gd^{3+} concentration is directly proportional to the ratio of absorbance at 550nm and 650nm, for Gd^{3+} concentration below 0.006 mM.

$$Gd^{free} \propto \frac{Abs^{658}}{Abs^{550}}$$

$$[Gd^{3+}] = A + B\frac{Abs^{658}}{Abs^{550}}$$

When Gd^{3+} concentration is above 0.006 mM, absorption peaks transform into another type with absorption maxima at 626 nm and 675 nm, as illustrated in figure S5b. These may result from structural change of saturated arzenazo-Gd^{3+} complex solution. The calibration curve is not usable for Gd^{3+} solution with a concentration over 0.006mM.



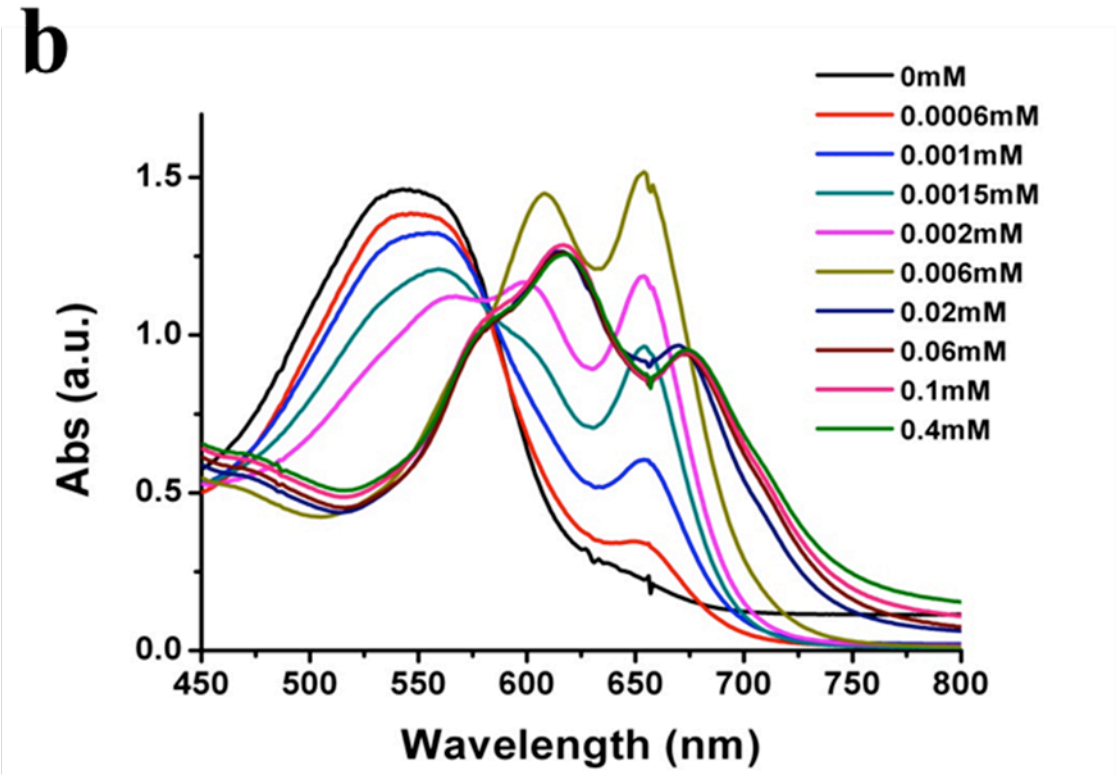


Figure S6. (a) Spectrophotometric determination of Gd^{3+} complex by arsenazo. The increase in Gd(III) concentration causes a decrease of the band intensity at 550nm and a consequent increase of the band at 615 nm and 658nm. The spectra were recorded in Gadolinium chloride aqueous solution at pH 5.8 in the presence of 0.6, 1, 1.5, 2, and 6μM of Gd^{3+} respectively. (b) Spectrophotometric changes of arsenazo with excess Gd^{3+}. Gd^{3+} concentration over 0.6μM causes a transformation of the band that is different from the previous bands.

A linear calibration curve is obtained over a concentration range from 0 mM to 0.006 mM as shown in figure S7. One can obtain the absorbance of a concentration-unknown arsenazo-Gd^{3+} solution and derive free Gd^{3+} concentration by applying Abs^{658}/Abs^{550} to the calibration equation, which is $Abs^{658}/Abs^{550} = 415.64\ [Gd^{3+}] + 0.0597$.

During the chelation of Gd^{3+}, a certain amount of Gd^{3+} was added to 7 mL of the MSiQD-DOTA dispersion. A 50µl aliquot was extracted from the batch and added to 200µl arsenazo solution and 1 mL HPLC water. The absorbance was measured to determine when chelation was complete. Figure S4 shows the changes in absorption spectra during the reaction. Pure arsenazo solution has one peak at 550nm. After adding 4mg Gd^{3+} for 1 hour, most of the free Gd^{3+} were captured by DOTA, and the spectrum shows no obvious peak for free Gd^{3+} at 658nm. More Gd^{3+} was added to obtain the other spectra. When all the available DOTA was saturated with Gd^{3+}, a large peak at 658 appeared, showing the existence of free Gd^{3+}.

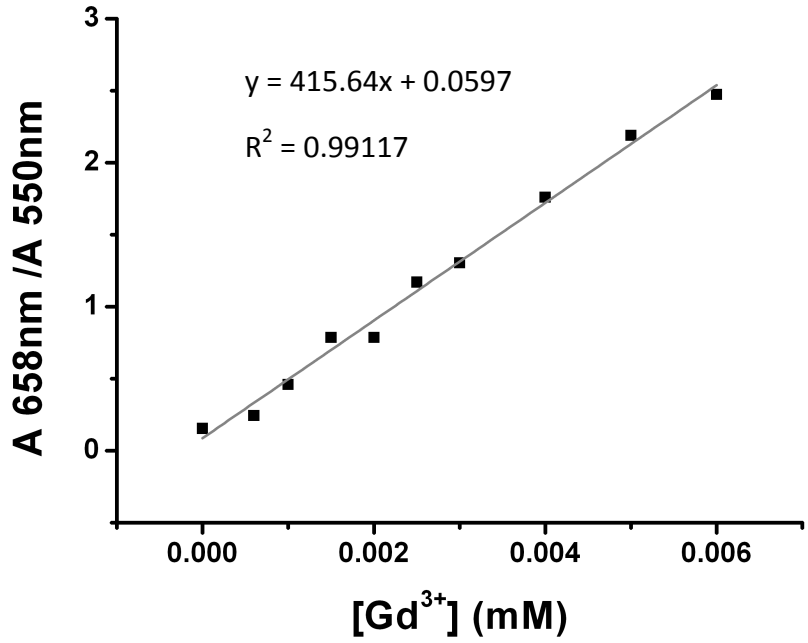


Figure S7. Calibration curve obtained from spectrophotometric changes of arsenazo absorption in the presence of different amount of Gd^{3+}.

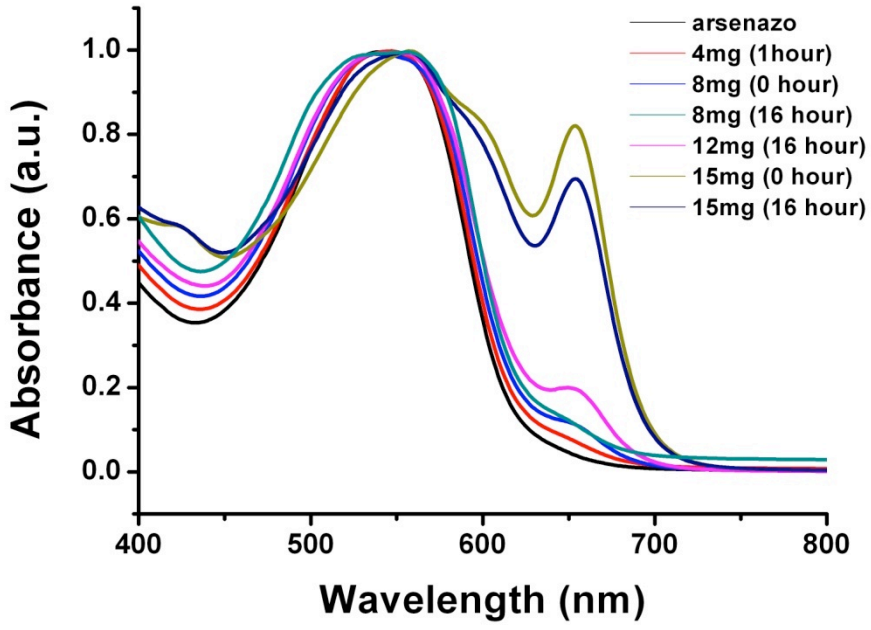


Figure S8. Absorbance spectra change during the reaction.

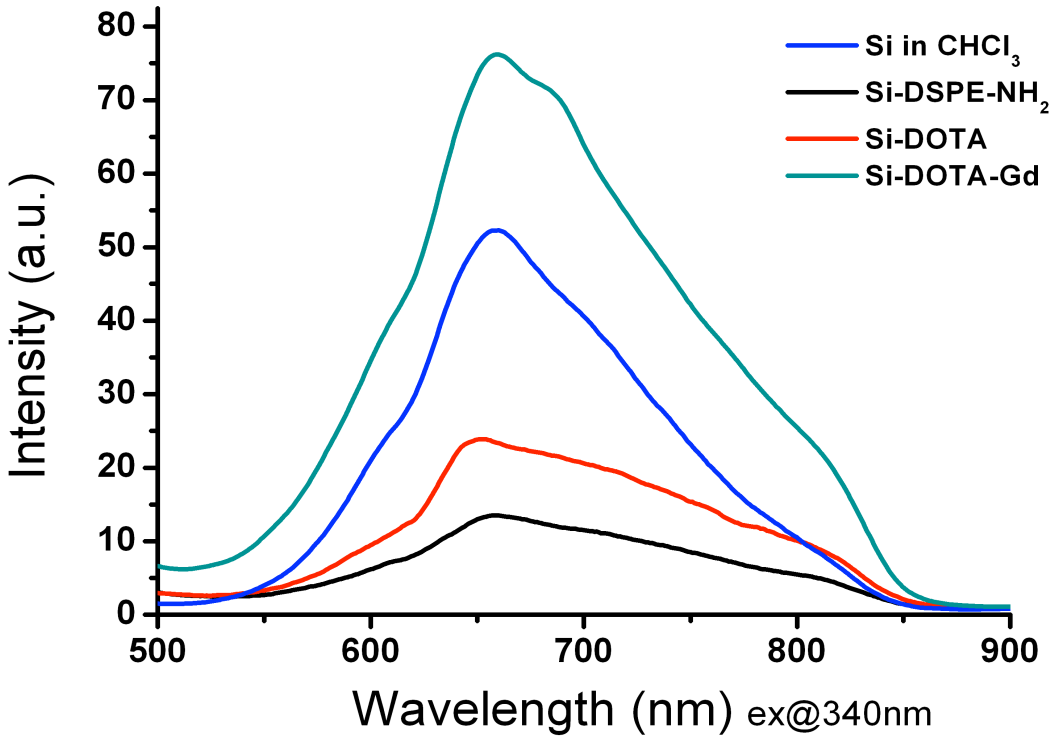


Figure S9. PL emission spectra intensity of MSiQD-NH_2, MSiQD-DOTA, and MSiQD-Gd^{3+}.