Electronic Supplemental Information for:

Chemical Insight Into The Origin of Red and Blue Photoluminescence Arising From Freestanding Silicon Nanocrystals.

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Figure S1. A summary of the characterization of the oxide embedded and hydride-terminated (H-Si NCs) silicon nanocrystals obtained from thermal treatment of HSQ. (**A**) X-ray powder diffraction pattern of Si NCs embedded in silica. The broad reflection at *ca*. 20^{o} arises from the amorphous silica-like matrix. (**B**) FT-IR spectrum of H-Si NCs. Absorptions at *ca*. 1050 cm^{-1} is attributed to Si–O–Si stretching and *ca*. 2100 and *ca*. 900 cm^{-1} are attributed to Si–H$_x$ stretching and bending vibrations, respectively. (**C**) PL spectrum of H-Si NCs. (**D**) Excited state life time of H-Si NCs upon exciting with 349 nm wavelength laser. (**E**) Bright field TEM micrograph of H-Si NCs with a diameter *ca.* 3.5 ± 0.4 nm. The image was acquired at 200kV accelerating voltage.

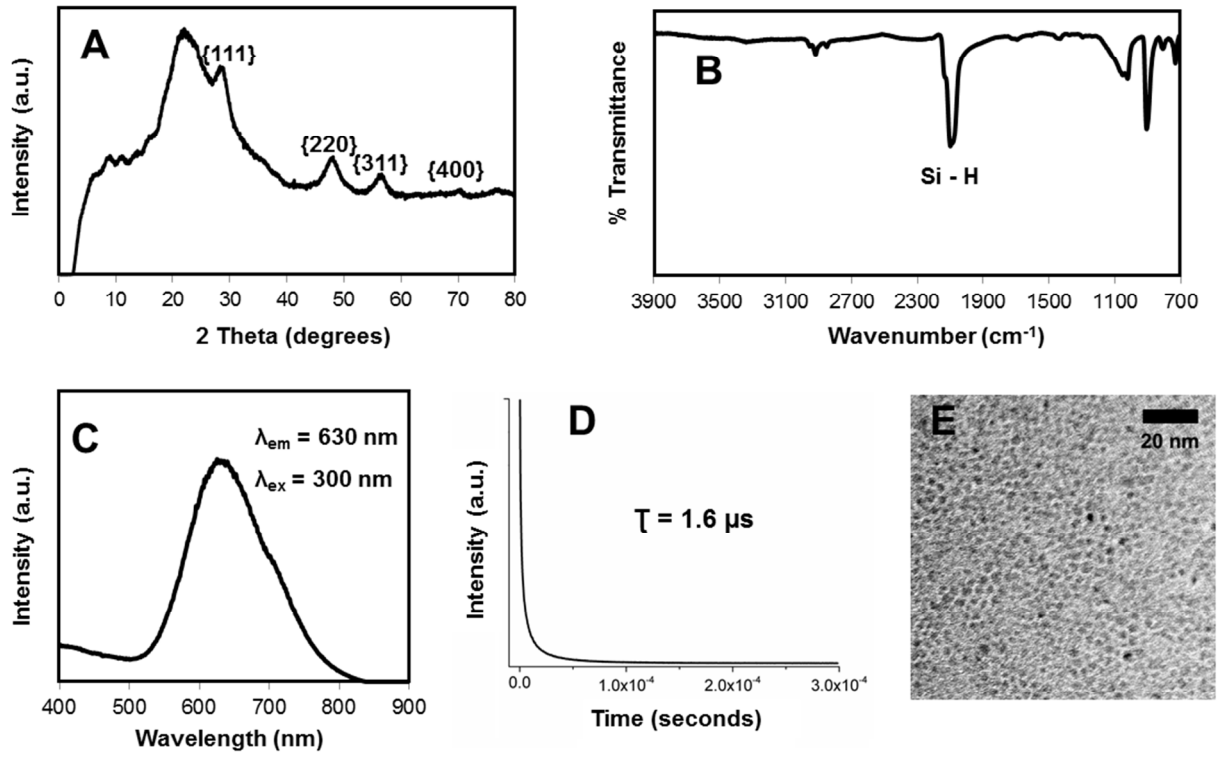

Figure S2. X-ray photoelectron spectra (XPS) of dodecyl surface functionalized Si NCs (Si NC-A). (**A**) Survey spectrum showing emissions arising from Si, C and O. (**B**) High resolution XP analysis of the silicon 2p spectral region. For clarity, only Si $2p_{3/2}$ emissions are shown.

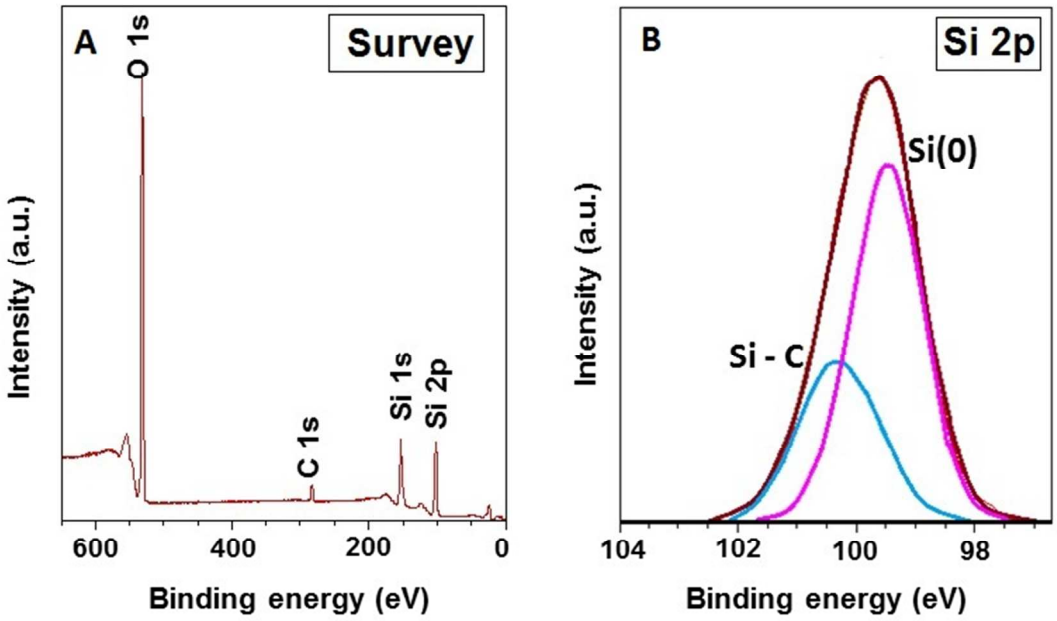

Figure S3. XPS spectra of the nitrogen 1s and silicon 2p spectral regions for H-Si NCs exposed to a variety of nitrogen sources: (A, B) TOAB functionalized Si NCs and (C, D) NH_4Br functionalized Si NCs. For clarity only Si $2p_{2/3}$ signals are shown.

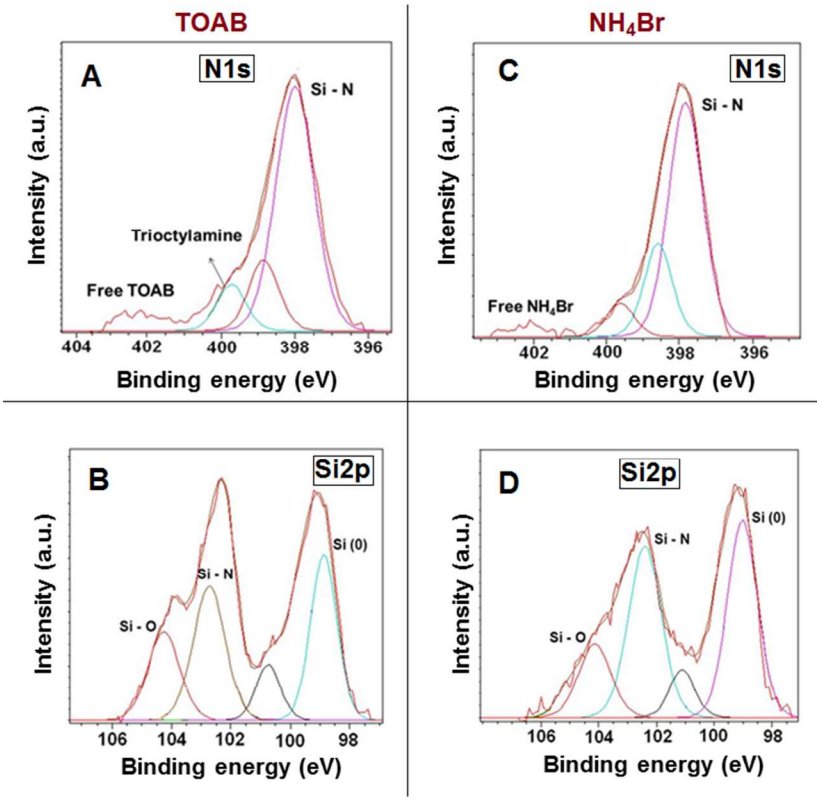

Figure S4. ^{1}H NMR of the byproducts obtained by reacting H-SiNCs with TOAB confirming the formation of trioctylamine and octane.

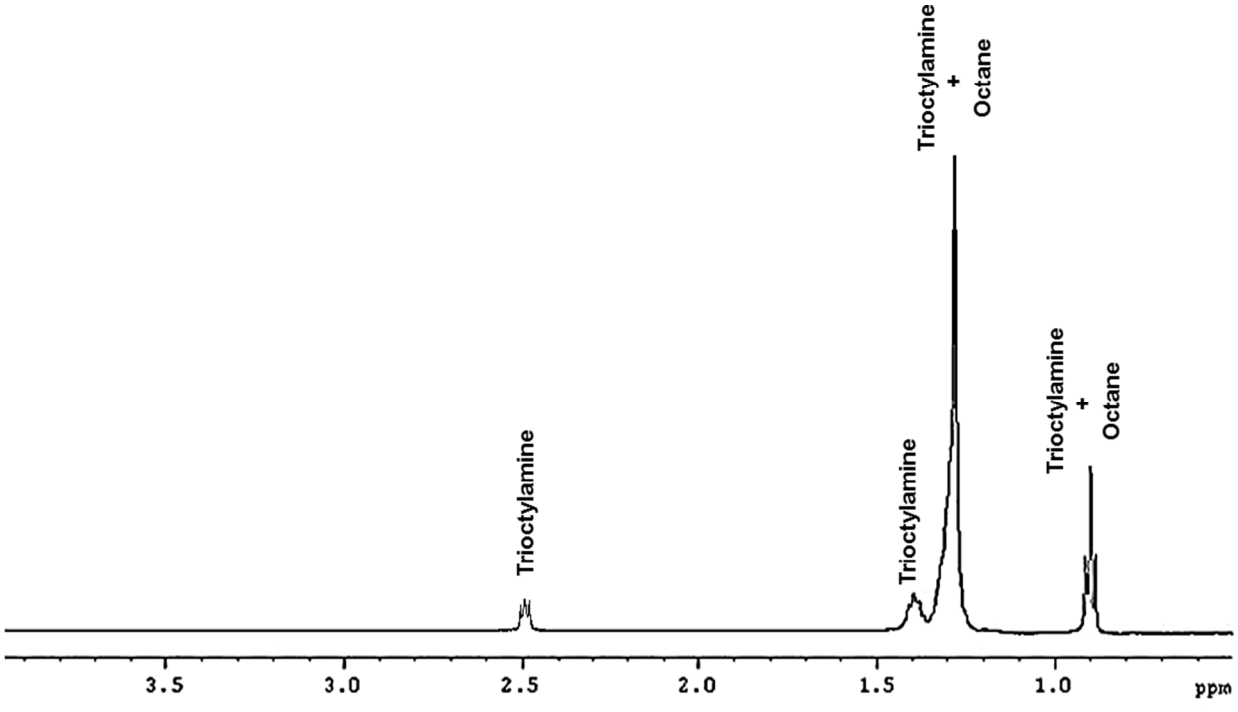

Figure S5. Photoluminescence decay of H-Si NCs reacted with (A) TOAB and (B) NH_4Br.

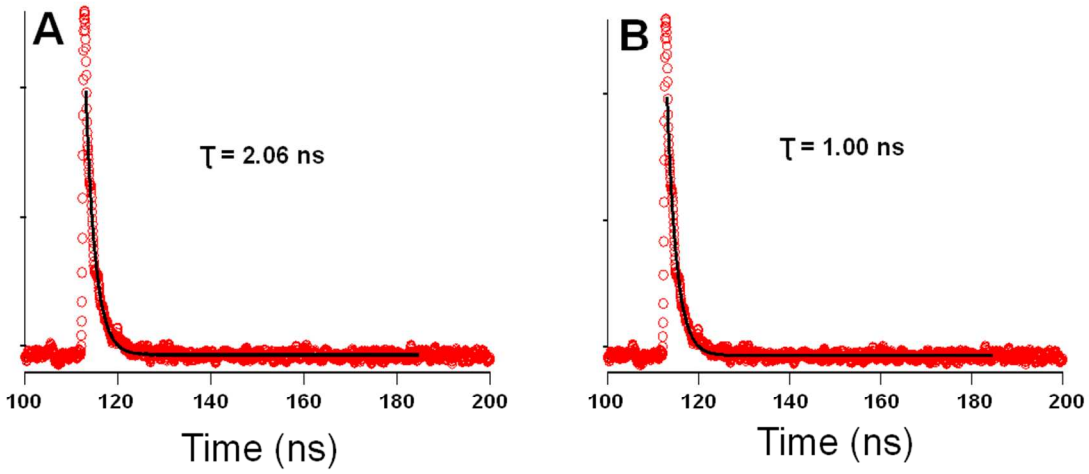

Figure S6. PL intensity at 420 nm *vs.* nitrogen concentration for H-Si NCs reacted with (A) TOAB and (B) NH_4Br.