Supporting Information for:

Tailoring B-Doped Silicon Nanocrystal Surface Chemistry via Phosphorous Pentachloride – Mediated Surface Alkoxylation

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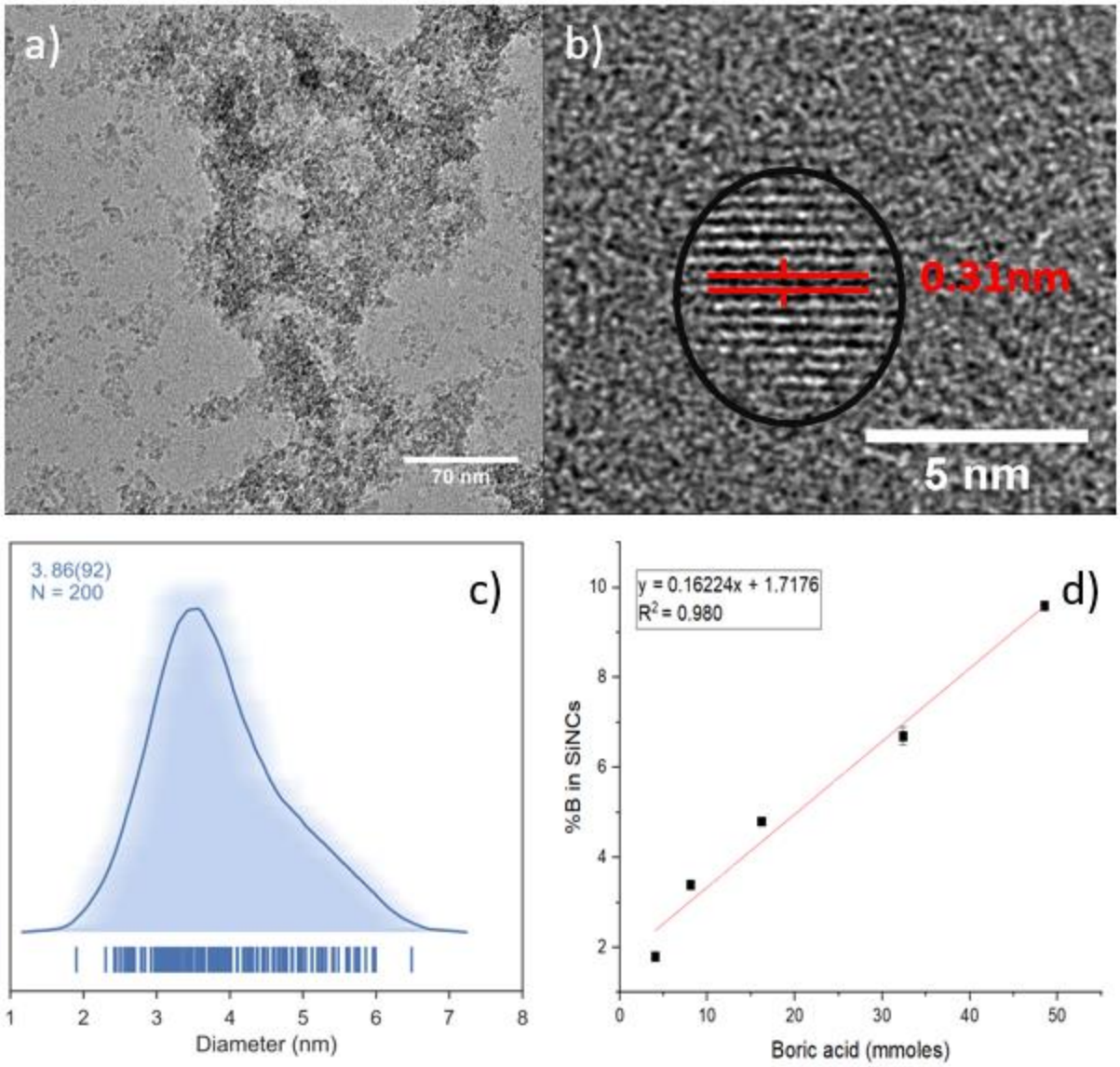

Figure S1 a) TEM of bare 9.6% B-doped SiNCs after HF etching with a measured average diameter of 3.86 ± 0.92 nm determined from the histogram in c). b) HRTEM provides measured lattice fringe of 0.31 nm that is characteristic of crystalline Si. d) Atomic % B was measured using ICP-MS and could be incorporated from 1.8-9.6% B in SiNCs.

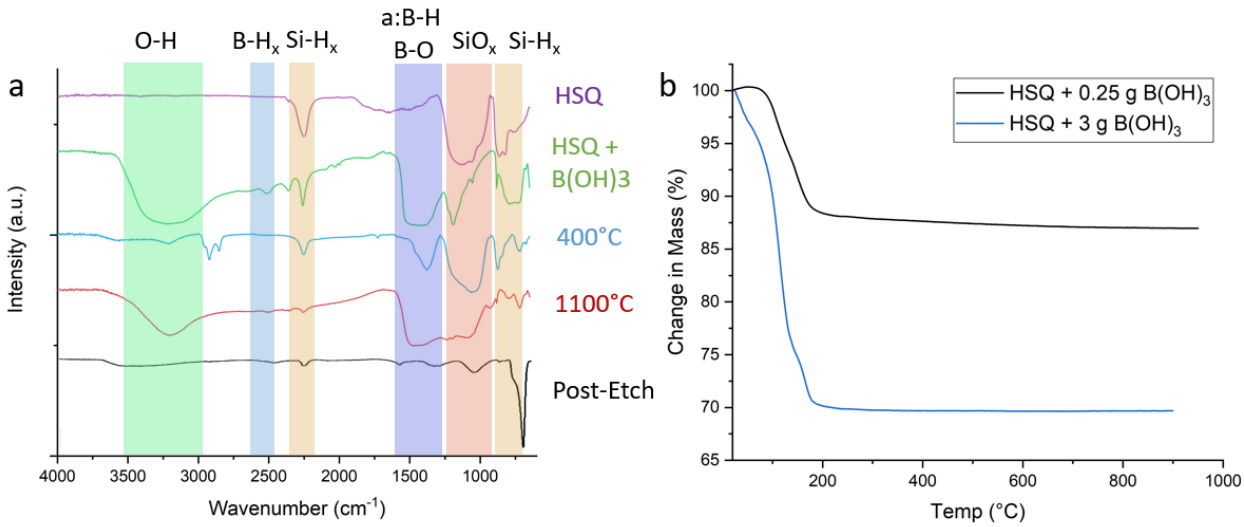

Figure S2 a) Fourier-transform infrared spectrum of undoped hydrogen silsesquioxane (HSQ), boric acid doped HSQ, the resulting composite after each thermal processing step and the resulting free-standing particles from Scheme 1. b) TGA of the lowest and highest concentration of B (0.25 g and 3 g of boric acid for 1.8 % and 9.6 % B).

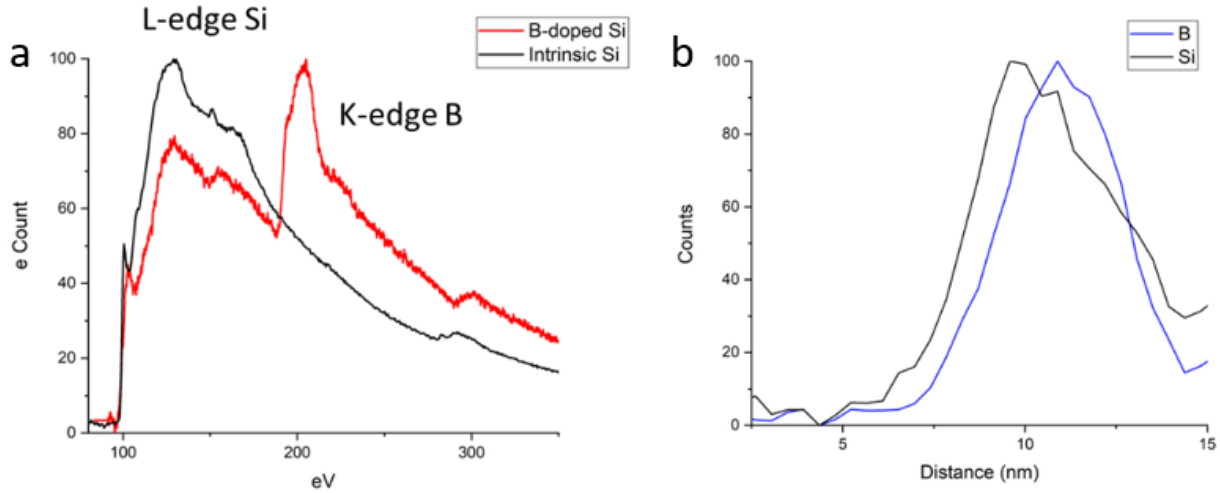

Figure S3 a) Electron energy loss spectroscopy (EELS) point spectrum of intrinsic Si and 9.6 % B SiNC showing L-edge of Si at 100eV and the K-edge of B in the doped sample at 200 eV b) EELS line-scan of a single SiNC with 9.6 % B.

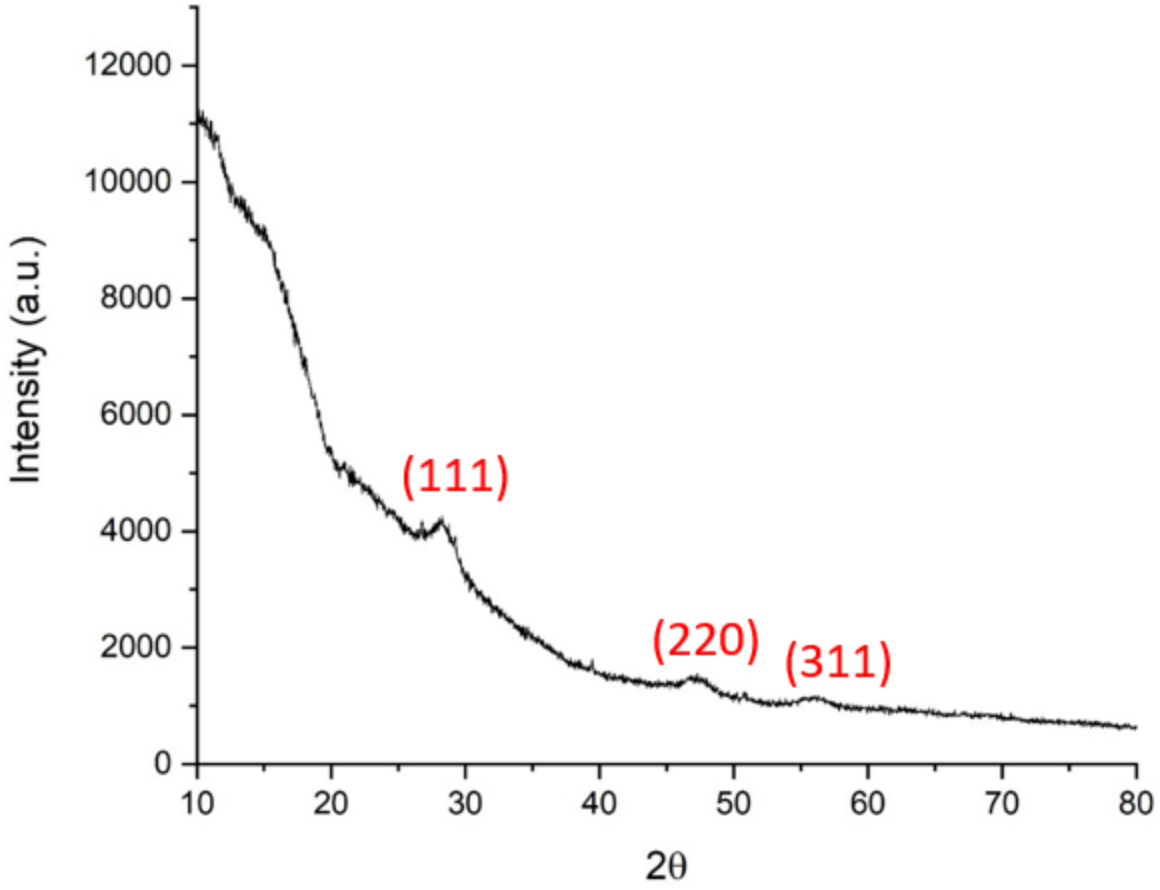

Figure S4 X-ray diffraction pattern of as-synthesized 9.6 atomic % B-doped SiNCs after HF etching, characteristic reflections for crystalline Si are observed.

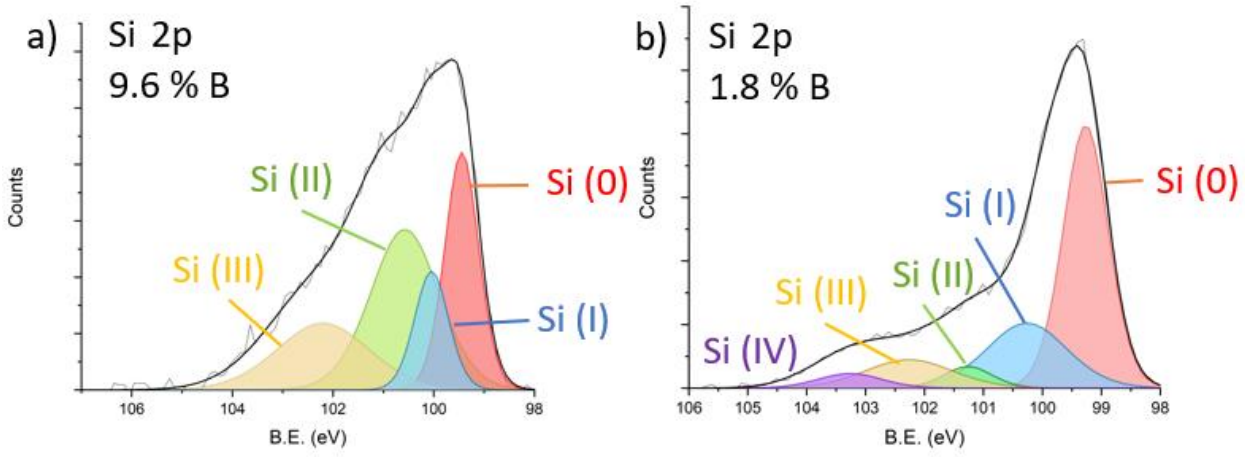

Figure S5 High resolution XP spectra of Si 2P region for a) 9.6 and b) 1.8 atomic % B doped SiNCs.

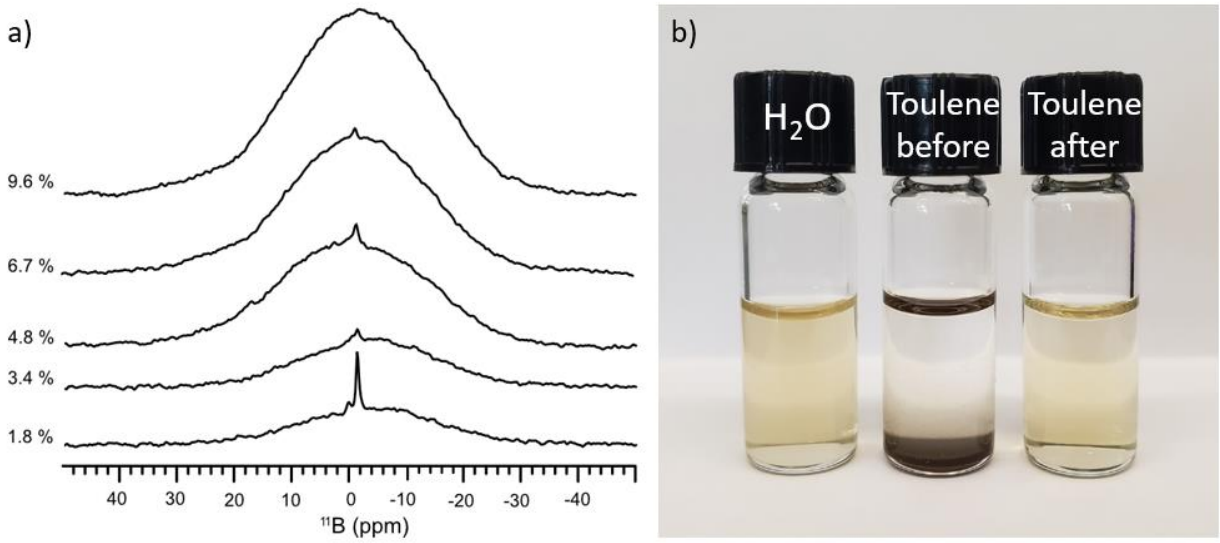

Figure S6 a) Direct polarization ^{11}B MAS NMR of B-doped SiNCs with indicated atomic % B (ICP-MS). b) B-doped SiNCs in indicated left: water, middle: toluene after thermal treatment only, right: toluene after PCl_5/thermal treatment.

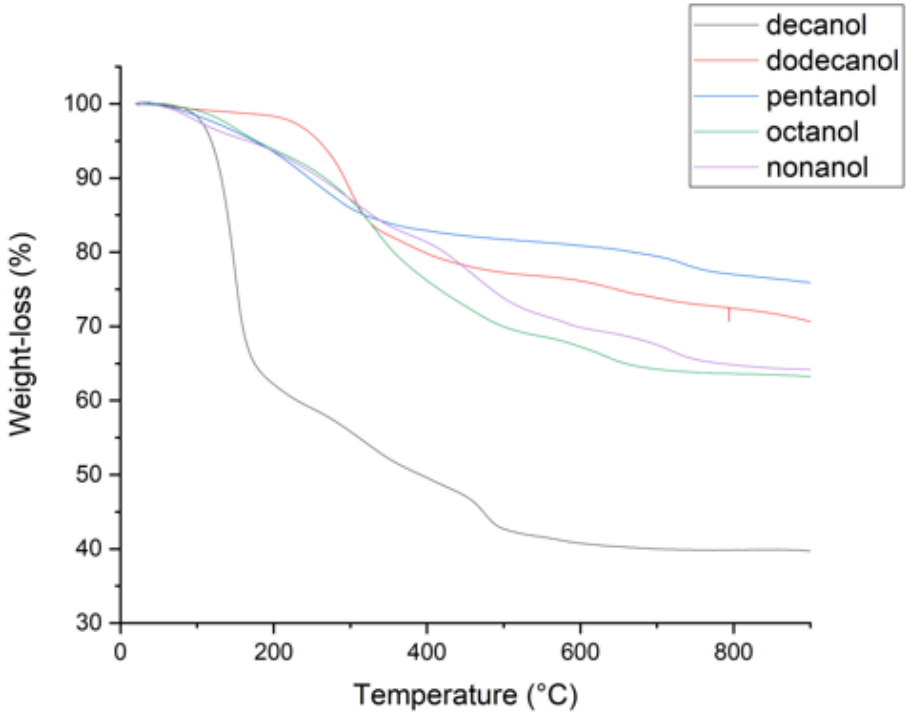

Figure S7 TGA weight-loss plots for 9.6 atomic % B-doped SiNCs functionalized with the indicated alkoxy ligands using the PCl_5/thermal method described in Scheme 2.

Table S1 Surface coverage of 9.6 at. % B-doped SiNCs with different ligands calculated using TGA analysis

Ligand	Theoretical Weight-loss (%)	Experimental Weight-loss (%)	Surface Coverage
1-pentanol	46.27	25.15	54.35
1-octanol	55.99	41.45	74.03
1-nonanol	58.50	48.07	82.78
1-decanol	60.70	58.20	95.90
1-dodecanol	64.54	30.90	47.91

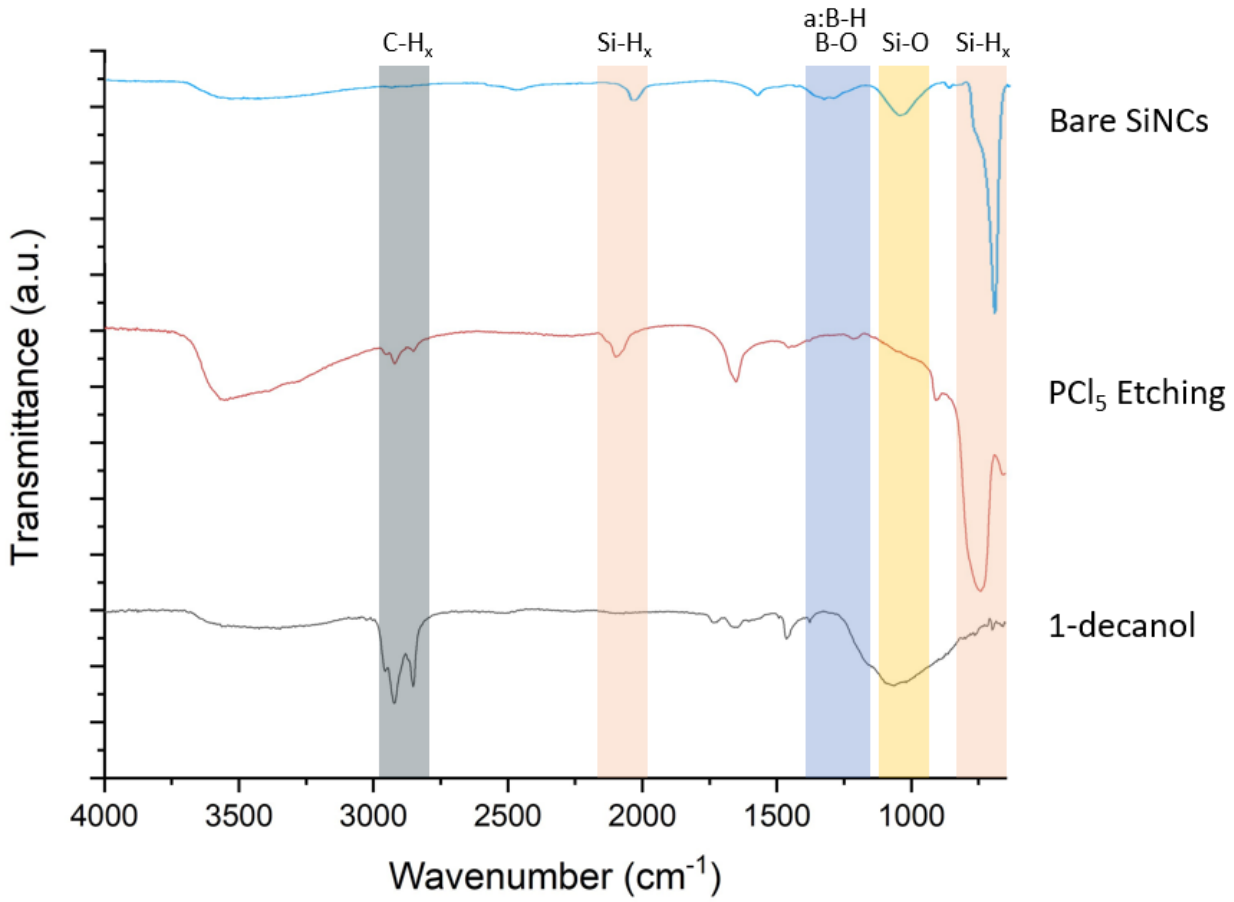

Figure S8 FTIR of 9.6% B-doped SiNCs before functionalization (bare SiNCs), after the PCl_5 etching step, and after reaction with 1-decanol with 180°C heating

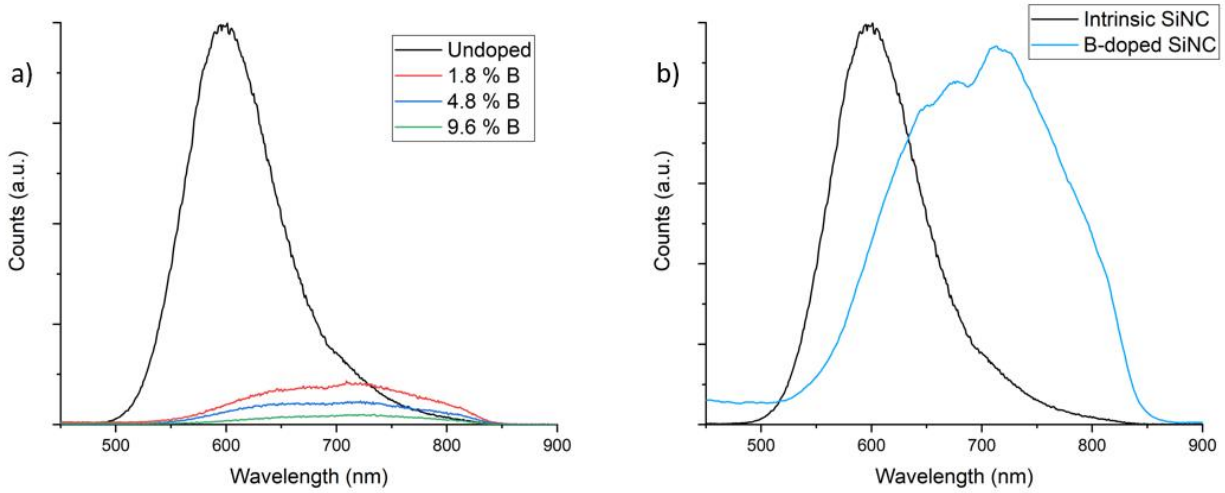

Figure S9 Photoluminescence emission spectra obtained using an excitation wavelength of 350 nm of a) intrinsic and 1.8 %, 4.8 % and 9.6% B-doped SiNCs after functionalizing with 1-decanol. b) Normalized spectra of intrinsic SiNC and 1.8% B-doped SiNCs, the doped particles show PL that ranges from 550 – 850 nm.

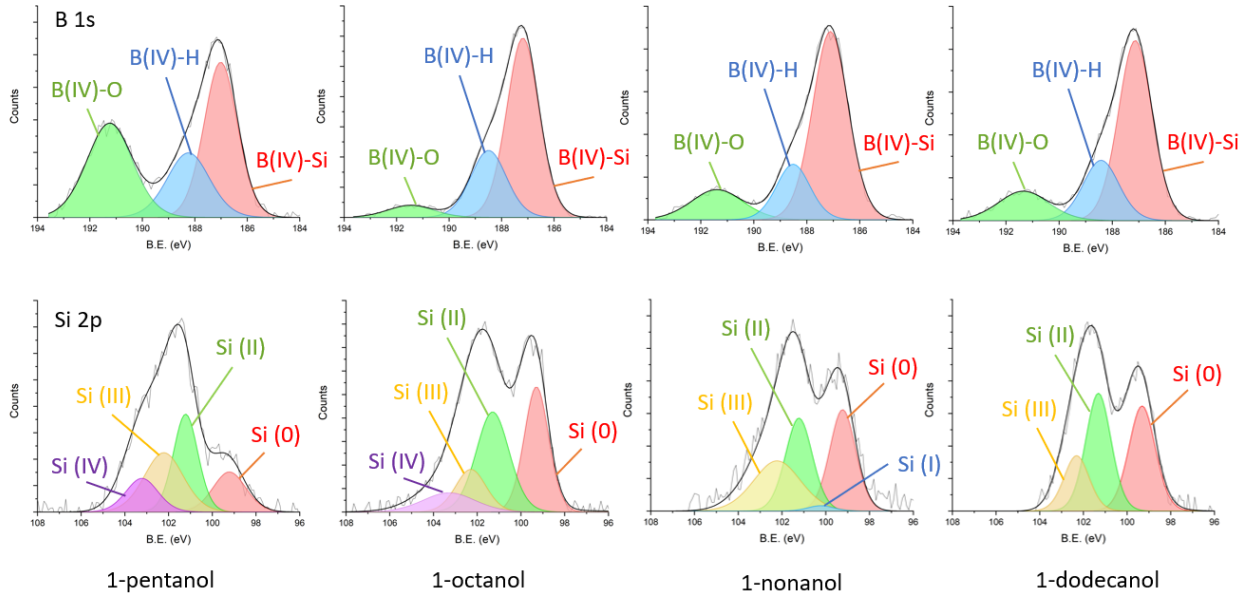

Figure S10 High resolution XP spectra of B 1s (top row) and Si 2p (bottom row) of 9.6% B-doped SiNCs after functionalization with the alkoxy ligands indicated in the figure.

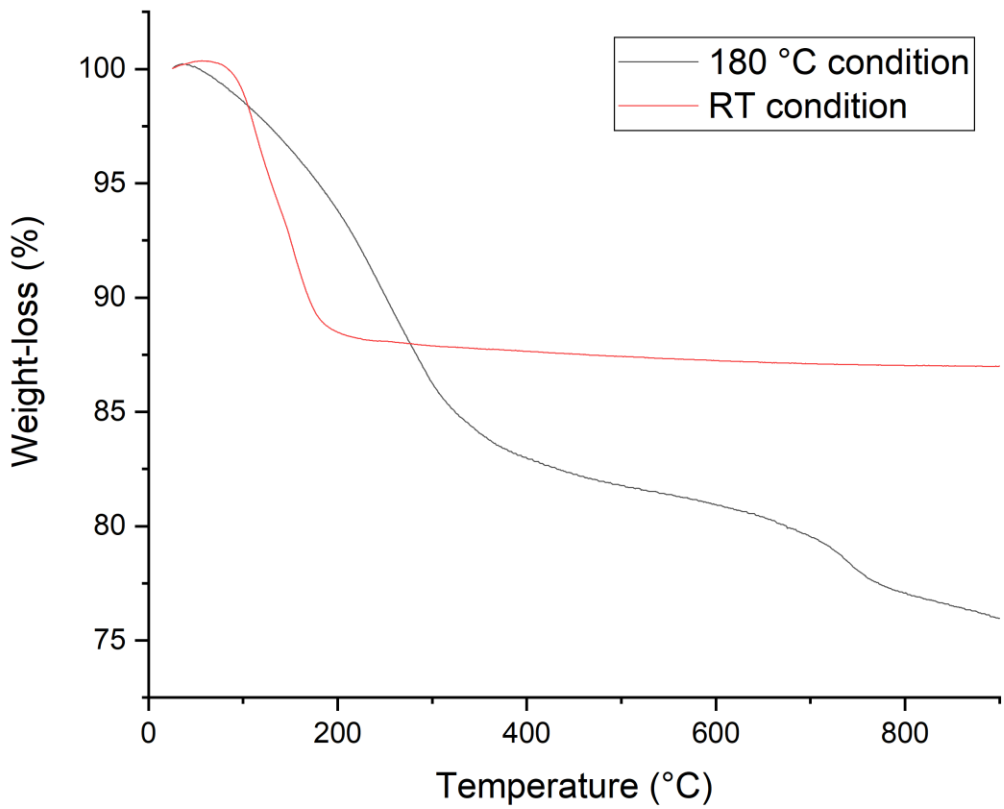

Figure S11 TGA weight-loss plots for functionalization reaction of 9.6% B-doped SiNCs with 1-pentanol for two different reaction conditions: without heating (red curve) and heated to 180 °C in a pressure sealed flask (black curve).

Table S2 Surface coverage of 9.6% B-doped SiNC with 1-pentonal with and without heating at 180 °C calculated using TGA analysis

Method	Theoretical Weight-loss (%)	Experimental Weight-loss (%)	Surface Coverage
Room temperature	46.27	13.38	28.92
Heating	46.27	25.15	54.35

Surface coverage calculation: The surface coverage from TGA weight-loss was calculated as follows:

$$\%\,Surface\ Coverage = \frac{\%\,Experimental\ weight\ loss}{\%\,Theoretical\ weight\ loss} \quad (1)$$

$$\%\,Theoretical\ weight\ loss = \frac{Ligands\ theoretical\ weight}{Ligands\ and\ SiNCs\ theoretical\ weight} x100 \quad (2)$$

$$SiNCs\ theoretical\ weight = \frac{N(Si)x\ M(Si)}{N_A} \quad (3)$$

$$Ligands\ theoretical\ weight = \frac{N(L)x\ M(L)}{N_A} \quad (4)$$

Where N(Si) = Total number of silicon atoms per nanocrystal

N(L) = Total number of ligands per nanocrystal surface

M(Si) = Molar mass of Si

M(L) = Molar mass of ligand

N_A = Avogadro's number

Substituting equation (3) and (4) into equation (2) simplifying results in equation (5)

$$\%Theoretical\ weight\ loss = \frac{N(L)\cdot M(L)}{N(L)\cdot M(L)+N(Si)\cdot M(Si)}x100 \quad (5)$$