Supporting Information for:

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

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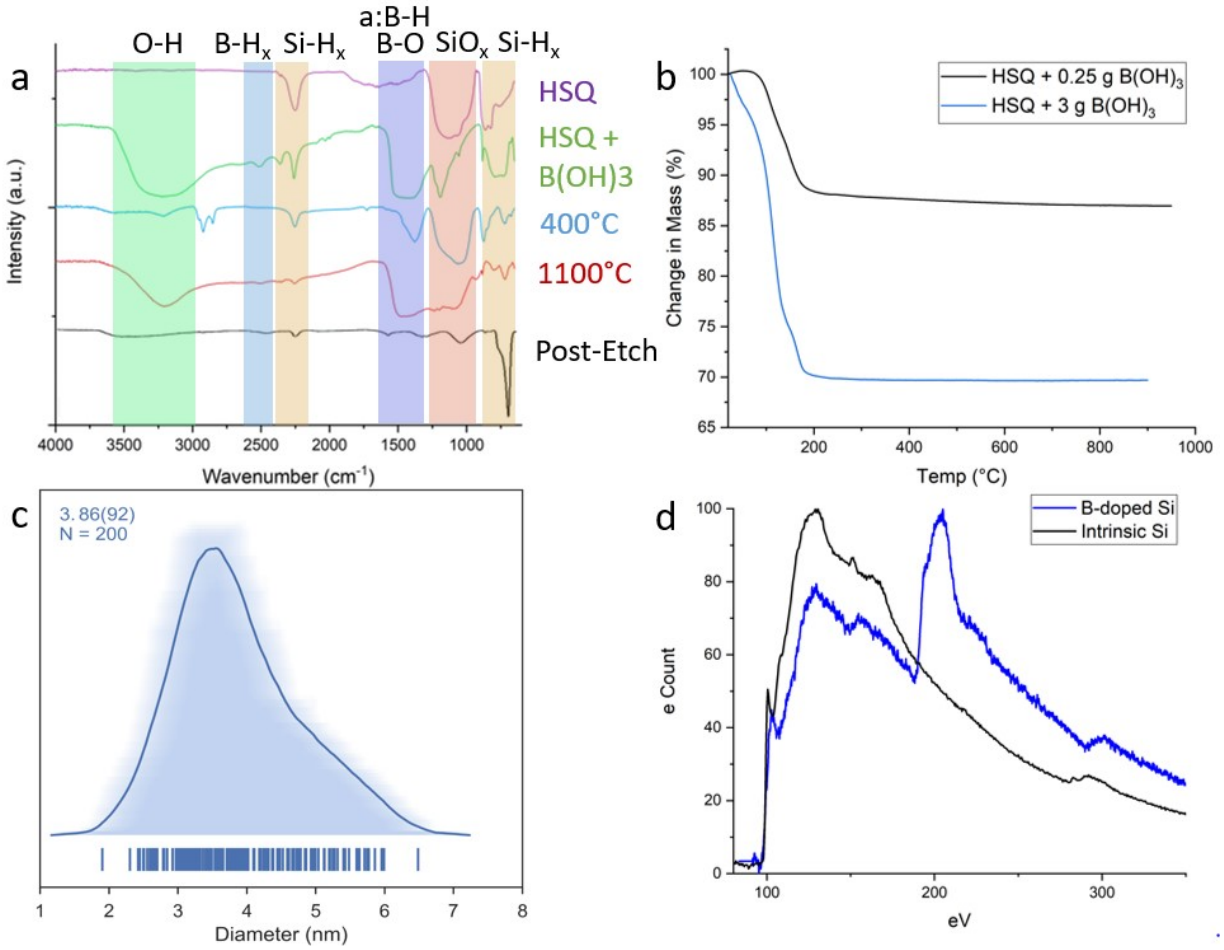

Figure S1 a) Fourier-transform infrared spectrum of undoped hydrogen silsesquioxane (HSQ), boric acid doped HSQ, the resulting composite after each thermal processing step and the resulting freestanding particles from Scheme 1. b) TGA of the lowest and highest concentration of B (0.25 g and 3 g of boric acid for 1.8 and 9.6 atomic % B). c) histogram for 9.6 atomic % B-doped SiNCs with resulting average diameter of 3.86 ± 0.92 nm. d) Electron energy loss spectroscopy (EELS) point spectrum of intrinsic Si and 9.6 atomic % B SiNC showing L-edge of Si at 100eV and the K-edge of B in the doped sample at 200 eV.

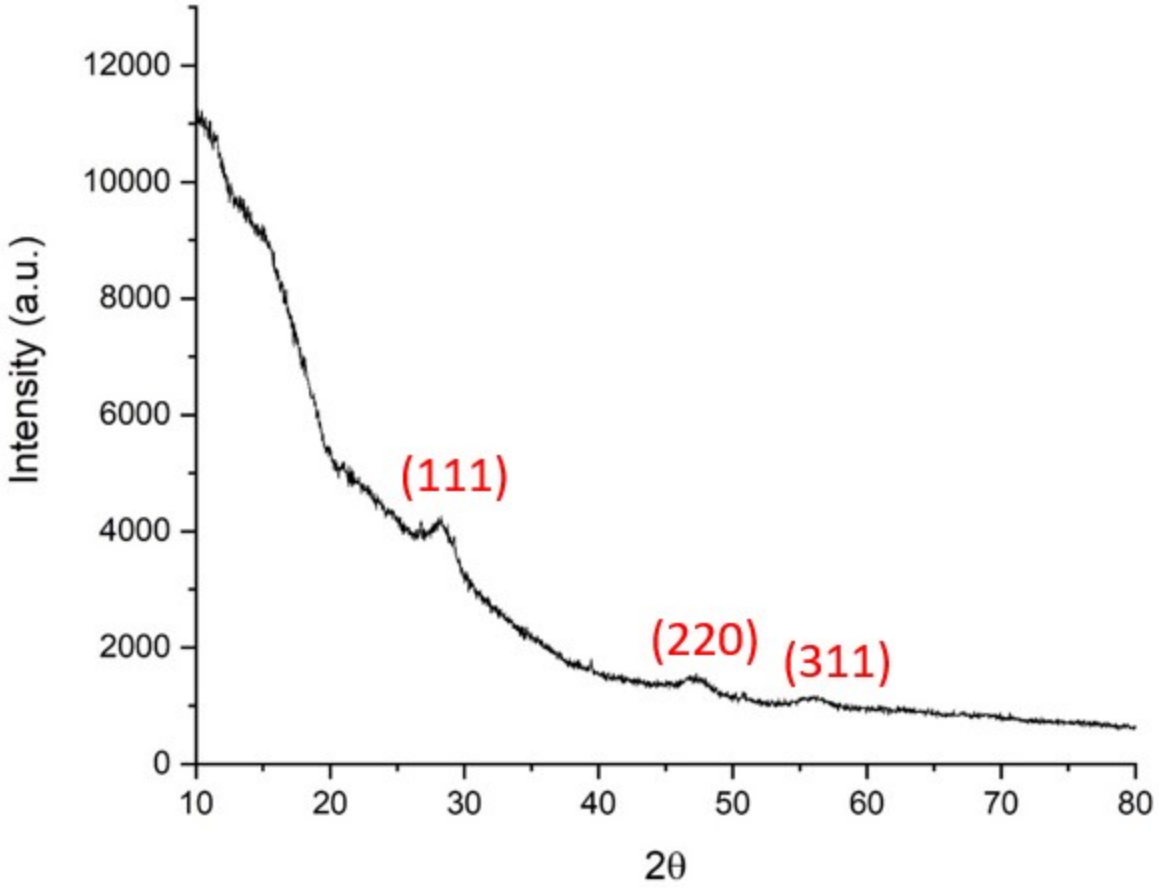

Figure S2 X-ray diffraction pattern of as-synthesized 9.6 atomic % B-doped SiNCs after HF etching, characteristic reflections for crystalline Si are observed.

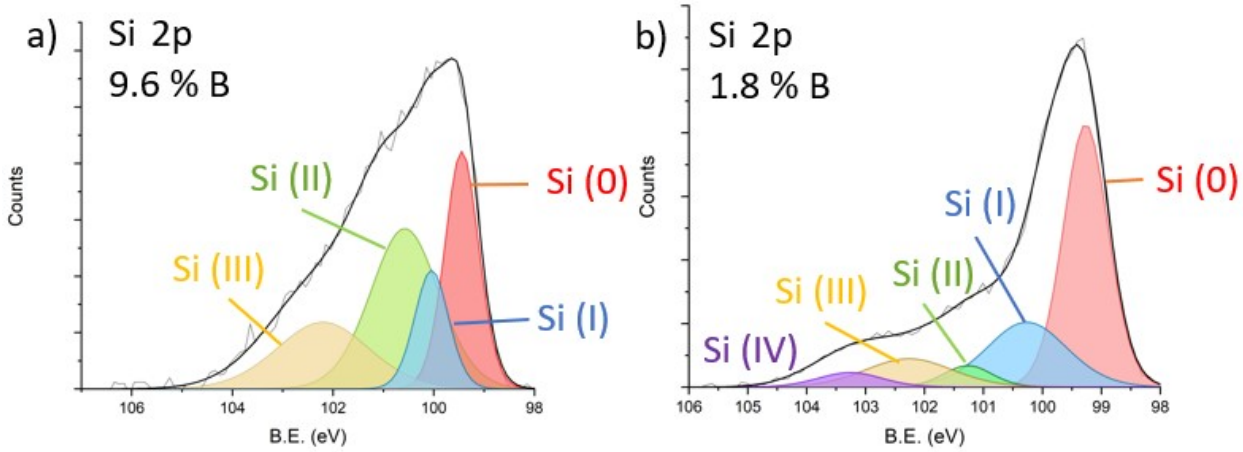

Figure S3 High resolution XP spectra of Si 2P region for a) 9.6 and b) 1.8 atomic % B doped SiNCs.

Table S1: Integrated values of "surface" and "core" B species found by taking the area under the fitted peaks centred at 189 eV and 187 eV in the B 1s spectra for samples with 9.6, 6.7, and 1.8 atomic % B.

Sample	Area of "surface" species (189 eV)	Area of "core" species (187 eV)
9.6 %B	334.7	116.3
6.7 %B	131.8	119.4
1.8 %B	40.2	118.0

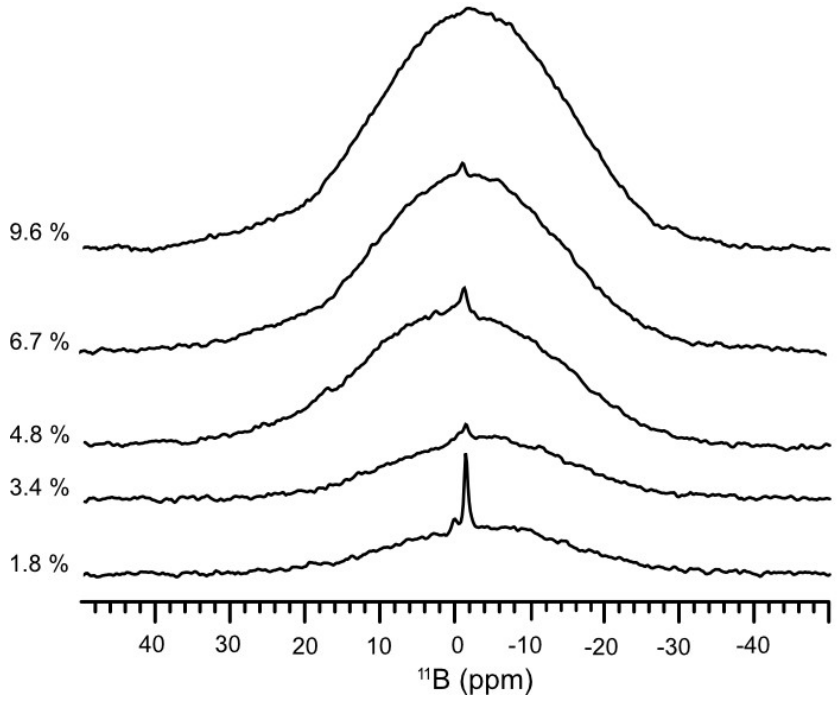

Figure S4 Direct polarization ^{11}B MAS NMR of B-doped SiNCs with indicated atomic % B (ICP-MS).

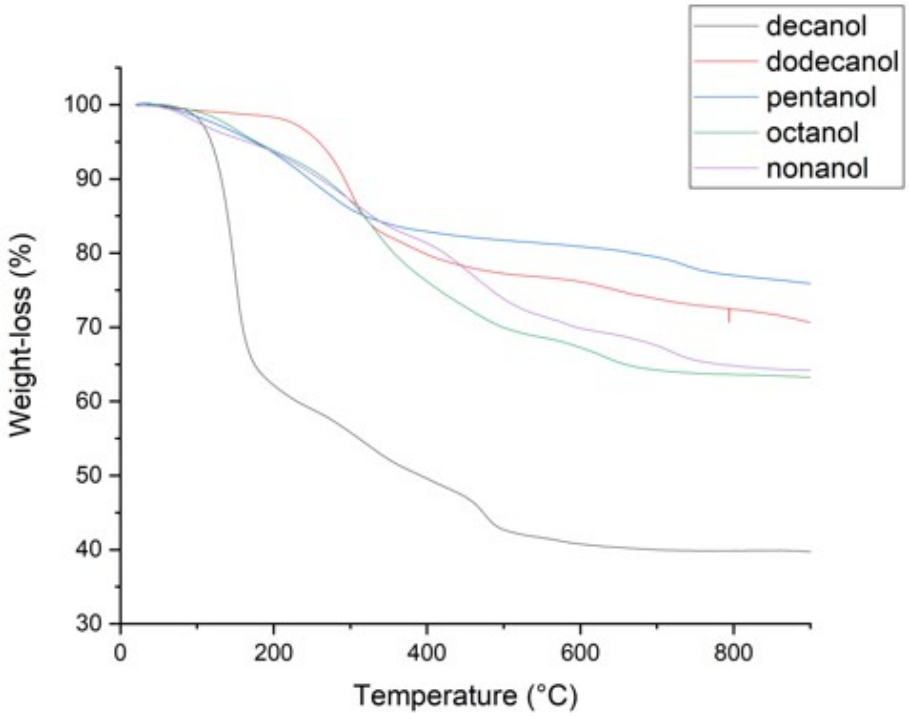

Figure S5 TGA weight-loss plots for 9.6 atomic % B-doped SiNCs functionalized with the indicated alkoxy ligands using the PCl_5/thermal method described in Scheme 2.

Table S2 Surface coverage of 9.6 atomic % 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

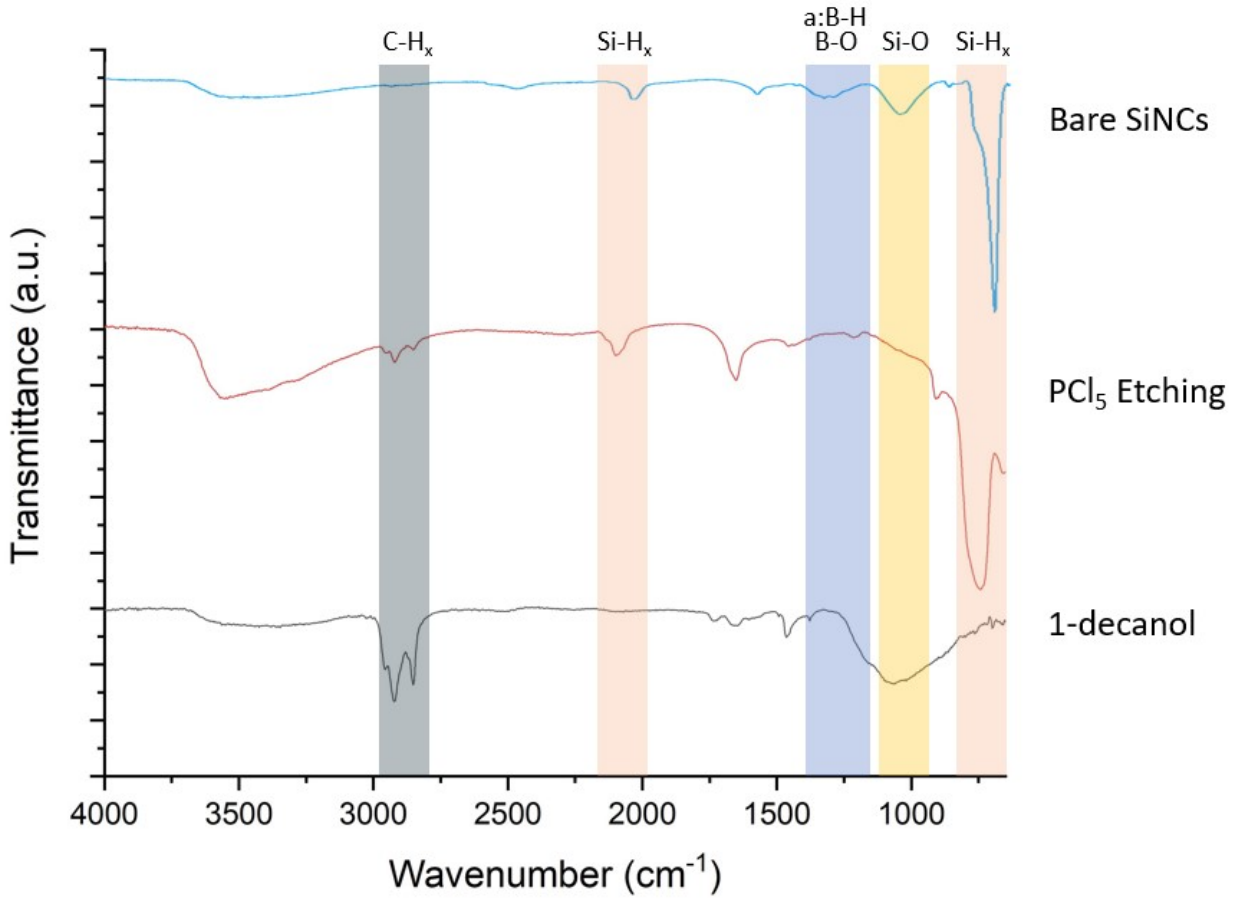

Figure S6 FTIR of 9.6 atomic % B-doped SiNCs before functionalization (bare SiNCs), after the PCl_5 etching step, and after reaction with 1-decanol with 180°C heating

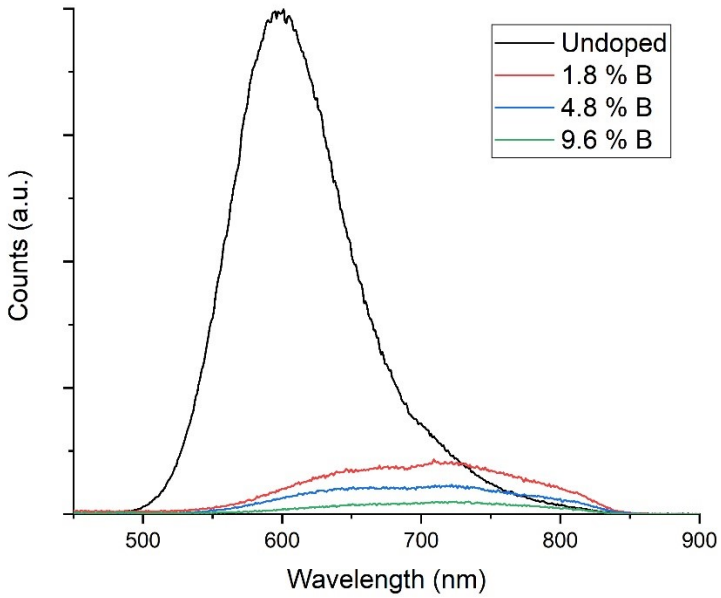

Figure S7 Photoluminescence emission spectra obtained using an excitation wavelength of 350 nm of intrinsic and 1.8, 4.8, and 9.6 atomic % B-doped SiNCs after functionalizing with 1-decanol.

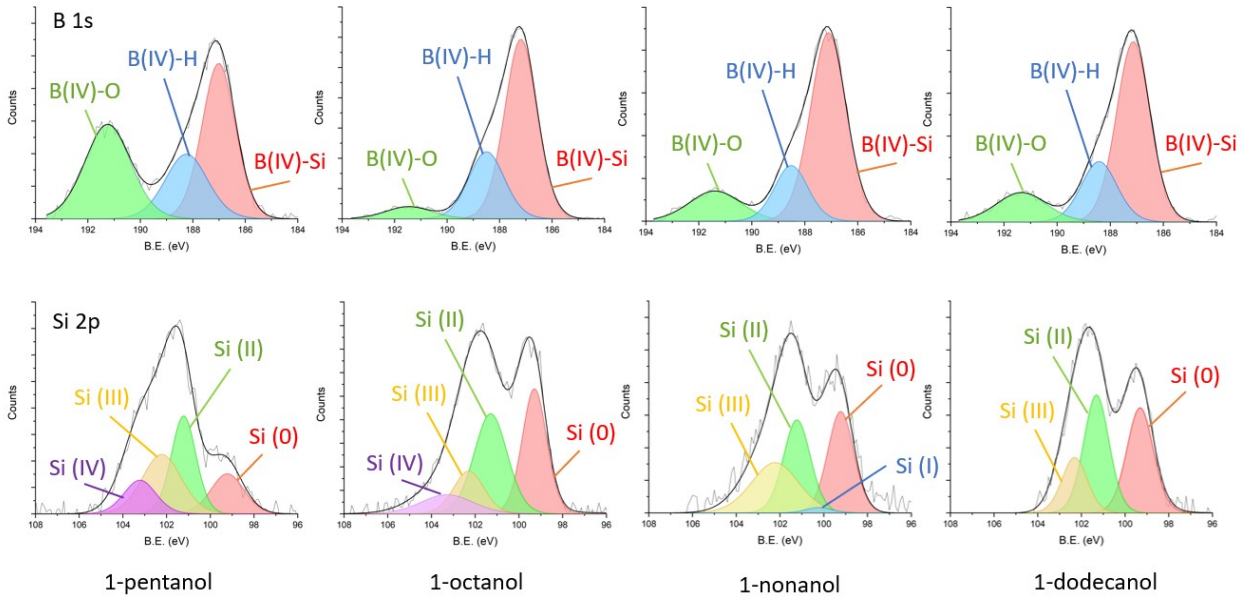

Figure S8 High resolution XP spectra of B 1s (top row) and Si 2p (bottom row) of 9.6 atomic % B-doped SiNCs after functionalization with the alkoxy ligands indicated in the figure.

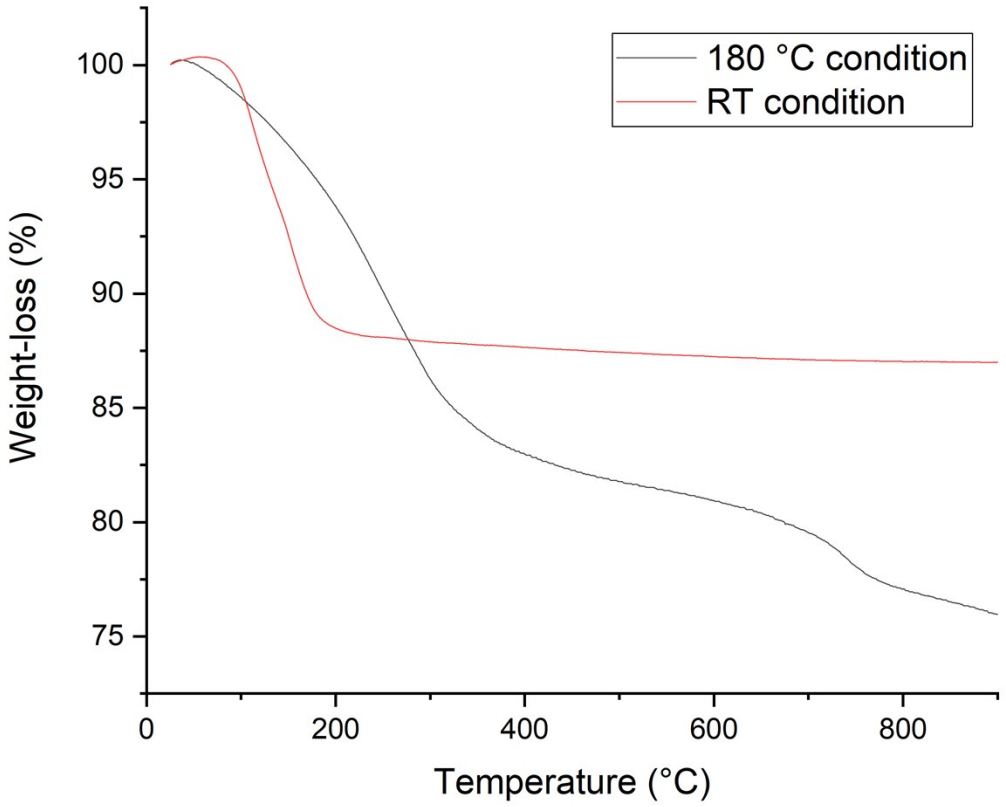

Figure S9 TGA weight-loss plots for functionalization reaction of 9.6 atomic % B-doped SiNCs with 1-pentanol for two different reaction conditions: without heating (red curve) and heated to 180 °C in a pressure sealed flask (black curve).

Table S3 Surface coverage of 9.6 atomic % B-doped SiNCs 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)

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