Supporting Information

Modulating Donor-Acceptor Transition Energies in Phosphorus-Boron co-Doped Silicon Nanocrystals via X- and L-Type Ligands

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NC size	Tube Size (ID)	30% B2H6/H2	PH3	100% SiH4	Ar	H2	Pressure	Forward Power
2.7 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	1.0 Torr	250 W
3.1 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	1.25 Torr	250 W
3.5 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	1.5 Torr	250 W
3.9 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	2.0 Torr	250 W
4.3 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	2.5 Torr	250 W
4.7 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	2.8 Torr	250 W
4.8 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	3.0 Torr	250 W
5.1 nm	19 mm	1.4 sccm	1.4 sccm	2.5 sccm	48 sccm	168 sccm	3.5 Torr	250 W

Table S1. Growth conditions for all PB:Si NCs in this report

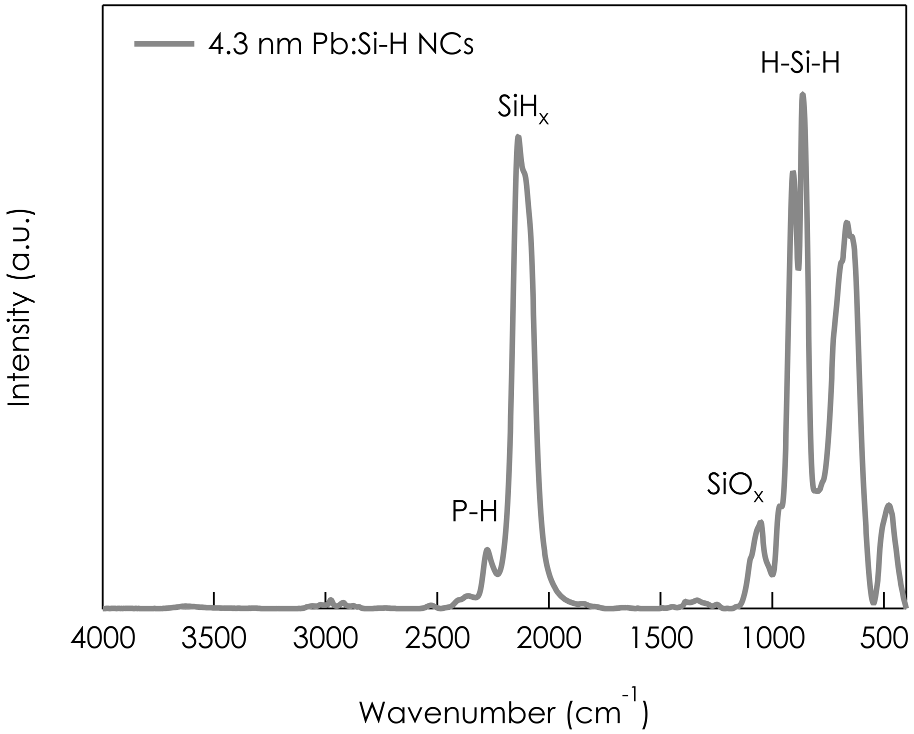


Figure S1. Representative FTIR spectrum of PB:Si–H NCs.

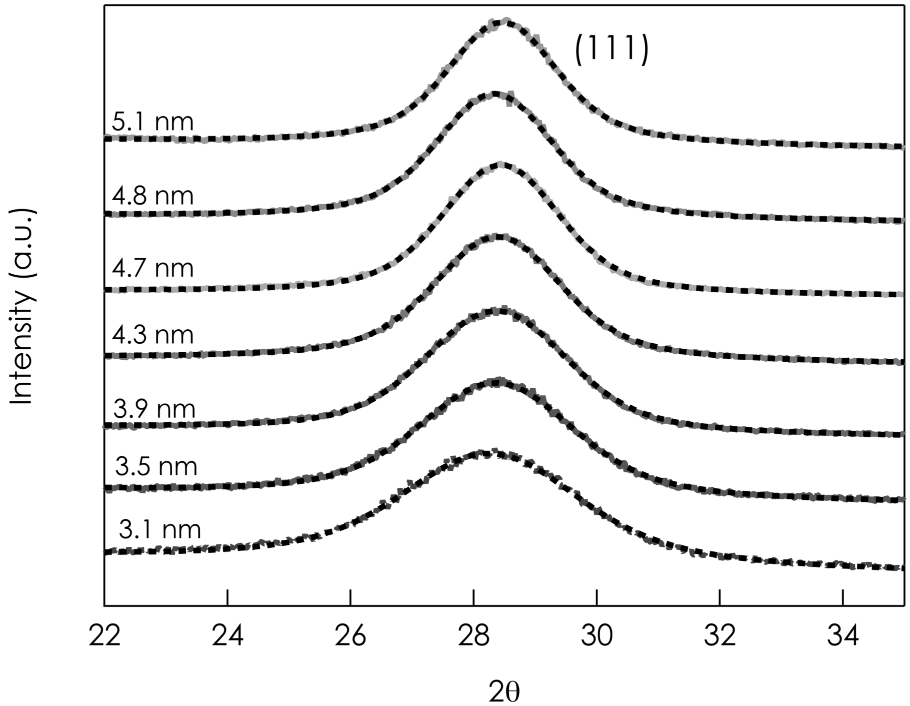


Figure S2. XRD patterns of the (111) crystalline peaks from all PB:Si–H NCs in this study (D_{NC} = 3.1-5.1 nm) . The black dashed line is a Voigt fit. The nanocrystal size is obtained using Scherrer analysis of the broadening of the (111) peak. We use the equation $NC_{diameter} = \frac{k \cdot \lambda}{w \cdot \cos(c)}$ where k is a shaping factor of 1.1, λ is wavelength of the X-rays (1.54 Å), and w and c are the FWHM and center of the (111) peak in radians, respectively.

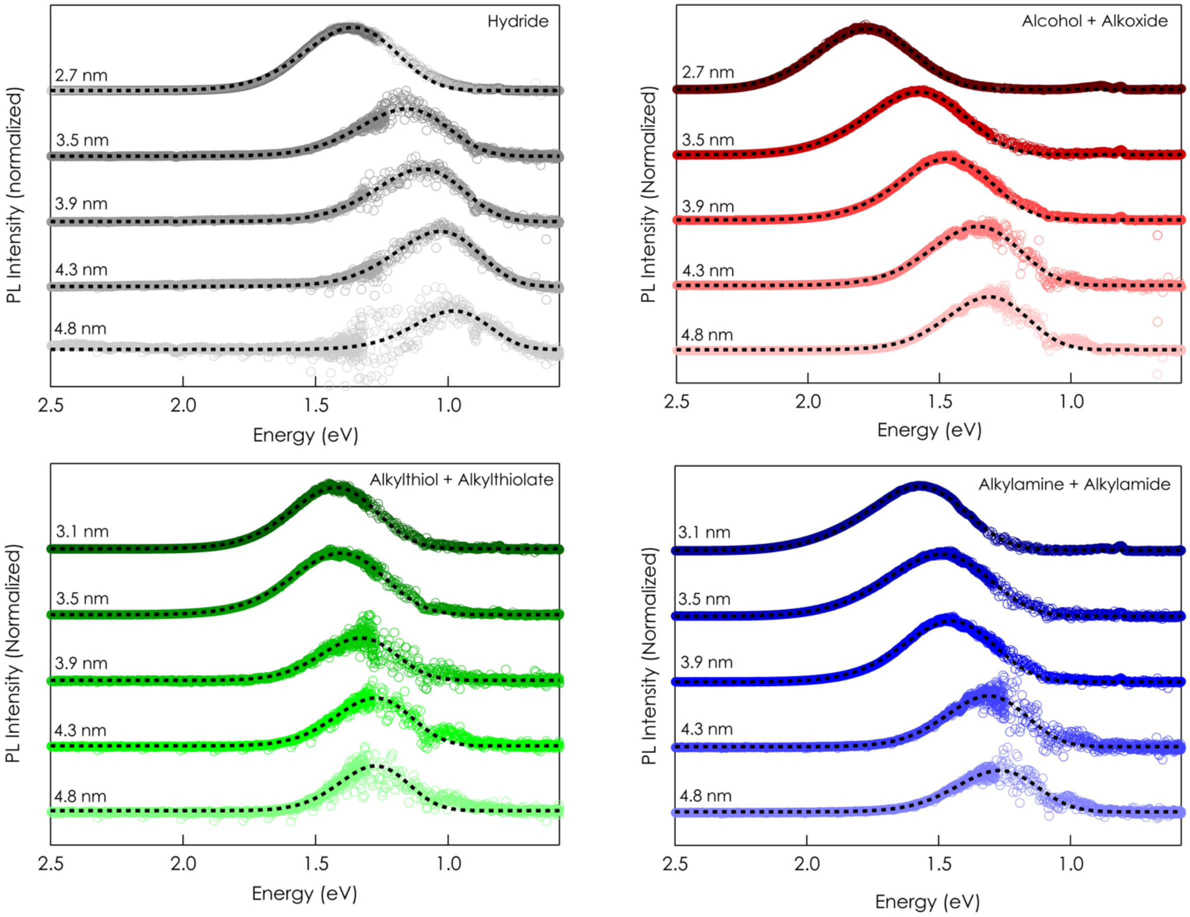


Figure S3. PL spectra from all PB:Si–X and L→PB:Si–X NCs in this study. Peak emission energies are summarized in Figure 1b.

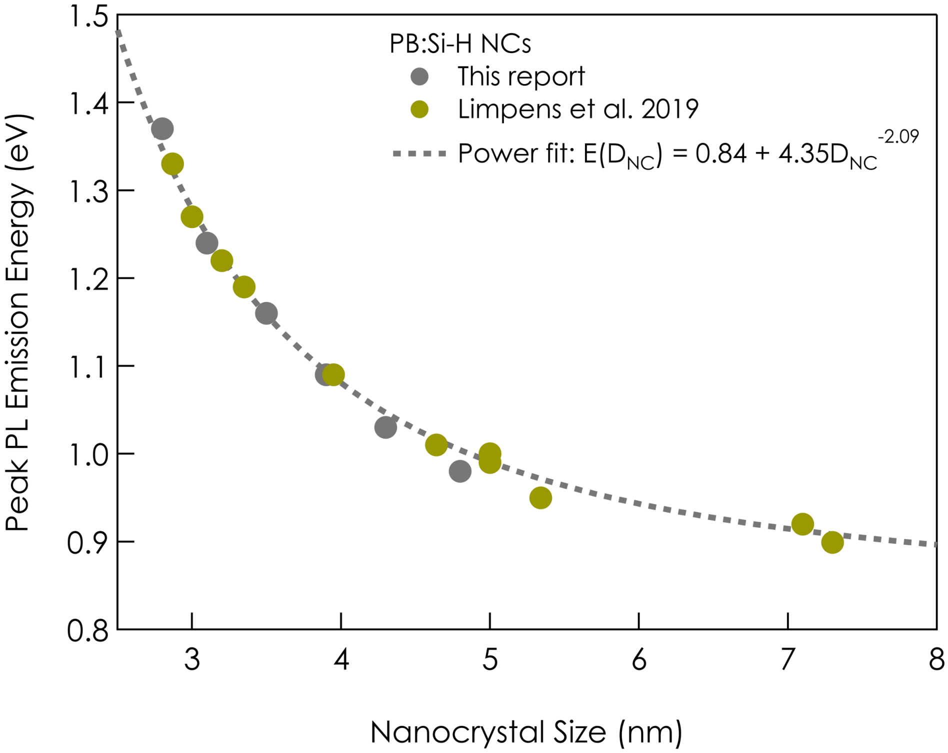


Figure S4. Peak emission energies from PB:Si–H NCs in this study and from our prior report.[1] The dashed grey trace is the power fit we previously developed.

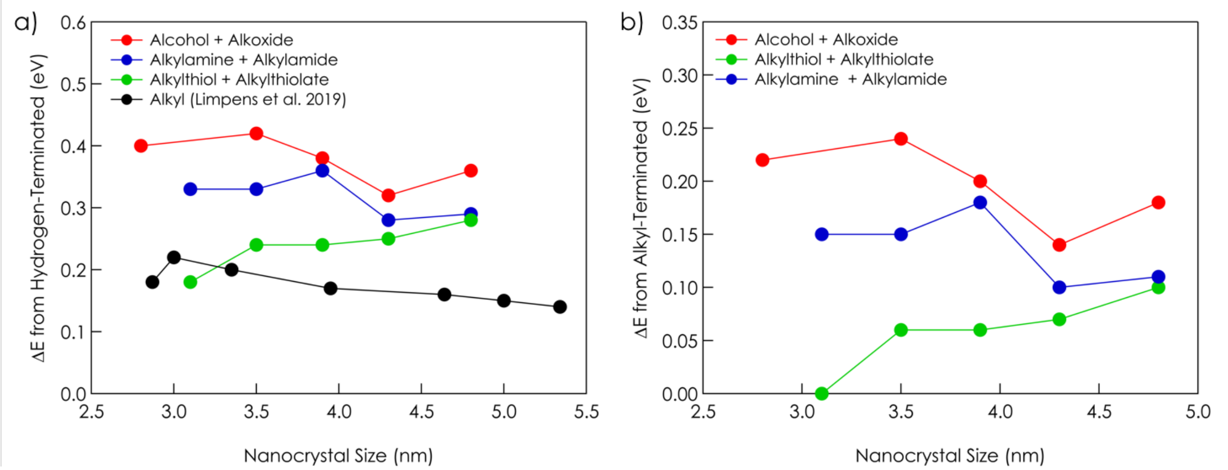


Figure S5. a) Shift in the peak PL energy for alkyl (black markers), alkylthiol + alkylthiolate (green markers), alkylamine + alkylamide (blue markers), and alcohol + alkoxide (red markers) terminations from PB:Si–H NCs of the same diameter. b) Shift in the peak PL energy from PB:Si–CH_2R NCs.

Figure S6. PB:Si–H directly dispersed in a solution of dodecanol and toluene showing the ability of PB:Si–H NCs to spontaneously solubilize under certain conditions. This spontaneous solvation likely results from reaction to form X-type *Si–OR and L-type RHO→*B interactions at the surface that result in the colloidal dispersion.

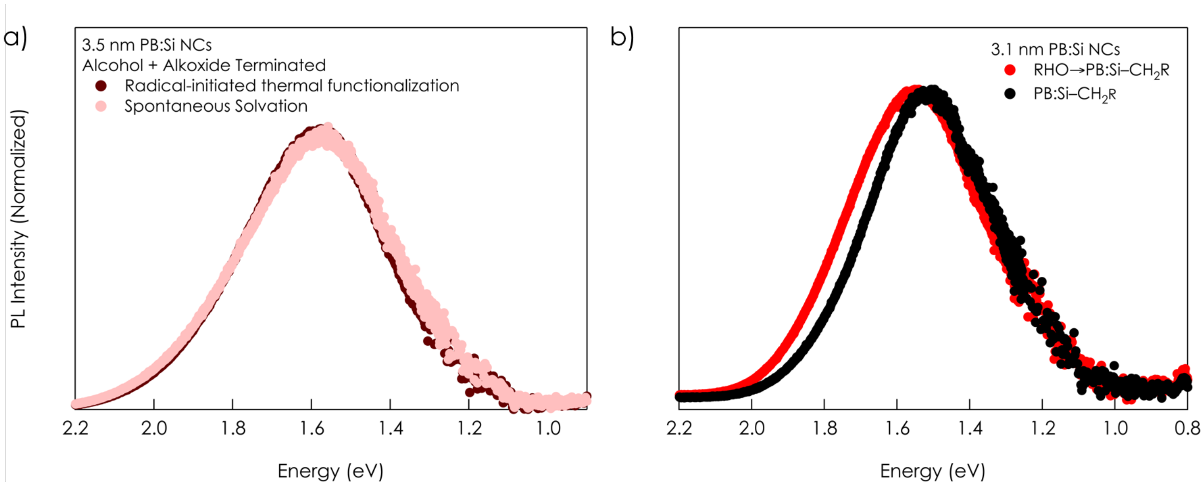


Figure S7. a) PL spectra from 3.5 nm RHO→PB:Si–OR NCs functionalized via spontaneous solvation in 1-dodecanol (light red trace) and via the radical-initiated thermal process (dark red trace). b) PL spectra from PB:Si–CH$_2$R (black trace) and RHO→PB:Si–CH$_2$R (red trace) NCs showing that a ~50 meV blue shift occurs upon subsequent L-type ligand functionalization with surface *B atoms.

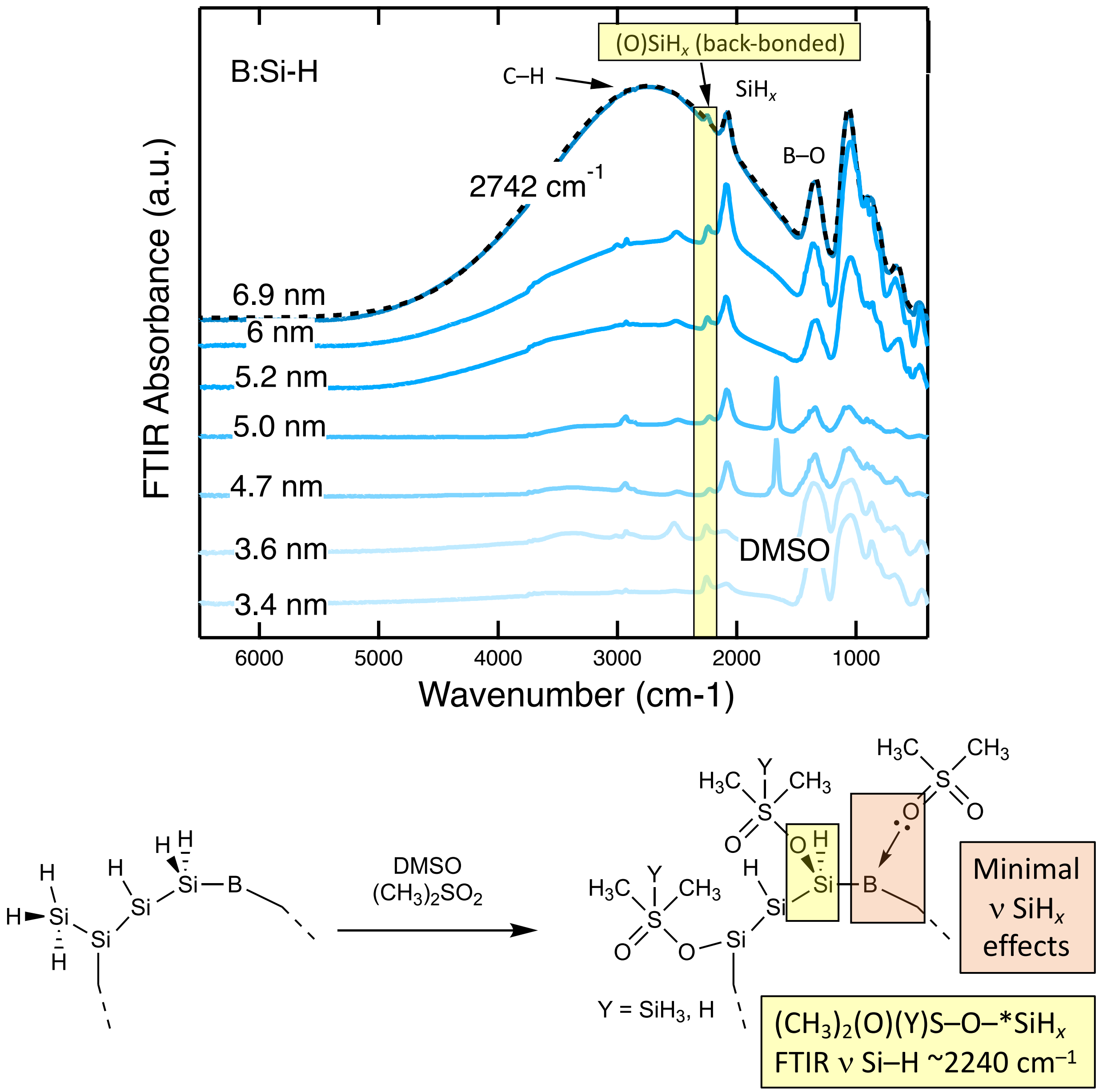


Figure S8. Top: FTIR data adapted from our prior report[2] on B:Si NCs showing the presence of surface oxide characteristic of hydro- and/or silylsilylation across the sulfoxide S=O bond in DMSO to give $(CH_3)_2(O)(Y)S–O–*SiH_x$ (Y = H for hydrosilylation and SiH_3 for silylsilylation). Bottom: Proposed mechanism of spontaneous reaction of DMSO with PB:Si–H NCs to give $(CH_3)_2SO_2 \rightarrow PB:Si–O–S(Y)(CH_3)_2$.

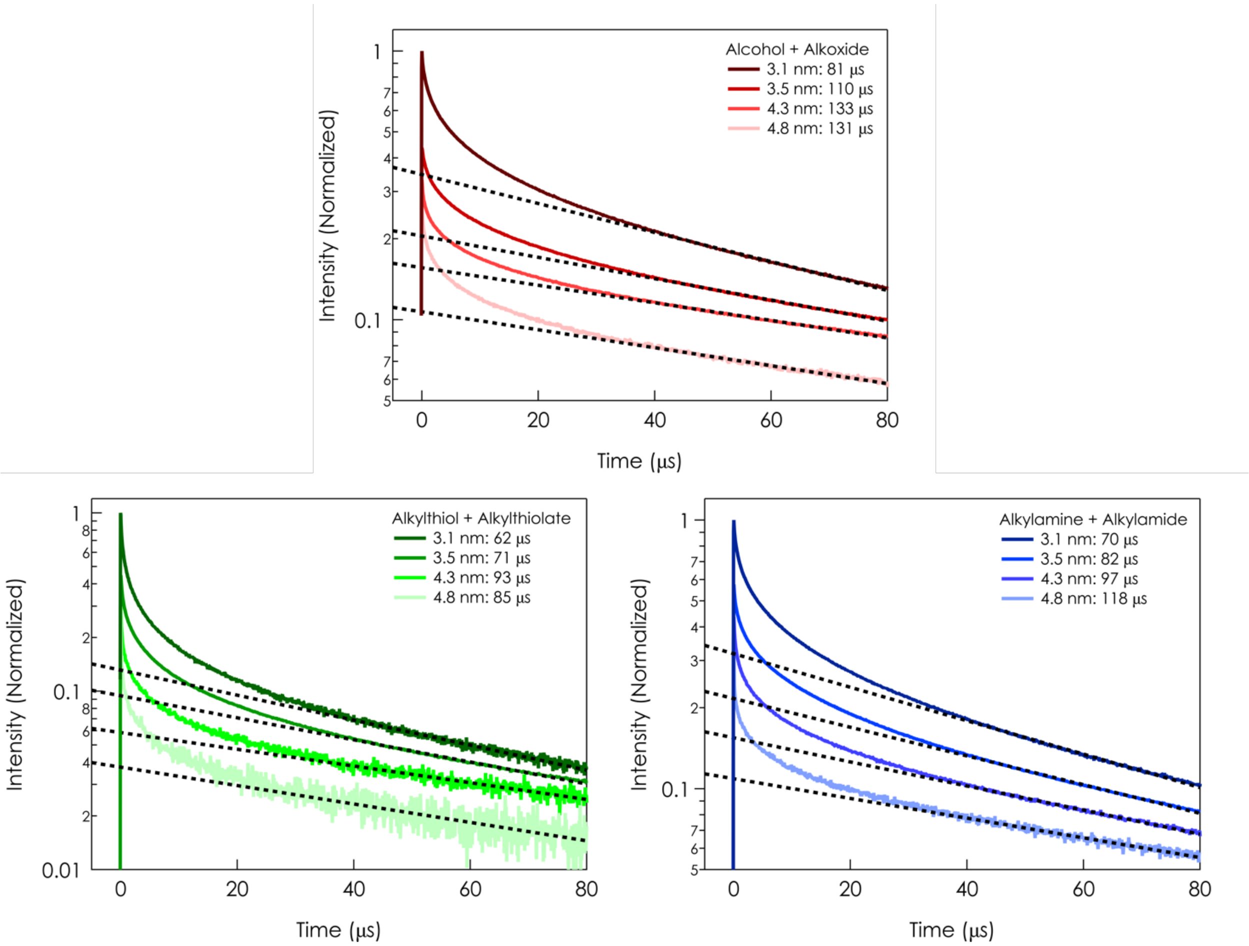
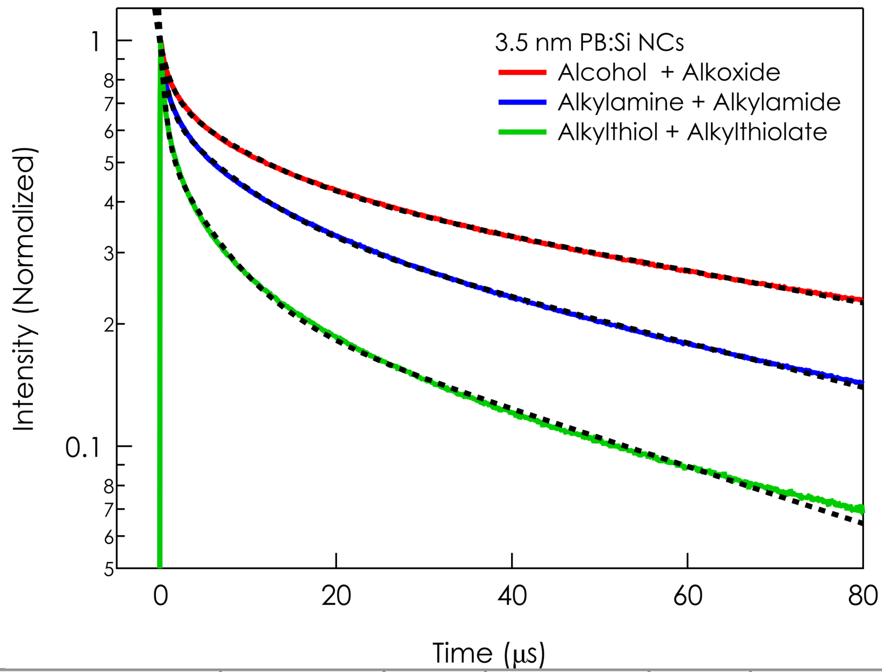


Figure S9. TRPL traces from all L→PB:Si–X NCs in this study. Figure 3b provides a summary of all lifetimes.



	t_1 (ms)	A_1	t_2 (ms)	A_2	t_3 (ms)	A_3
Alcohol + Alkoxide	1.1	0.8	10.0	0.3	110.1	0.5
Alkylamine + Alkylamide	0.9	0.8	9.0	0.3	80	0.4
Alkylthiol + Alkylthiolate	0.6	0.1	6.0	0.3	62	0.2

Figure S10. Top) TRPL traces from Figure 3 fit with a tri-exponential fit. Bottom) Lifetime and relative amplitudes from fits.

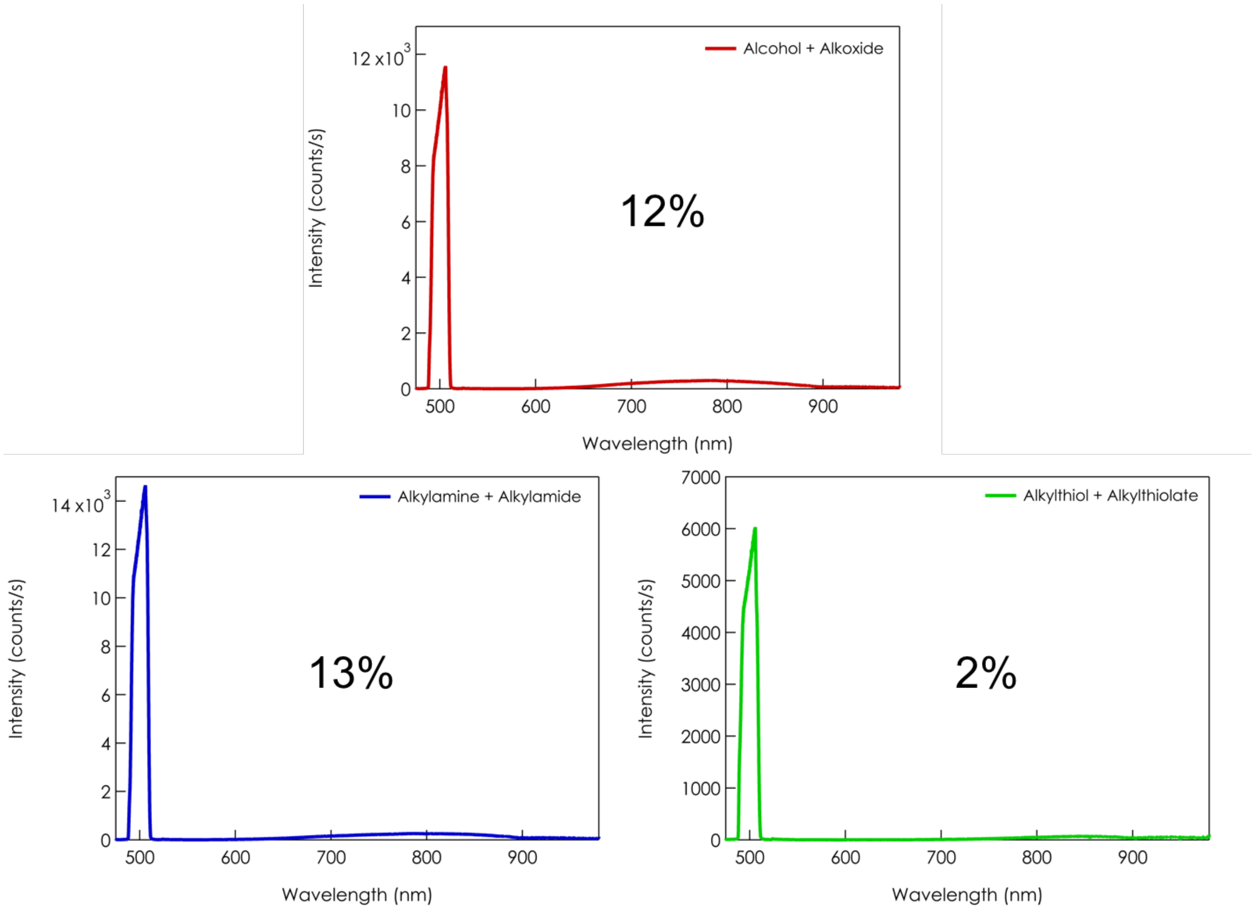


Figure S11. PLQY spectra for alcohol/alkoxide, alkylamine/alkylamide, and alkylthiol/alkylthiolate terminated 3.1 nm L→PB:Si–X NCs. The PLQY is determined by $PLQY = \frac{\#\ of\ emitted\ photons}{\#\ of\ absorbed\ photons}$. The number of absorbed photons is calculated by integrating the excitation laser peak (centered at 500 nm) and subtracting that from the integrated laser peak of a blank sample (cuvette with toluene). The emitted photons are calculated by integrating the emission spectrum (centered around 800 nm). See methods for further details.

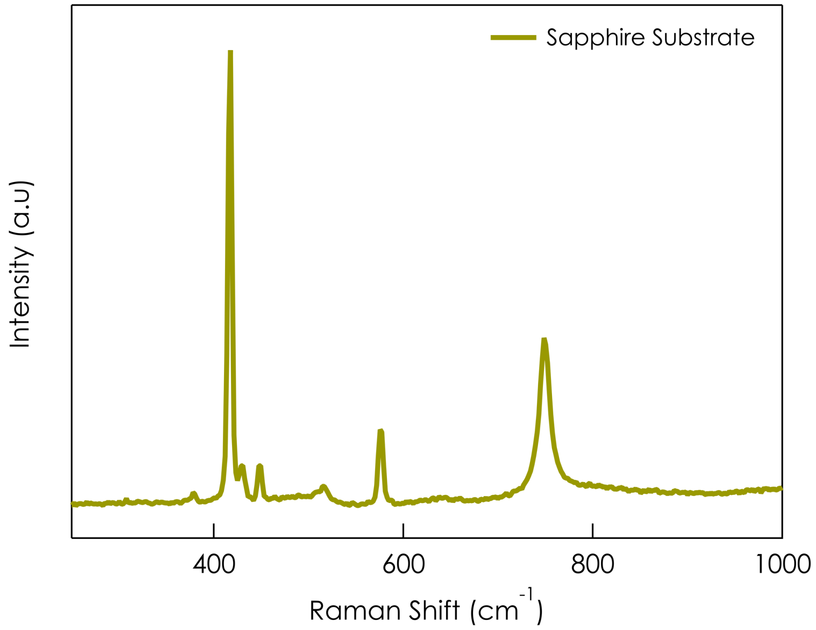


Figure S12. Raman spectrum of a blank sapphire substrate.

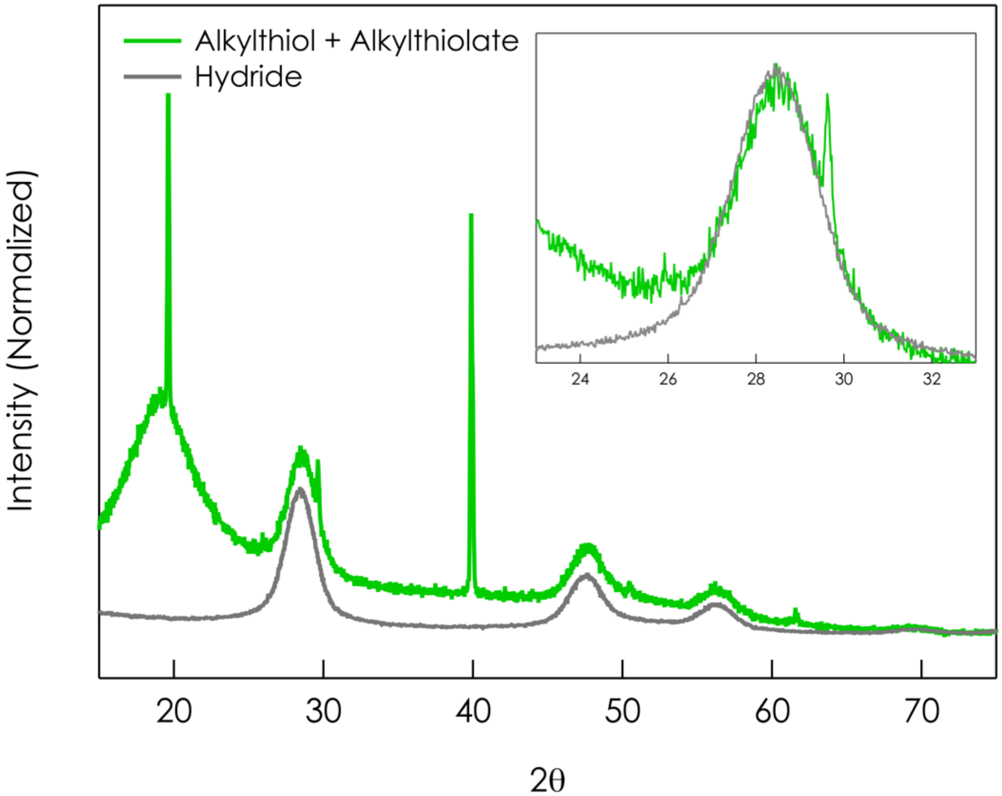


Figure S13. XRD spectra of as-synthesized PB:Si–H NC compared to RHS→PB:Si–SR functionalized PB:Si NCs.

References:

1. R. Limpens, G. F. Pach and N. R. Neale, *Chem. Mater.*, 2019, **31**, 4426-4435.
2. R. Limpens, G. F. Pach, D. W. Mulder and N. R. Neale, *J. Phys. Chem. C*, 2019, **123**, 5782-5789.