

SUPPORTING INFORMATION FILE

Unraveling the Mechanism Underlying Surface Ligand Passivation of Colloidal Semiconductor Nanocrystals: A Route for Preparing Advanced Hybrid Nanomaterials

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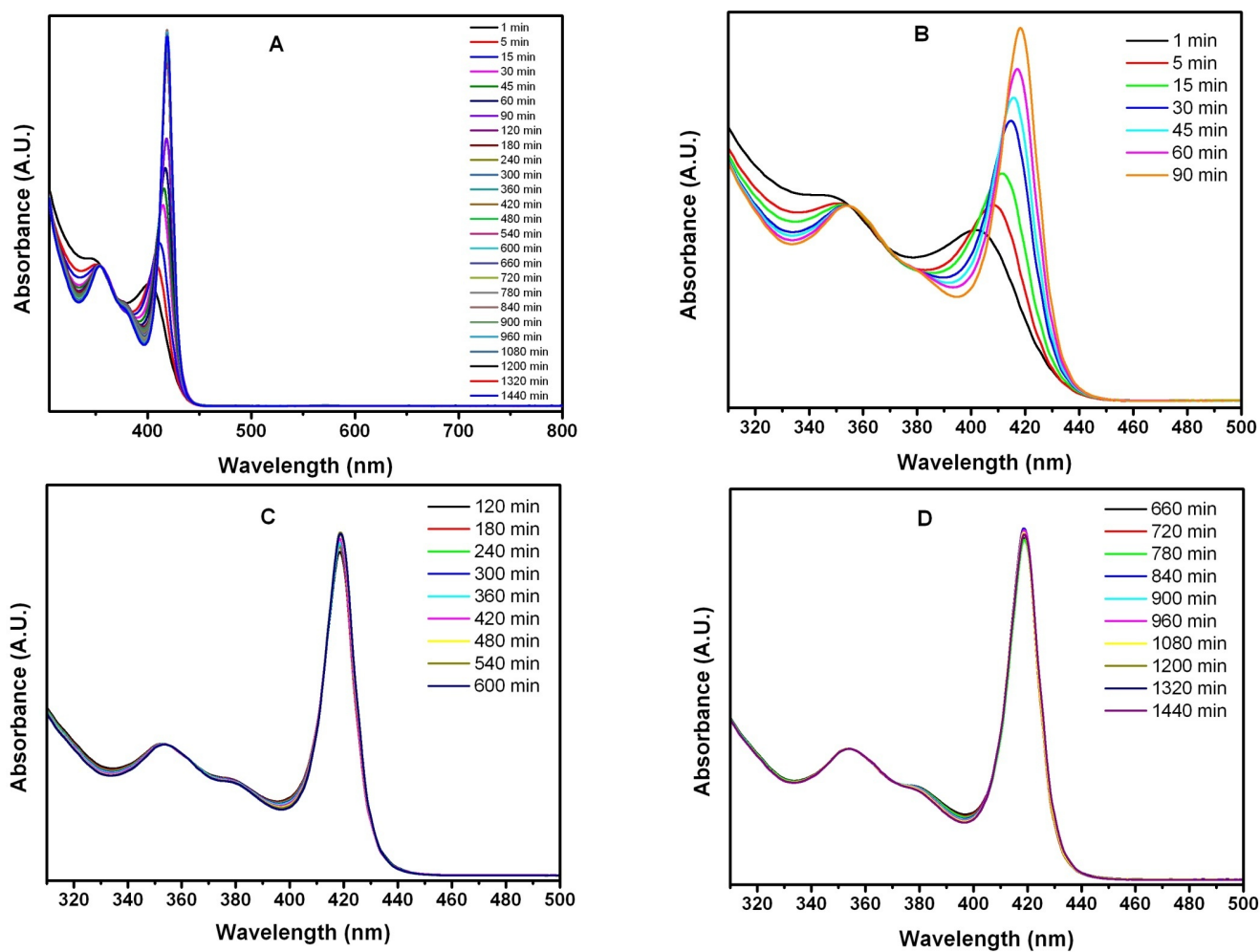


Figure S1: Time-dependent UV-vis absorption spectra of $(\text{CdSe})_{33/34}$ CSNC formation at room temperature. Over the time interval 240-1440 min, no significant changes in the absorption peak positions or shapes were observed.

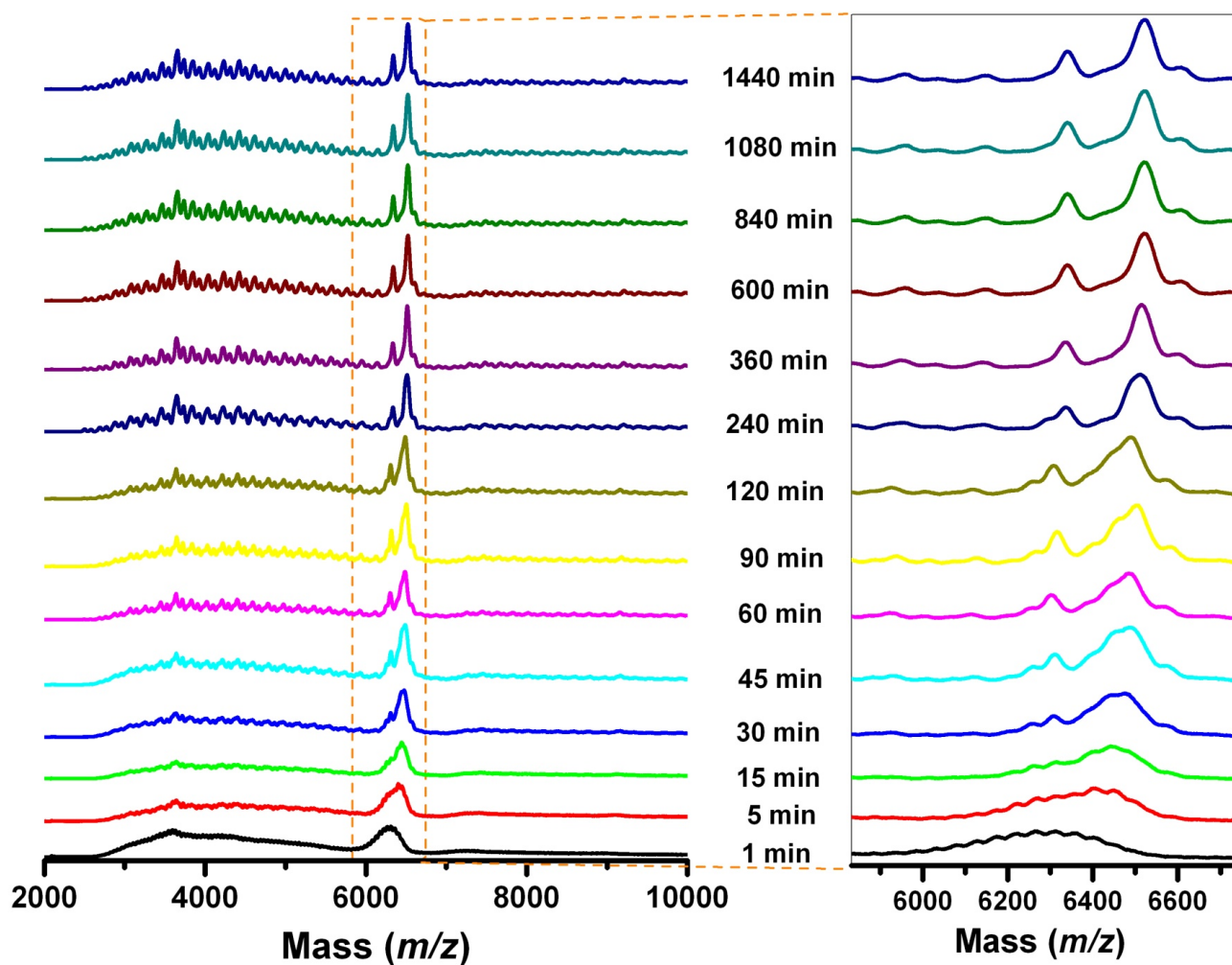


Figure S2: Time-dependent MALDI-TOF-MS analysis of $(\text{CdSe})_{33/34}$ CSNCs during their formation. Over the time interval 240-1440 min, no significant changes in the MS peak positions or shapes were observed.

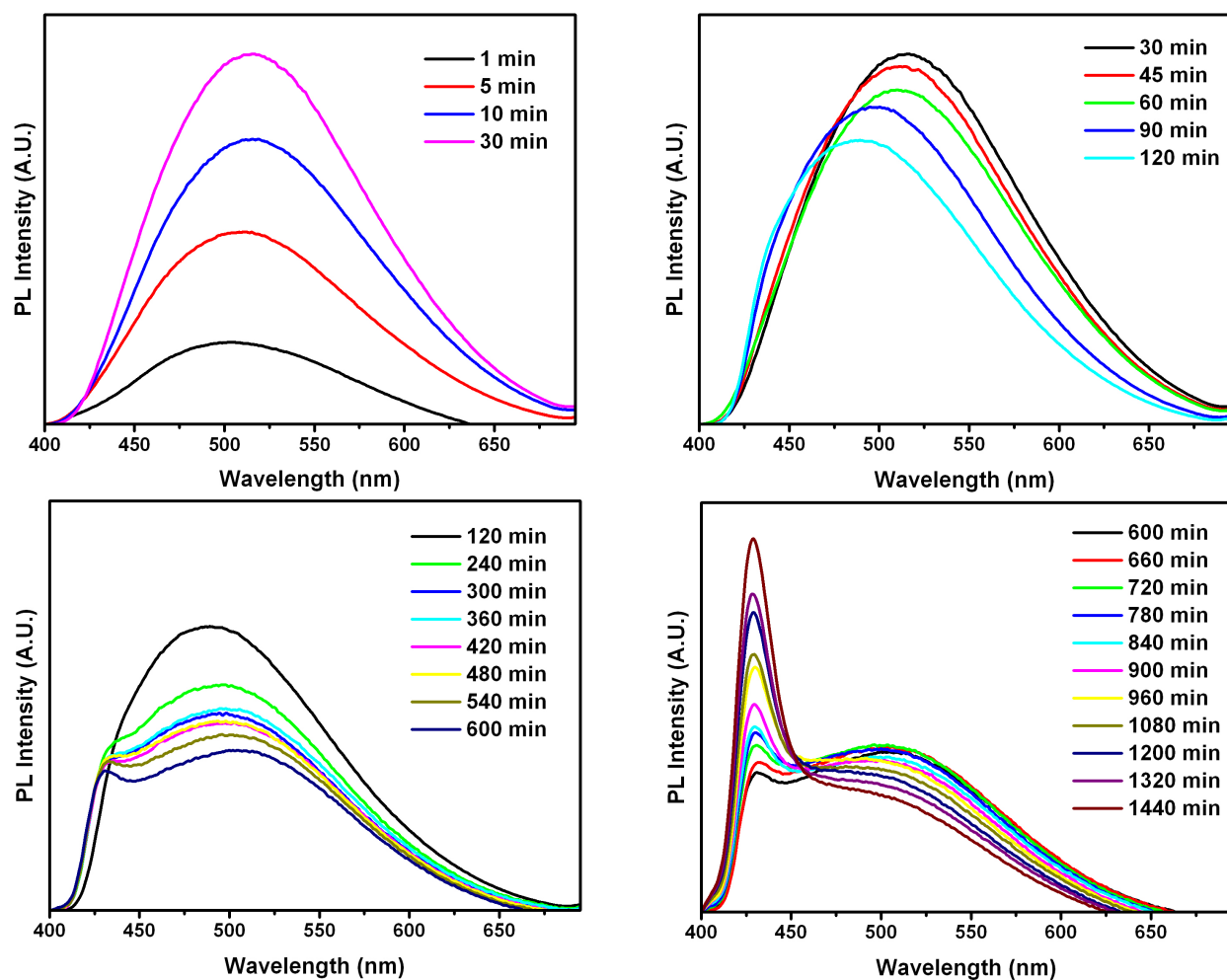


Figure S3: Time dependent PL spectra of $(\text{CdSe})_{33/34}$ CSNC formation at room temperature. Throughout the synthesis, we continually observed changes in the the broadband PL peak positions and shape. However after 600 min, the band-edge peak position remained constant and the intensity of the peak increased over the time.

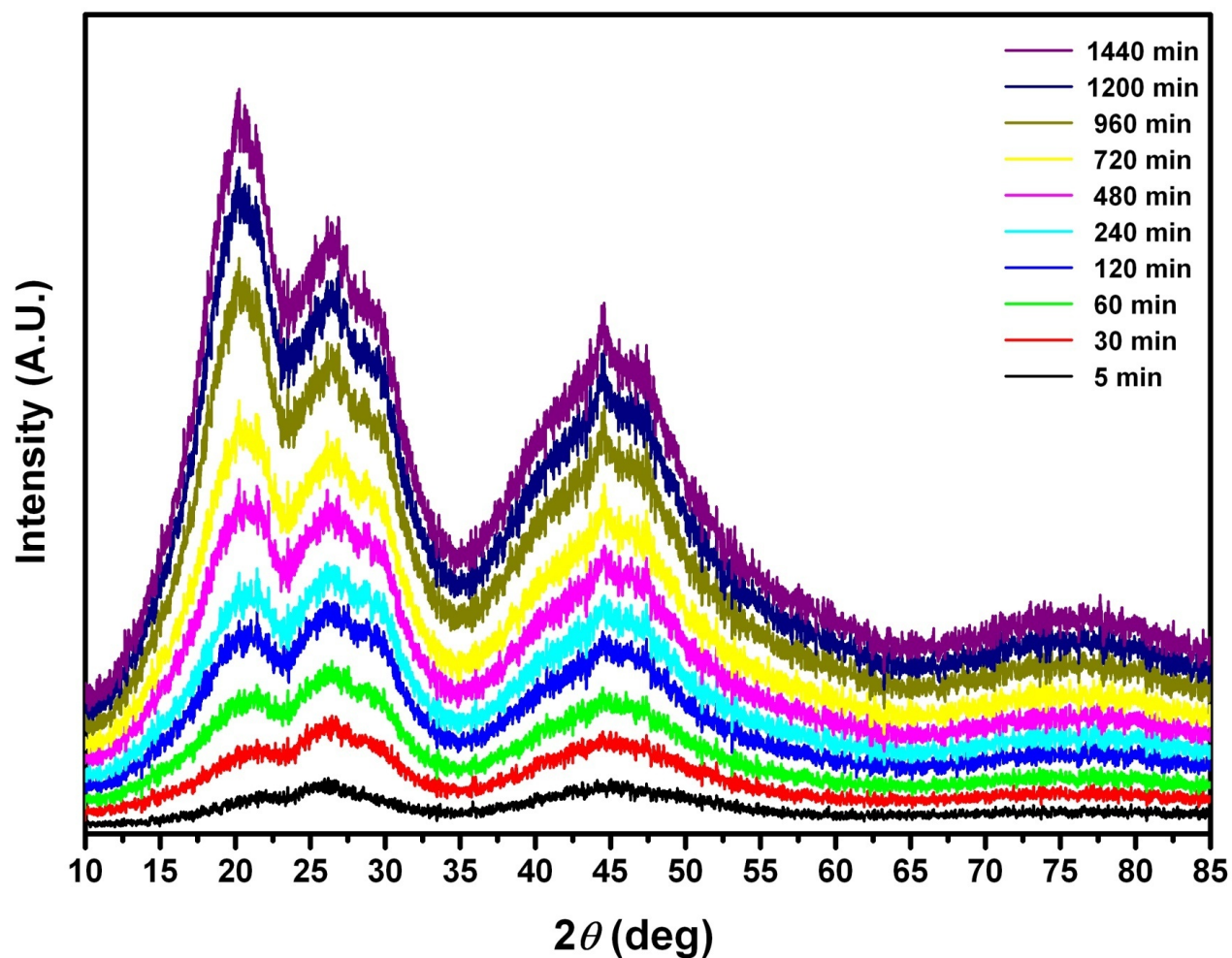


Figure S4: Time-dependent XRD spectra of $(\text{CdSe})_{33/34}$ CSNC formation. The peaks are characteristic of wurtzite crystal structure. Over the time interval 240-1440 min, no significant changes in the XRD peak positions or shape were observed.

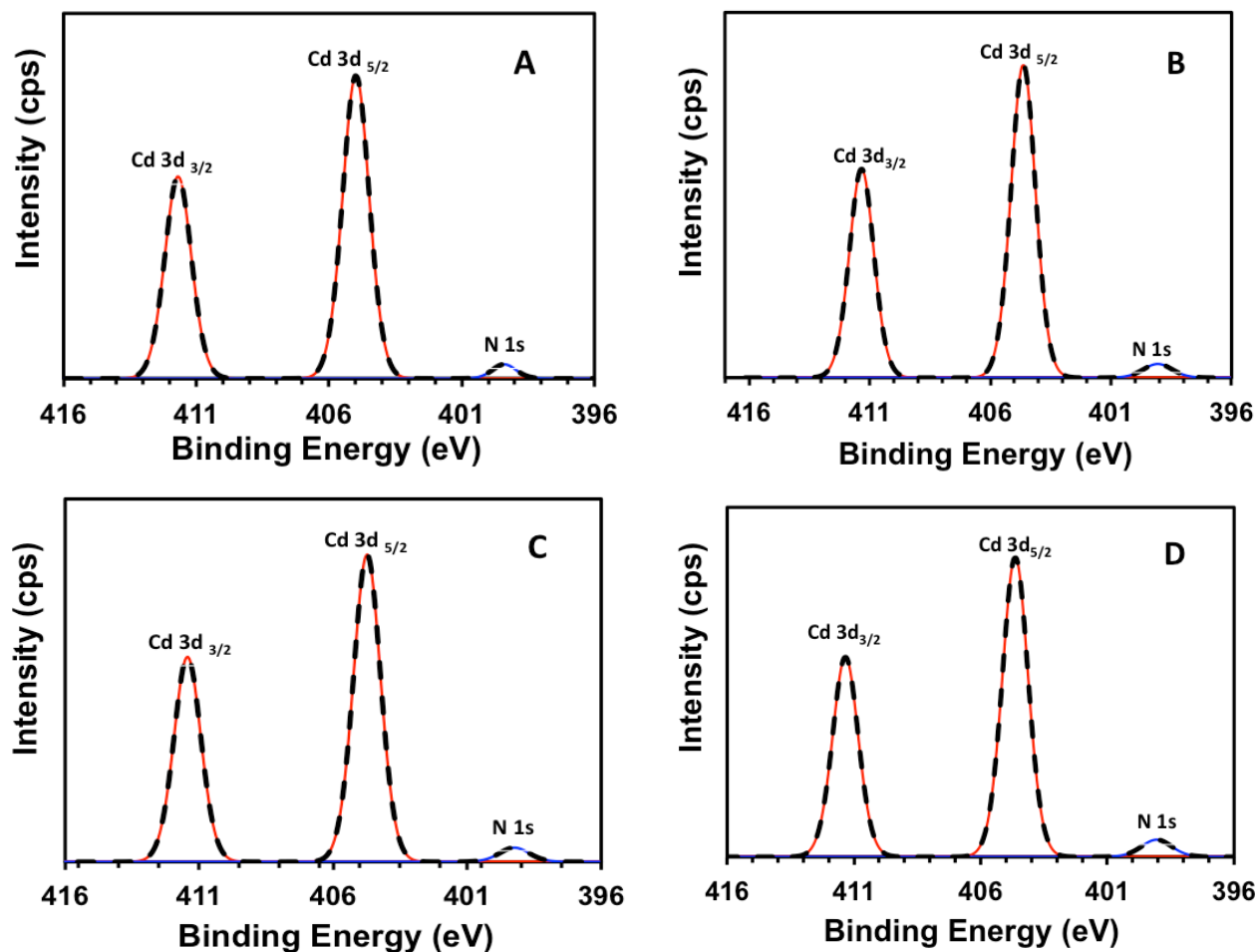


Figure S5: Time-dependent XPS spectra of OLA-passivated (CdSe)_{33/34} CSNCs: (A) 240, (B) 600, (C) 900, and (D) 1200 min after the injection of Se precursor at room temperature.

Table S1: Time-dependent determination of number of OLA per (CdSe)_{33/34} CSNC through XPS analysis.

Time (min)	Integrated Cd 3d Peak Area	Integrated N 1s Peak Area	Cd:N Ratio	# OLA Ligands/ CdSe Nanocrystal
240	3124.7	579.0	5.93	6.3
300	3114.0	788.4	3.95	8.6
420	3126.4	1042.2	3.23	10.5
600	3180.7	1144.2	2.78	12.4
720	3123.8	1269.2	2.41	14.1
840	3174.6	1469.7	2.16	15.7
960	3180.7	1423.5	2.19	16.2
1200	3119.7	1616.4	1.93	17.6
1440	3110.4	1654.4	1.88	18.0

Table S2: Time-dependent determination of number of OLA per (CdSe)_{33/34} CSNC through ¹H NMR analysis using ferrocene as an internal standard.

Time (min)	NMR 5.35 integration	# OLA Ligands / CdSe Nanocrystal
240	0.09	7.2
300	0.16	9.3
420	0.30	11.4
600	0.39	13.1
720	0.49	15.8
840	0.65	16.4
960	0.75	17.3
1200	0.78	18.1
1440	0.84	18.4

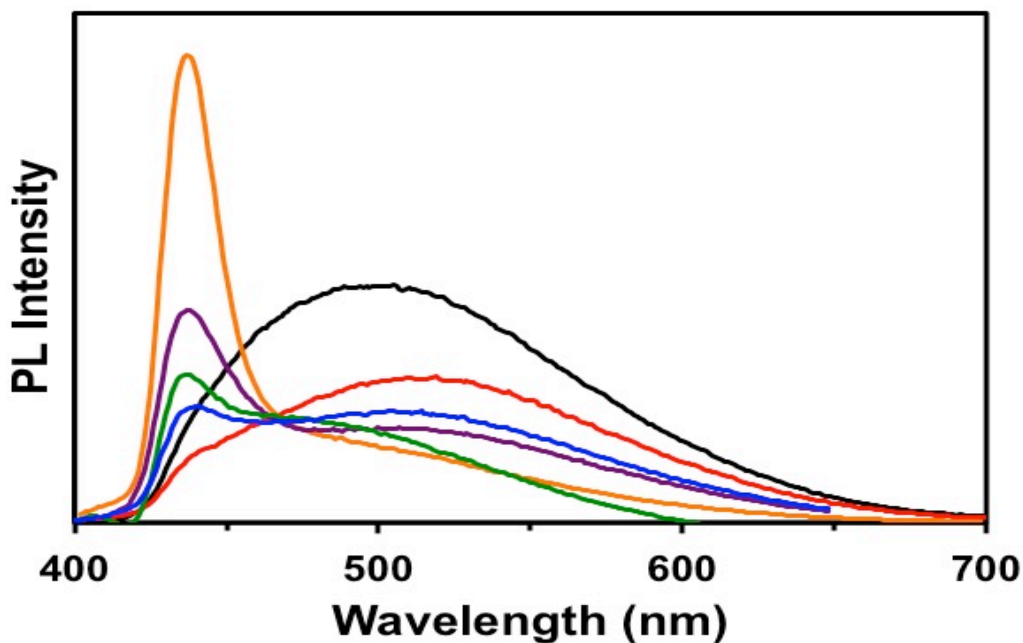


Figure S6A: Ex-situ surface modification of (CdSe)_{33/34} CSNCs with ex-situ addition of OLA at room temperature. Black: 0 min (as synthesized and purified CSNCs). Time-dependent changes after addition of 5 mM OLA: Red, 240 min; Blue, 480 min; Green, 720 min; Purple, 1440 min; and Orange, 2880 min.

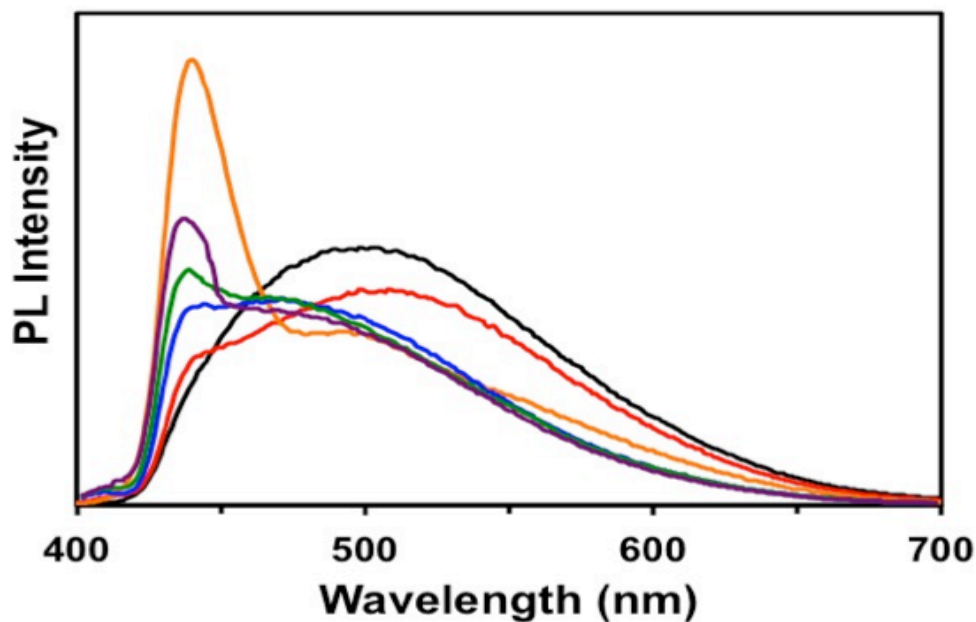


Figure S6B: Ex-situ surface modification of (CdSe)_{33/34} CSNCs with OCA at room temperature. Black: 0 min (as synthesized and purified CSNCs). Time-dependent changes after addition of 5 mM OCA: Red, 120 min; Blue, 240 min; Green, 480 min; Purple, 720 min; and Orange: 1080 min.

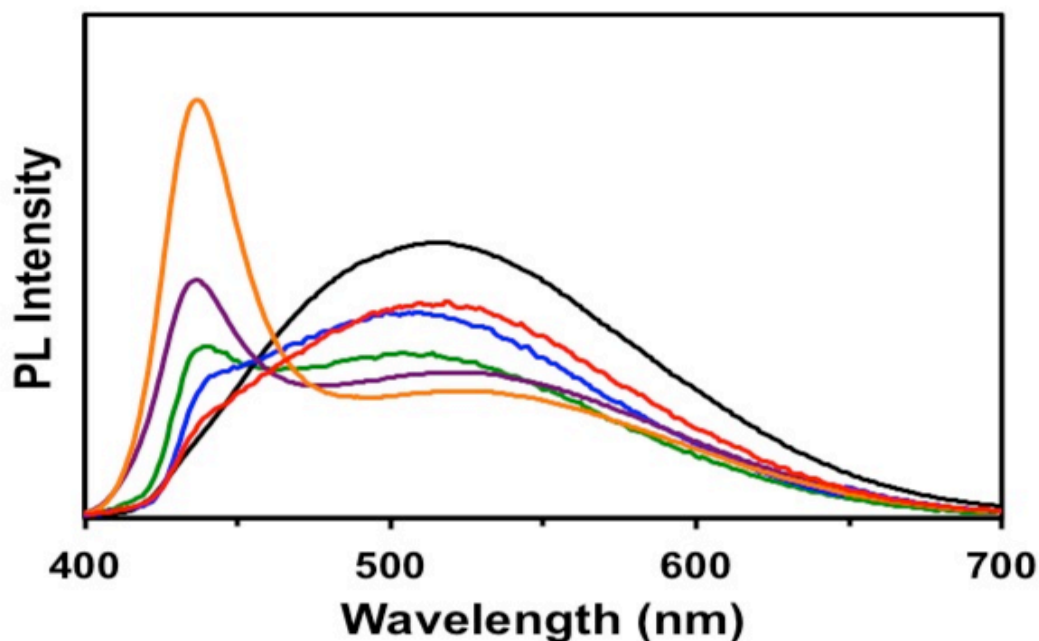


Figure S6C: Ex-situ surface modification of (CdSe)_{33/34} CSNCs with DCA at room temperature. Black: 0 min (as synthesized and purified CSNCs). Time-dependent changes after addition of 5 mM DCA: Red, 120 min; Blue, 240 min; Green, 400 min; Purple, 720 min; and Orange, 1440 min.

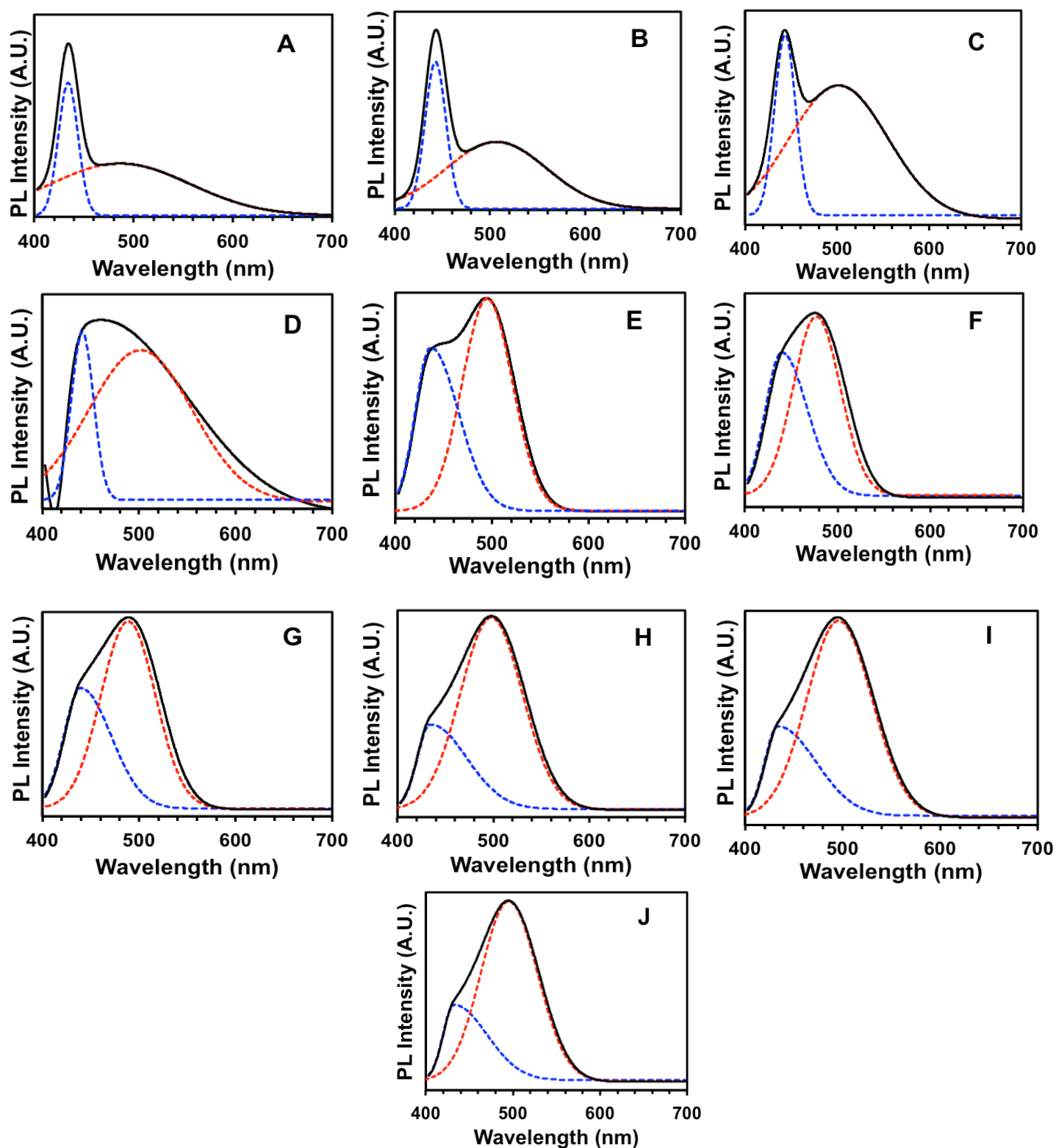


Figure S7: Ex-situ surface modification of $(\text{CdSe})_{33/34}$ CSNCs with OLA at room temperature. A stock solution of $0.12 \mu\text{M}$ $(\text{CdSe})_{33/34}$ CSNCs was prepared in toluene. Various

concentrations of OLA examined: (A) 2000 μM , (B) 1000 μM , (C) 500 μM , (D) 200 μM , (E) 50 μM , (F) 20 μM , (G) 5 μM , (H) 1 μM , (I) 0.5 μM , and (J) 0.2 μM were added, and the reactions were monitored by PL until a stable intensity was observed.

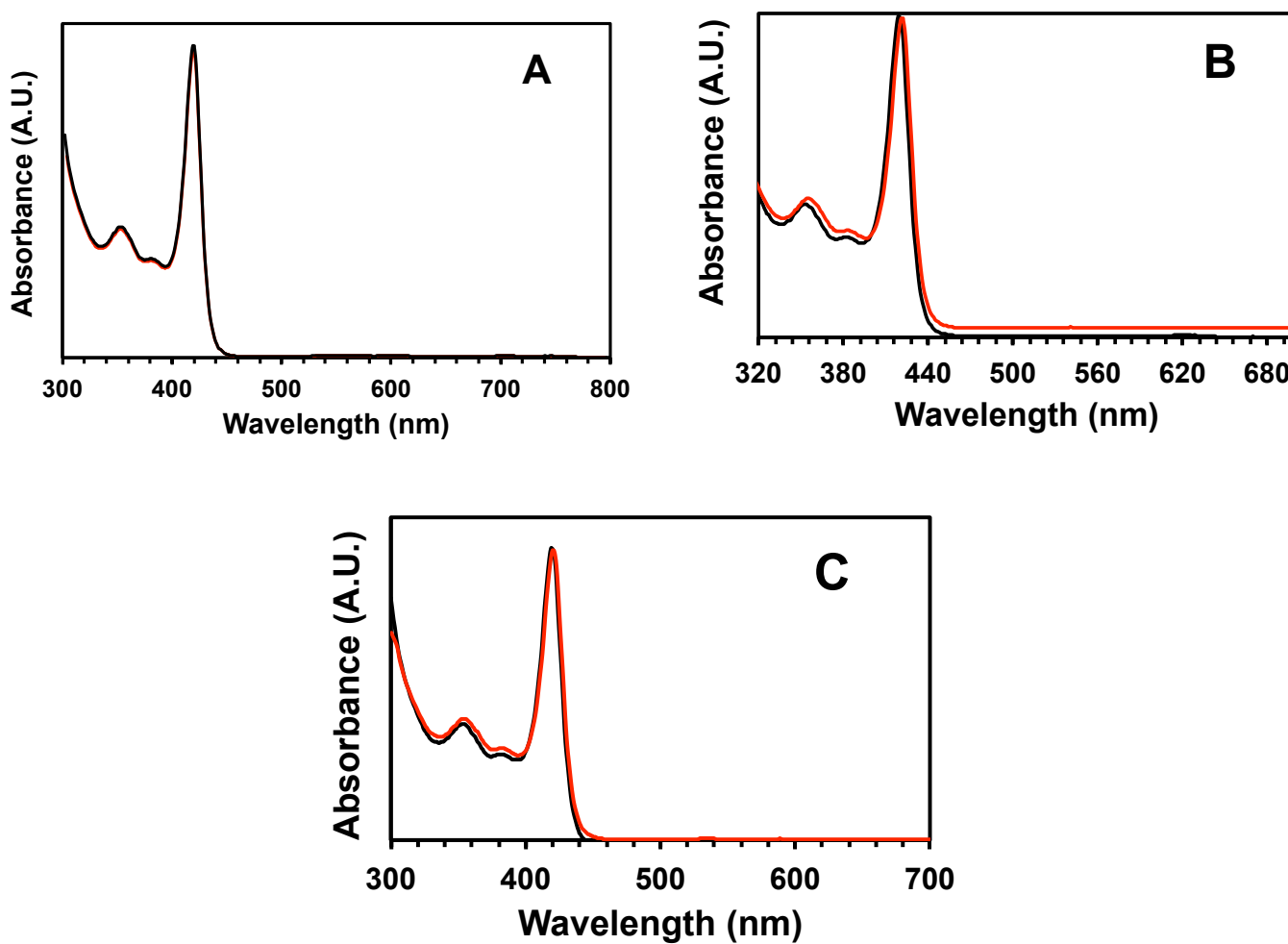


Figure S8. UV-vis spectra of OLA-passivated (black lines) and mixed (A) OLA-/AHA-, (B) OLA-/HXA-, and (C) OLA-/APTES-passivated (red lines) $(\text{CdSe})_{33/34}$ CSNCs.

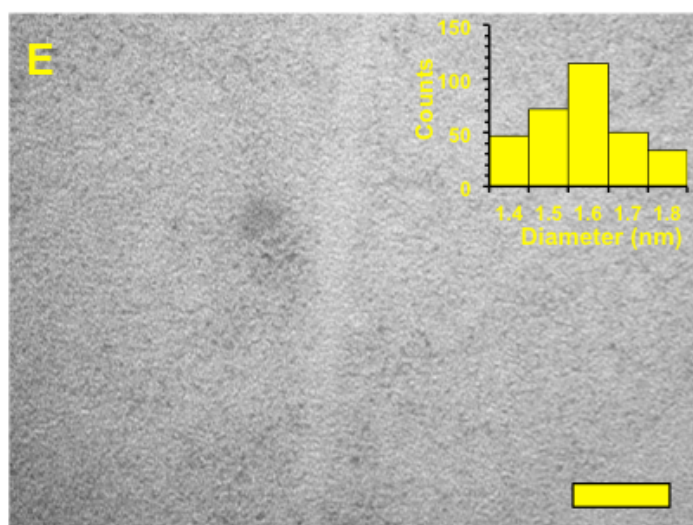
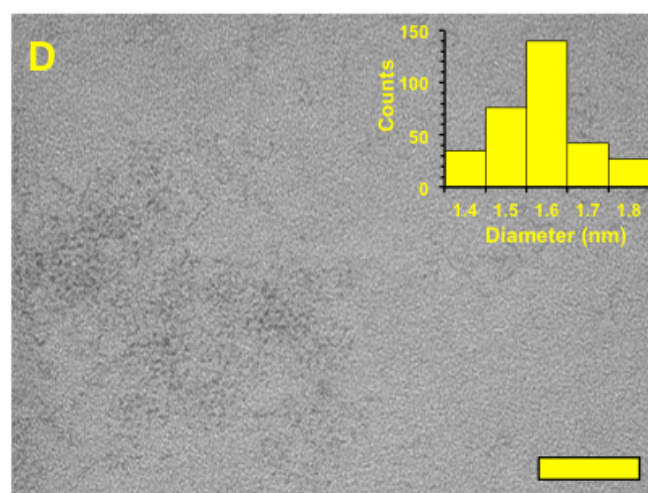
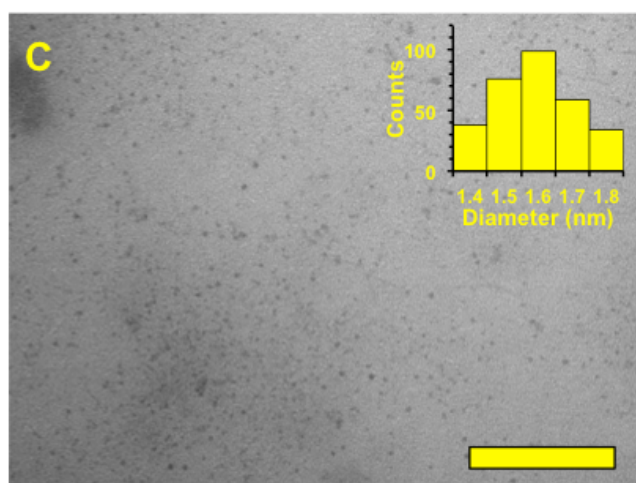
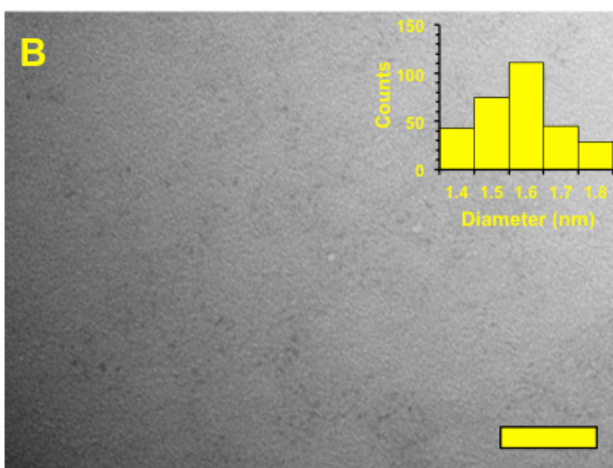
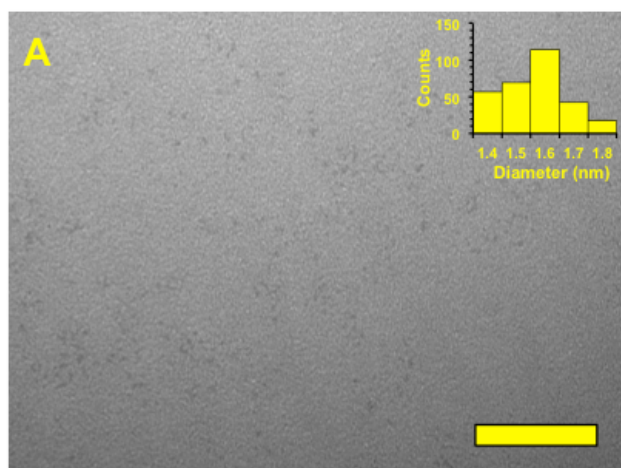


Figure S9. TEM image of (A) partially OLA-passivated, and mixed (B) OLA-/AHA-, (C) OLA-/AAB-, (D) OLA-/HXA-, and (E) OLA-/APTES-passivated (red lines) (CdSe)_{33/34} CSNCs.

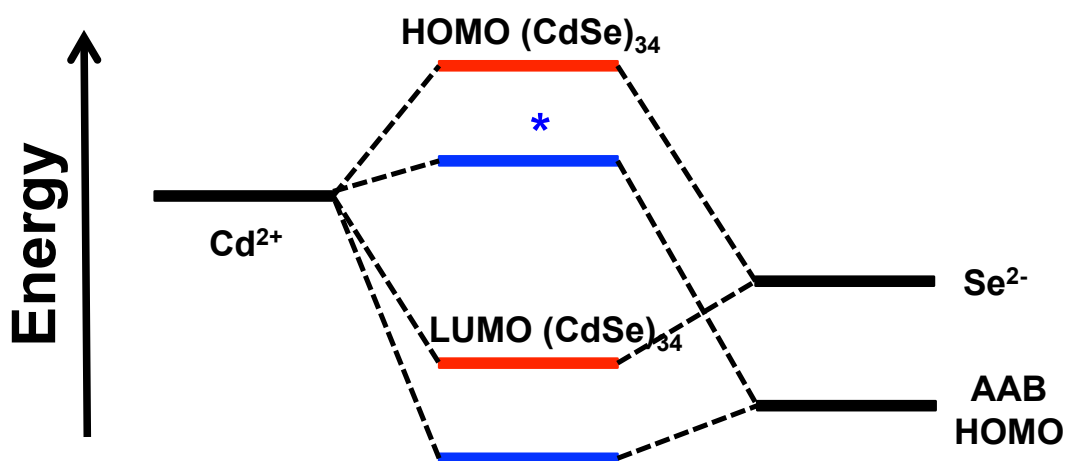


Figure S10. Simplified molecular orbital diagram depicting interaction of AAB with $(\text{CdSe})_{33/34}$ CSNC as previously proposed for CdSe CSNC-aniline conjugates by Weiss and coworkers.¹ AAB is a weak s-donating ligand. Therefore the interaction between a surface Cd site and amine from AAB will form an antibonding orbital (blue star) below the HOMO of the CSNC and this antibonding orbital acts as a mid-gap trap state where a photoexcited electron may become trapped, resulting in a broadened PL band.

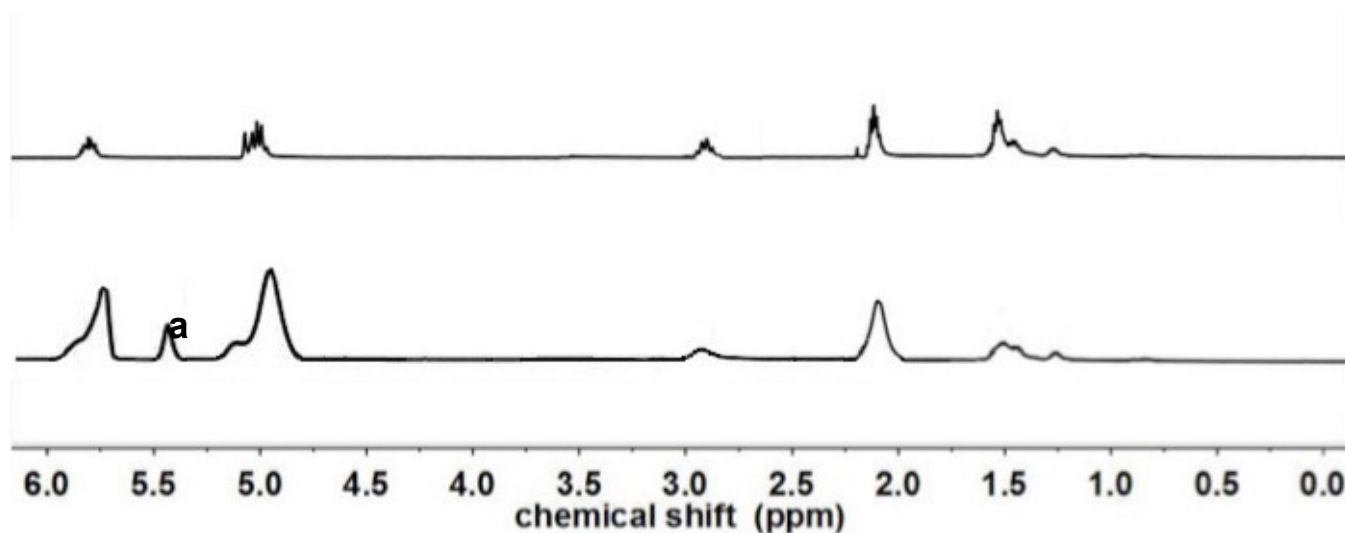


Figure S11. ^1H NMR spectrum of mixed OLA-/HXA-passivated $(\text{CdSe})_{33/34}$ CSNCs (bottom). The characteristic vinyl (a, $-\text{CH}=\text{CH}-$) resonance of OLA at 5.34 ppm, and double bond ($-\text{CH}=\text{CH}_2$) resonances at 5.83 and 4.88 ppm from HXA were observed. The NMR peak broadening is because of spin-spin relaxation and dipole broadening from surface bound ligand. A sharp resonances of $-\text{CH}=\text{CH}_2$ are observed for pure AHA (top). The NMR data equivocally prove the mixed surface ligation of $(\text{CdSe})_{33/34}$ CSNCs.

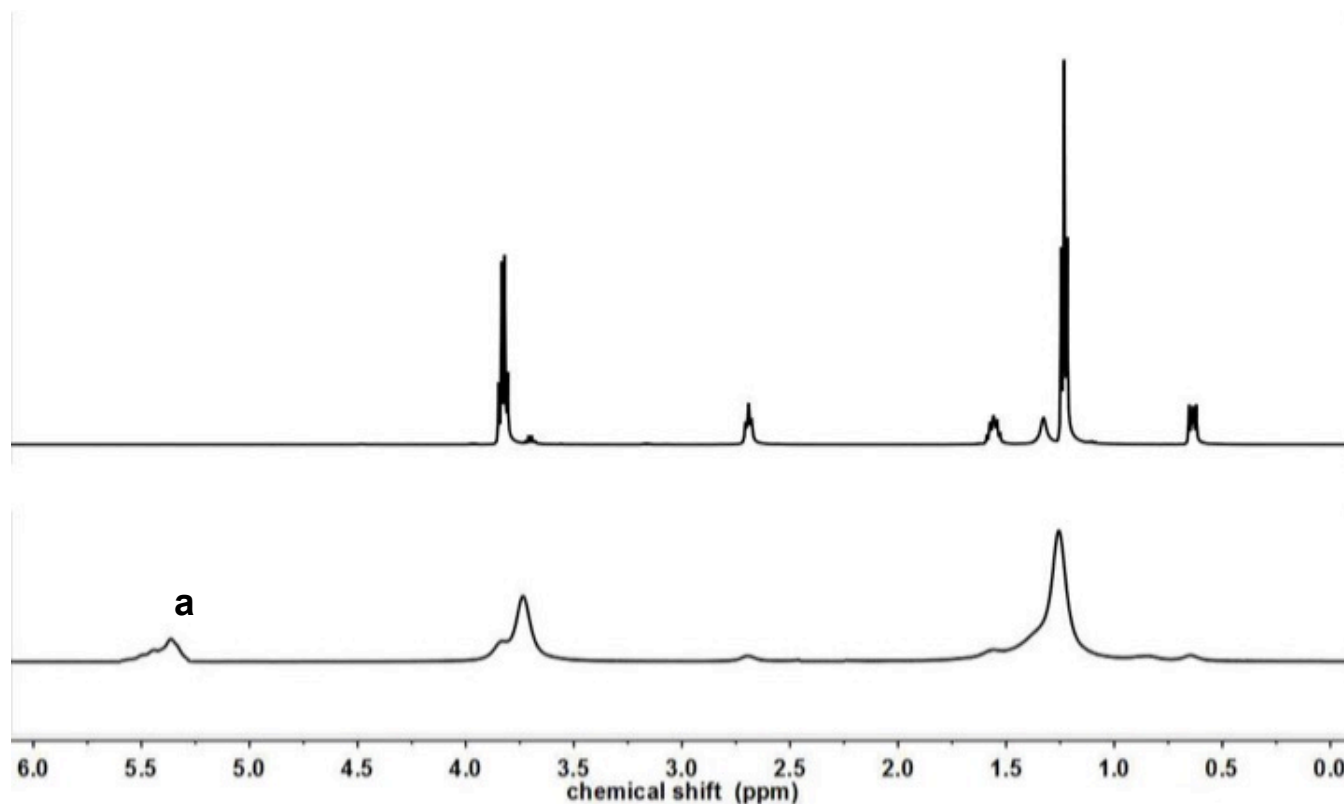


Figure S12. ^1H NMR spectrum of mixed OLA-/APTES-passivated $(\text{CdSe})_{33/34}$ CSNCs (bottom). The characteristic vinyl (a, $-\text{CH}=\text{CH}-$) resonance of OLA at 5.34 ppm and a-methylene ($-\text{Si}-\text{O}-\text{CH}_2$) resonance at 3.83 ppm from APTES are observed. The NMR peak broadening is because of spin-spin relaxation and dipole broadening from surface bound ligand. A sharp resonance of $-\text{Si}-\text{O}-\text{CH}_2$ is observed for pure APTES (top). The NMR data equivocally prove the mixed surface ligation of $(\text{CdSe})_{33/34}$ CSNCs.

Reference

1. Morris-Cohen, A. J.; Vasilenko, V.; Amin, V. A.; Reuter, M. G.; Weiss, E. A. Model for adsorption of ligands to colloidal quantum dots with concentration-dependent surface structure. *ACS Nano* **2011**, 6, 557-565.