Supporting information

Organoborane Se and Te precursors for controlled modulation of reactivity in nanomaterial synthesis

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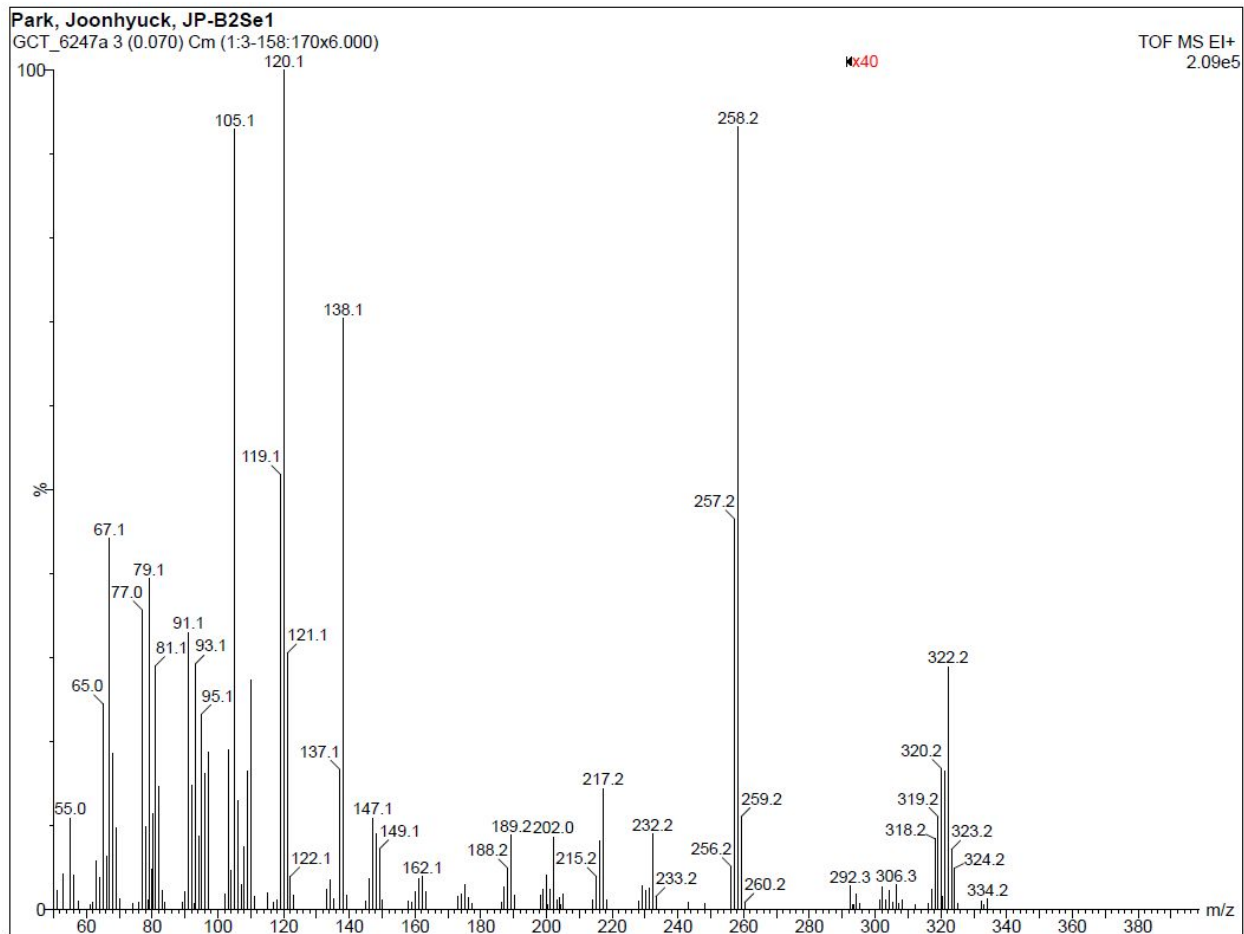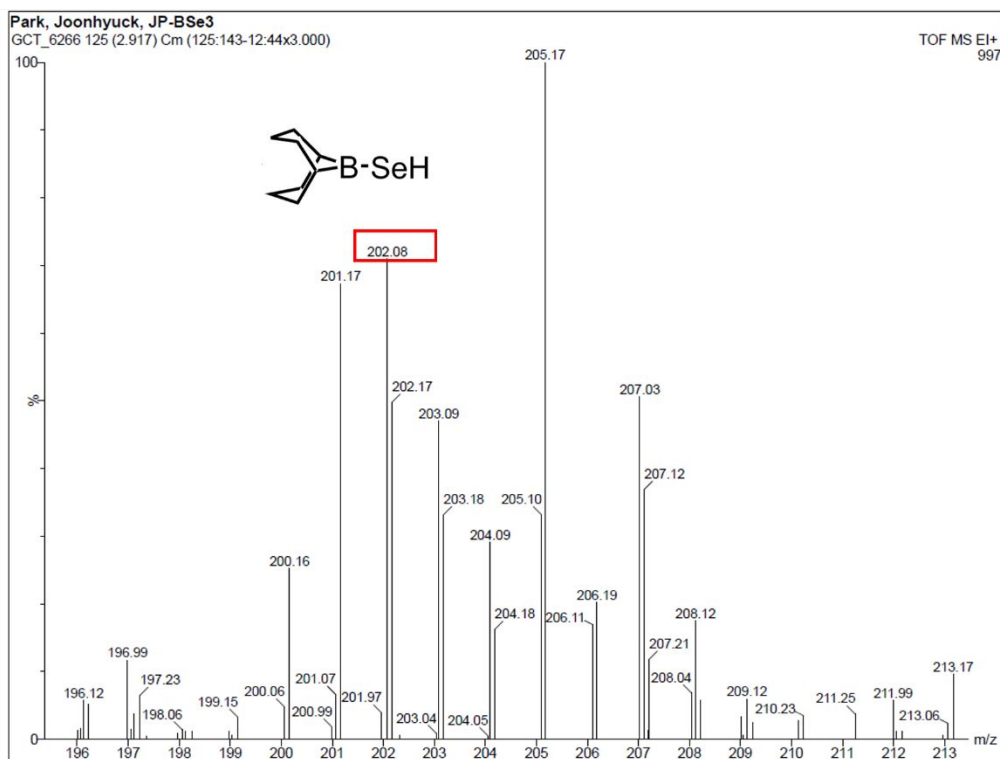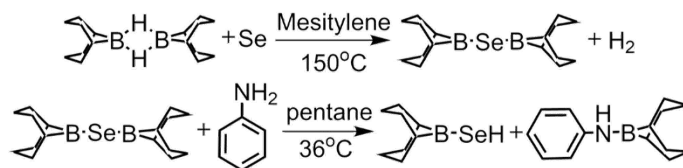
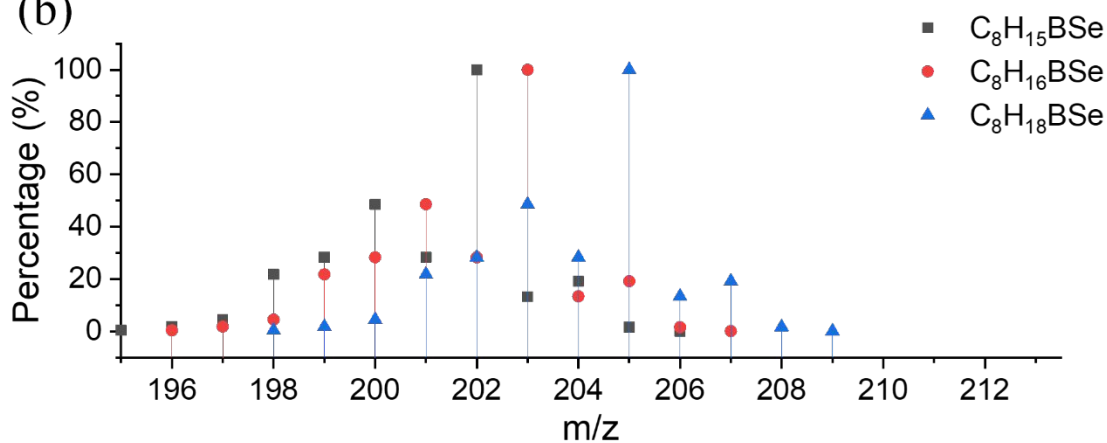Figure S1. ESI mass spectrum of (BBN)$_2$Se

Figure S2. Mass spectrum of BBN-SeH from either (a) experimental or (b) simulation data. The peak at 202.08 matched the exact mass of BBN-SeH (M). The peaks at 203.09 and 205.17 are attributed to $[M+H]^+$ ($C_8H_{16}BSe$) and $[M+3H]^+$ $C_8H_{18}BSe$). The simulation data was obtained from the website of mass spec plotter, https://www.sisweb.com/mstools/isotope.htm.
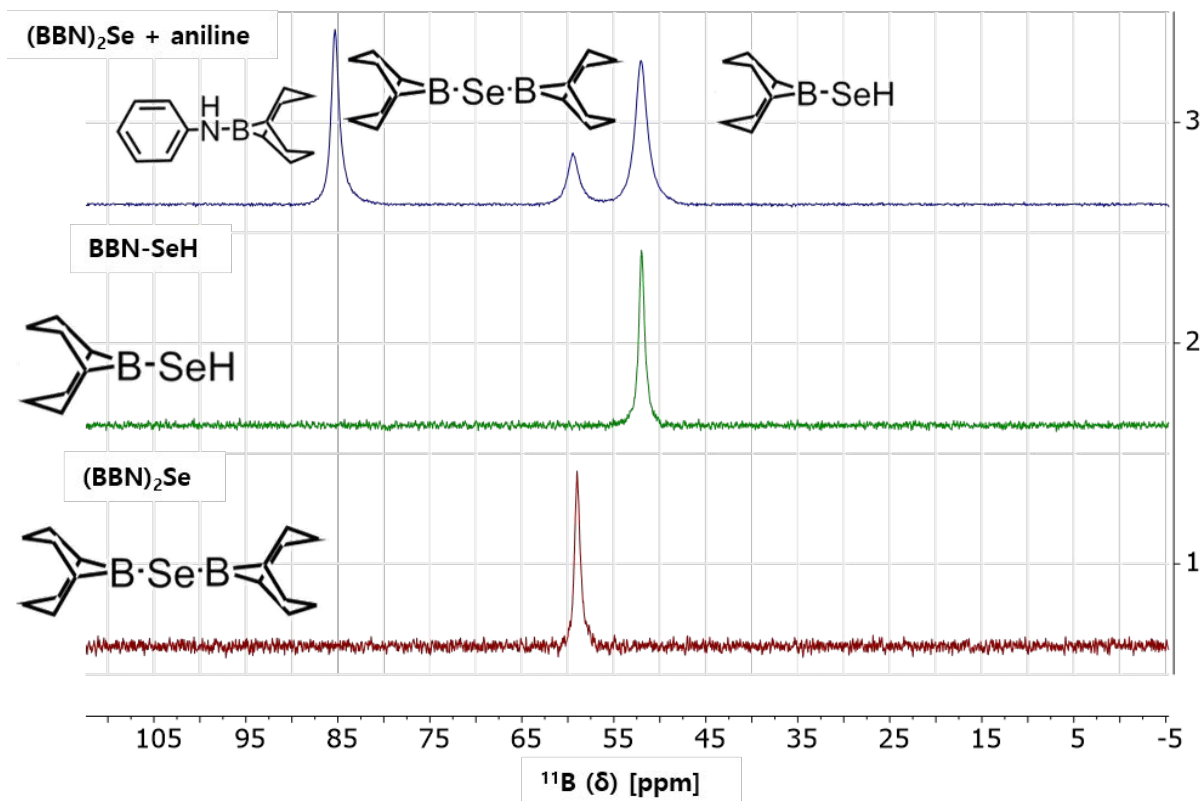
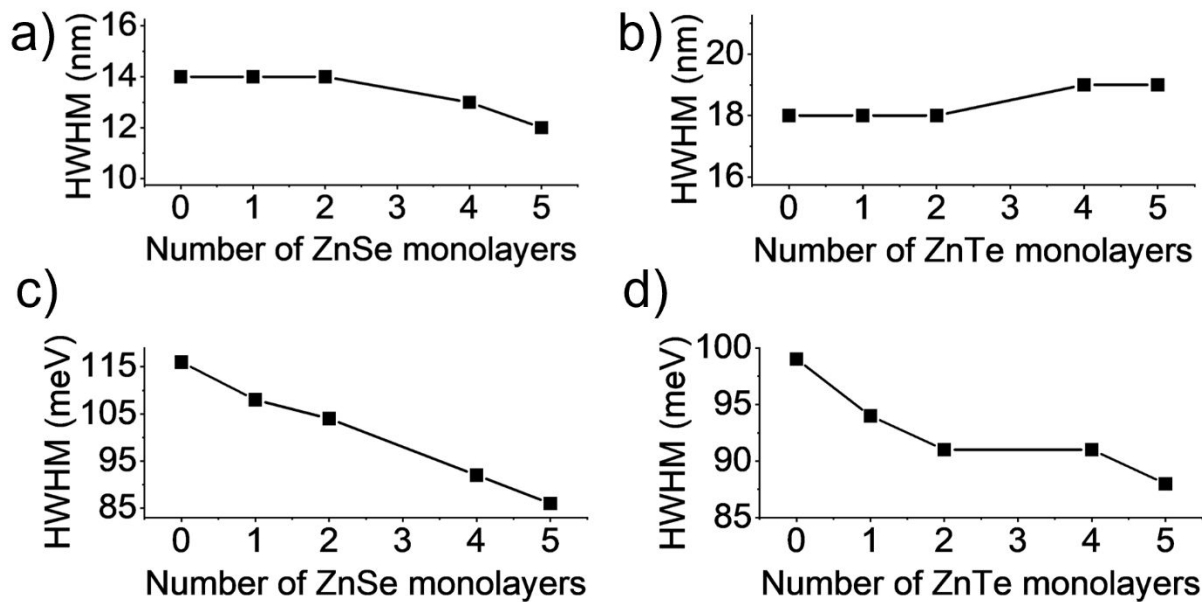Figure S3. ^{11}B NMR spectra of *in situ* formation for BBN-SeH

Figure S4. Evolution of the HWHM of the first absorption peak during growth. (a, c) ZnSe QDs (a: in nm, c: in meV) (b) ZnTe QDs (b: in nm, d: in meV)

Figure S5. Absorption spectra of ZnSe QDs during the QD growth with TOP-Se as a precursor
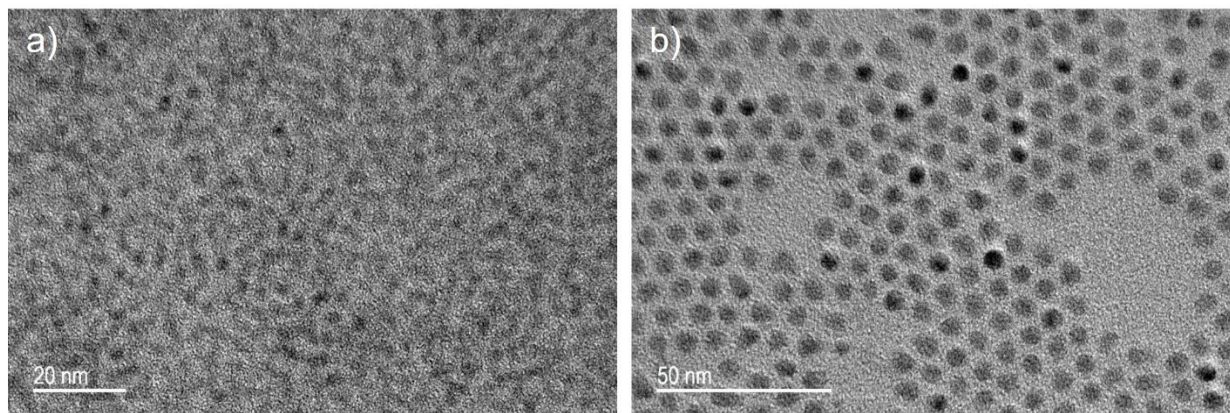
Figure S6. TEM images of (a) premade ZnSe QD cores and (b) ZnSe QD after ZnSe growth

Figure S7. Placement of our experimental data on the fitted function plotting size versus the first absorption peak (1s peak) as reported by Toufanian et al., Chem Mater 2021. Our experimental data sit right on top of the fitted curve.
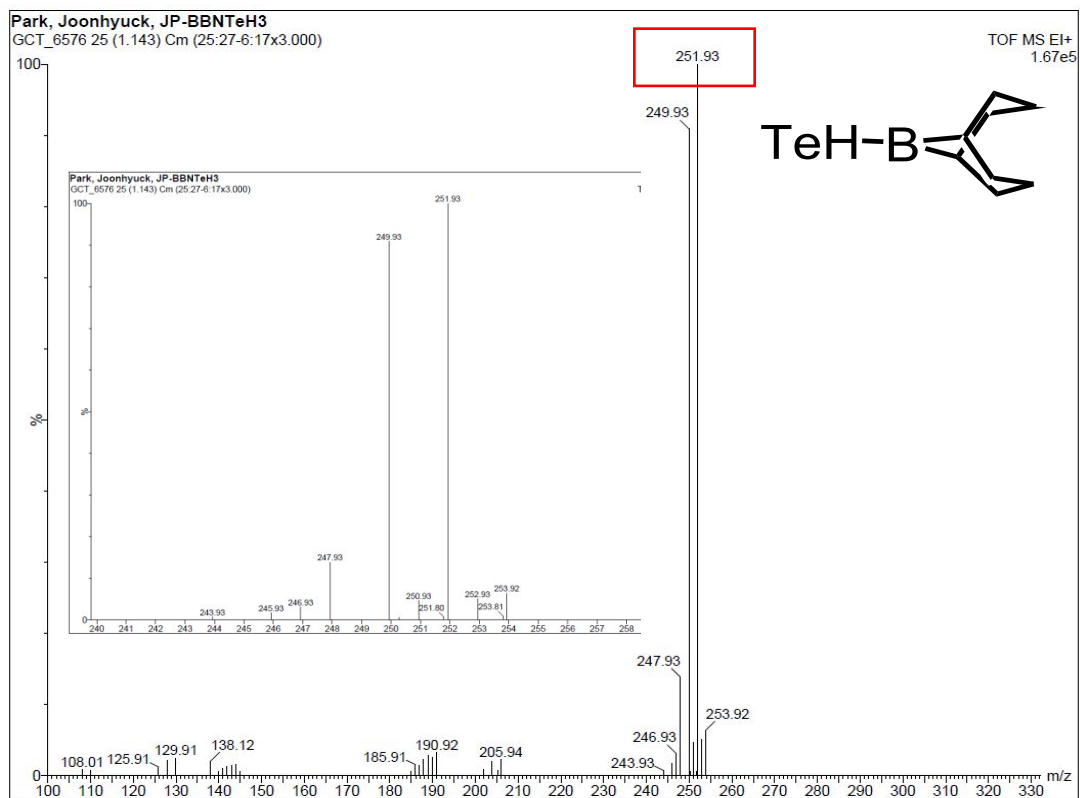
Figure S8. ESI mass spectrum data of BBN-TeH
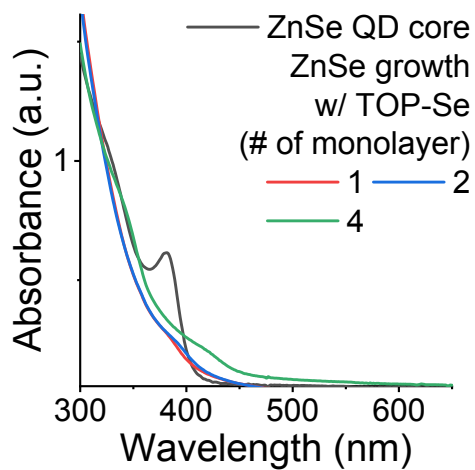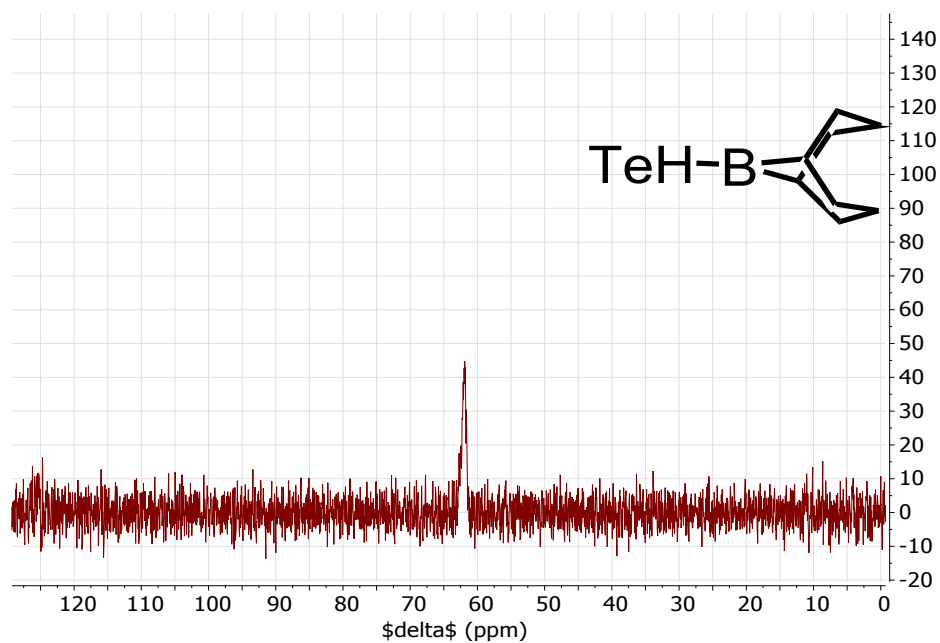

Figure S9. ^{11}B NMR spectrum of BBN-TeH
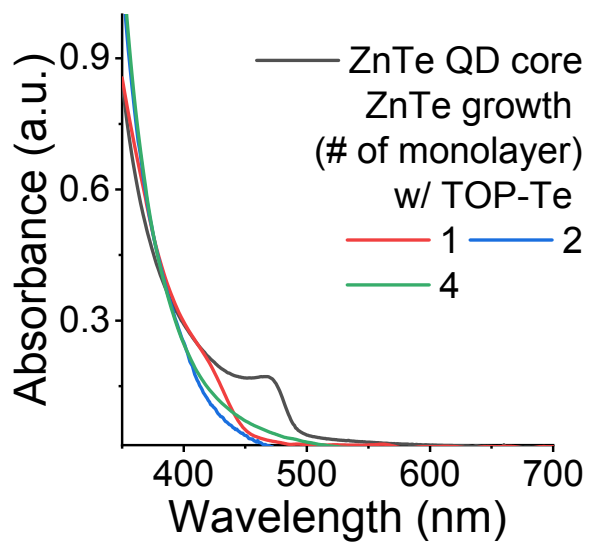
Figure S10. Absorption spectra of ZnTe QDs during the QD growth with TOP-Te as a precursor

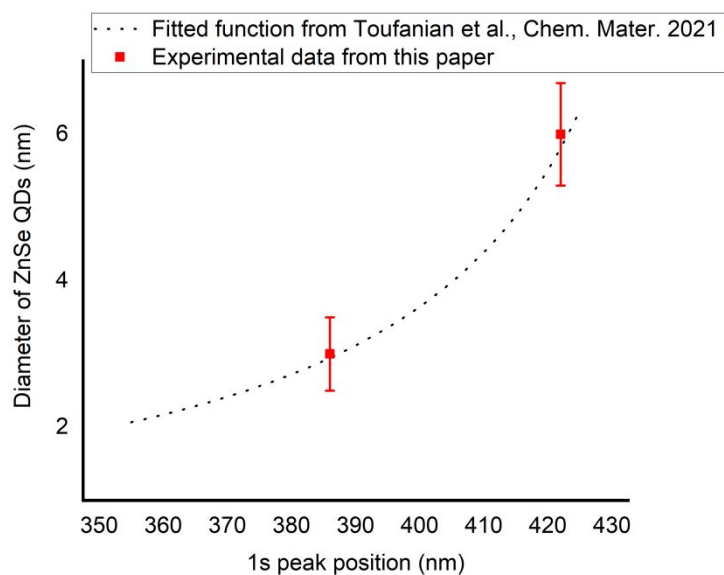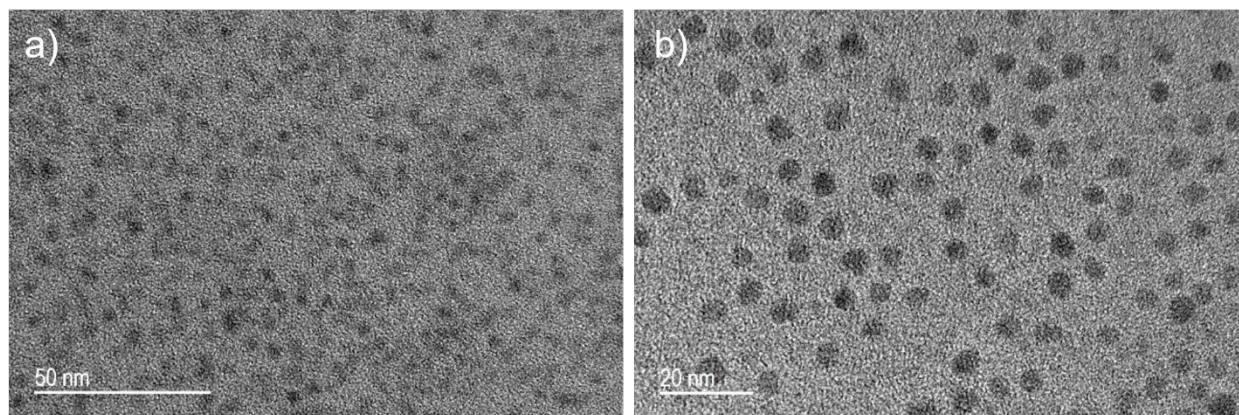Figure S11. TEM images of a) premade ZnTe QD cores and b) ZnTe QD after ZnTe growth
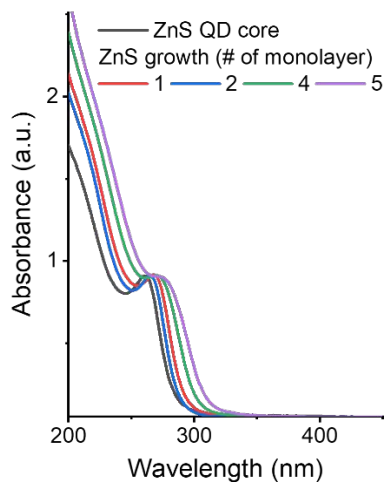
Figure S12. Absorbance spectrum of ZnS QD by using BBN-SH as a S precursor
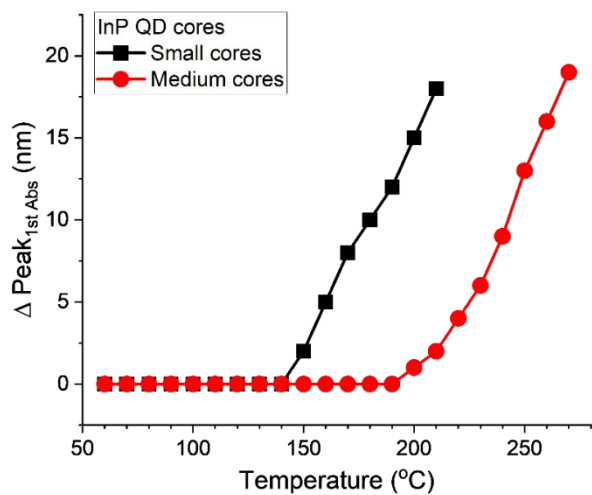
Figure S13. Melting temperature of InP QDs of different sizes. The peak of the first absorption of the InP QD cores is monitored while increasing the temperature [small size (d: 1.7 nm, black square), medium size (d: 2.4 nm, red circle)]. A red-shifted first absorption indicates that the InP QD cores become unstable, leading to Ostwald ripening.
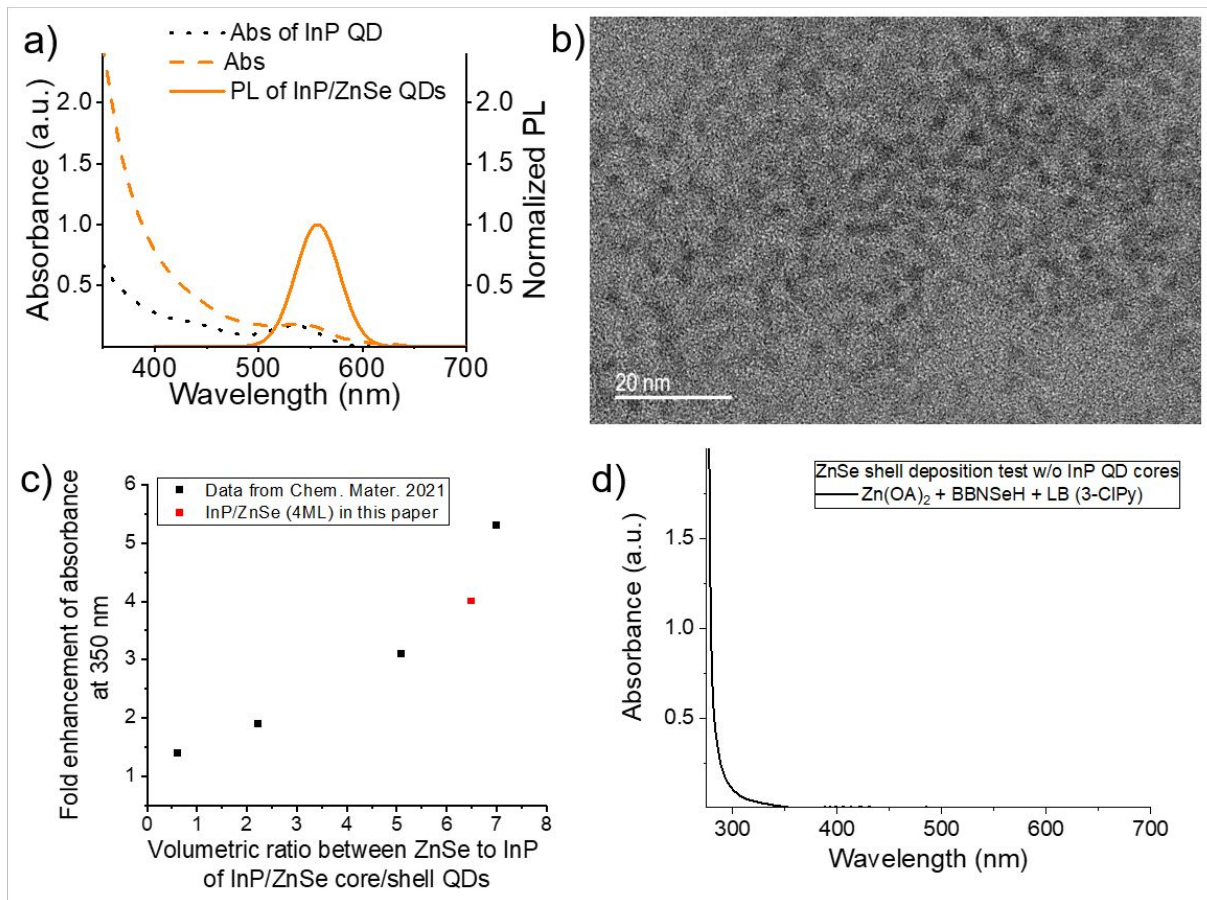
Figure S14. ZnSe shell growth on medium-size (2.4 nm in diameter) InP QD cores using BBN-SeH as a precursor. a) Absorption and photoluminescence spectrum of InP QD cores and InP/ZnSe core/shell QDs. b) TEM image of InP/ZnSe QDs. c) Fold enhancement of absorbance at 350 nm as the volumetric ratio between ZnSe shell layers and InP QD cores are varied. Black dots are from the data in the previous literature (Toufanian *et al., Chem Mater.* **2021**, *33*, 1964-1975) and a red dot is the value obtained from our InP/ZnSe core/shell QDs. d) ZnSe shell deposition test without InP QD cores confirms no significant change in the reaction vessel during the shell deposition processes.
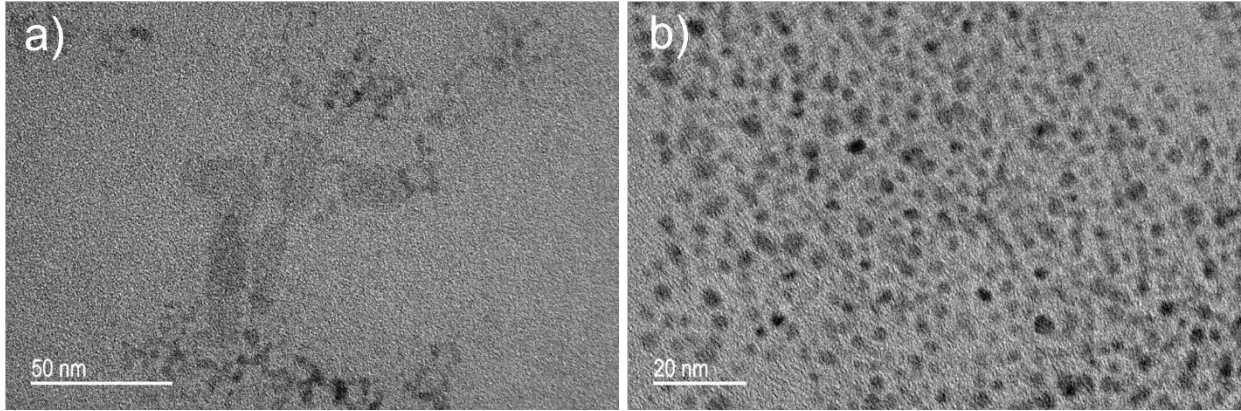
Figure S15. Conventional ZnSe NPLs synthesis resulting a mixture of ZnSe QDs and NPLs. a), b) TEM images showing the broad size distribution.
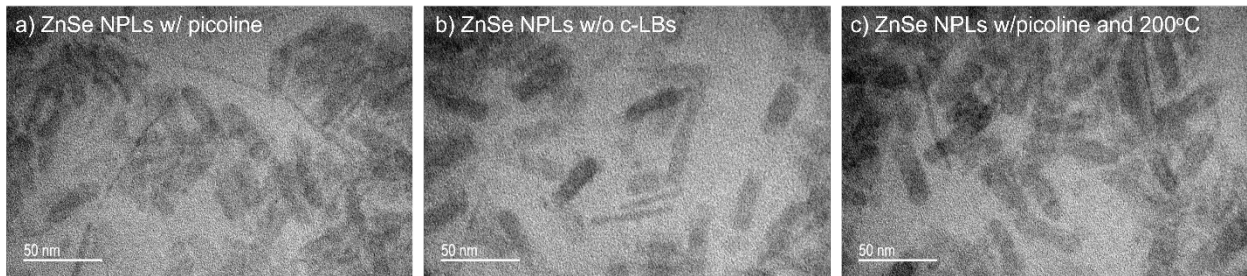
Figure S16. TEM images of a) ZnSe NPLs w/ picoline, b) ZnSe NPLs without c-LBs, and c) ZnSe NPLs w/picoline after heating up to 200°C.
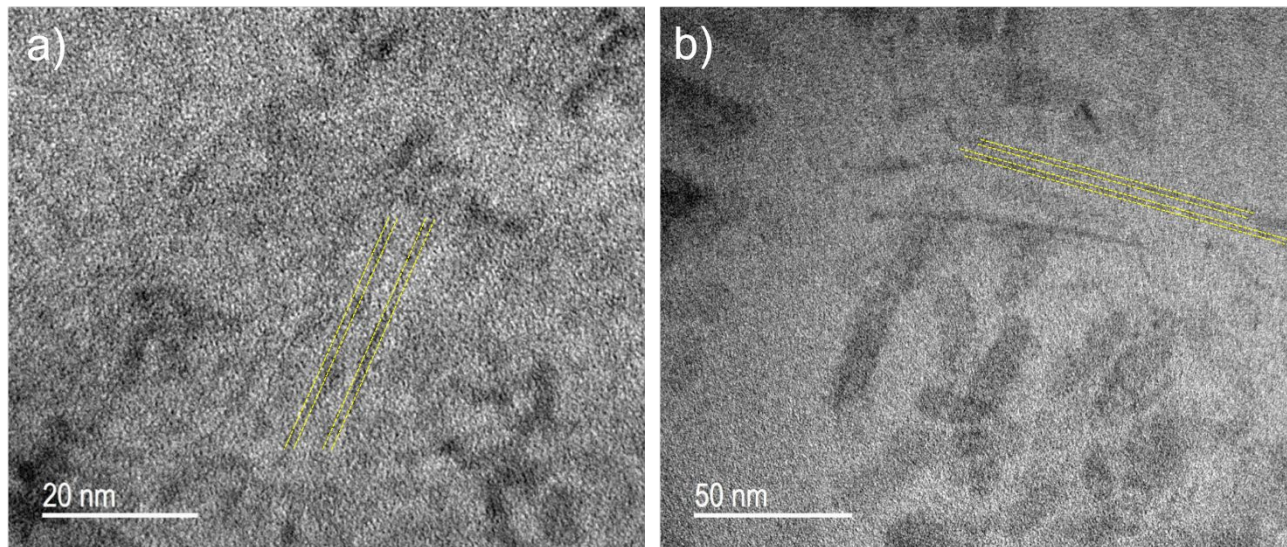
Figure S17. TEM images of the stacked a) 3ML ZnSe NPLs (316 and 305 nm absorption peak, scale bar: 20 nm) and b) 4ML ZnSe NPLs (345 and 328 nm absorption peak, scale bar: 50 nm). The thickness of the 3ML (1.1 (±0.6) nm) and 4ML ZnSe NPLs (1.4 (±0.7) nm) were measured at 30 different regions of interest.
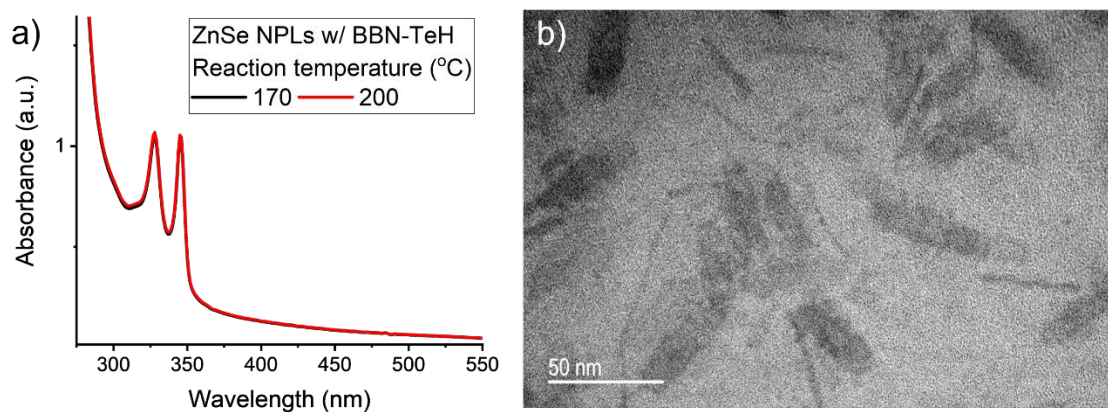
Figure S18. Thermally stable 345 nm ZnSe NPLs. After heating up to to 200°C, a) the absorption spectrum and b) TEM image of 345 nm ZnSe NPLs in the presence of BBN-TeH were confirmed.

	ZnSe		ZnTe	
	Size (std dev)	Aspect ratio (std dev)	Size (std dev)	Aspect ratio (std dev)
Before growth	3.0 (±0.5) nm	1.03 (±0.04)	2.8 (±0.4) nm	1.04 (±0.04)
After growth	6.0 (±0.7) nm	1.06 (±0.05)	5.8 (±0.8) nm	1.09 (±0.08)

Table S1. Summary of size and aspect ratio of ZnSe QDs and ZnTe QDs before and after growth.

ICP-AES	ZnSe QDs		$ZnSe/ZnSe_{0.97}Te_{0.03}$ QDs w/ TOPSe	$ZnSe/ZnSe_{0.955}Te_{0.045}$ QDs w/ TOPSe	$ZnSe/ZnSe_{0.91}Te_{0.09}$ QDs w/ TOPSe
	As-synthesized	w/ TOPSe pretreat			
Zn(%)	**52.4**	**50.1**	**50.0** (50.0)	**50.1** (50.0)	**50.1** (50.0)
Se(%)	**47.4**	**49.8**	**49.0** (49.0)	**48.4** (48.5)	**47.0** (47.0)
Te(%)	-	-	**0.9** (1.0)	**1.5** (1.5)	**2.9** (3.0)

Table S2. ICP-AES measurement results for ZnSe QDs and $ZnSe/ZnSe_{1-x}Te_x$ QDs (x=0, 0.03, 0.045, and 0.09). The values in parenthesis are the expected values calculated under the assumption of quantitative conversion of the precursors.

Experimental Section

Materials and Methods

Materials: oleylamine (OLAm, 70%), 1-octadecene (ODE, 90%), trioctylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 97%), oleic acid (OA, 90%), 4-(dimethylamino)pyridine (DMAP, 99%), picoline (99%), 3-chloropyridine (3-ClPy, 99%), 1,4-diazabicyclo[2.2.2]octane (DABCO,

99%), 1-methylpyrolidine (98%), 1-phenylimidazole (97%), aniline (99%), indium(III) acetate

(In(Ac)$_3$, 99.99%), zinc nitrate hexahydrate (99%), myristic acid (99%), lithium aluminum hydride

solution (LiAlH$_4$, 2 M in THF), zinc stearate (10~12% Zn basis), and 9-borabicyclo[3.3.1]nonane

dimer were purchased from Sigma Aldrich. 4-(trifluoromethyl)pyridine (99%) was purchased

from Oakwood Chemical. Selenium shot, zinc acetate (anhydrous, 99.98%), selenium powder

(99.999%), and cadmium oxide (CdO, 99.999%) were purchased from Alfa Aesar.

Tributylphosphine (TBP) was purchased from Strem Chemicals. Tellurium (powder, 99+%) and

[tris(trimethylsilyl)]phosphine ((TMS)$_3$P, 98%) were purchased from Acros Organics. All reagents

were used as received unless noted. Toluene was prepared by a solvent purification system (SPS).

Other solvents were of reagent grade or higher and were used without further purification. 1.5 M

trioctylphosphine selenide (TOP-Se) was prepared by dissolving 0.15 mmol of selenium shot in

100 mL of TOP under inert atmosphere and stirring vigorously overnight, forming a 1.5 M TOP-

Se solution. 1.0 M trioctylphosphine telluride (TOP-Te) was prepared by dissolving 0.1 mmol of

tellurium powder in 100 mL of TOP under inert atmosphere and stirring vigorously overnight,

forming a 1 M TOP-Te solution. 0.1 M zinc oleate solution was prepared by dissolving 10 mmol

of zinc acetate in 20 mmol of OA, 10 mmol of OLAm, and 91 mL of ODE. (BBN)$_2$Se were

synthesized using the previously reported method. (Köster, R., Seidel, G., Siebert, W. & Gangnus,

B. in Inorg. Synth. Vol. 29 (Wiley, New Jersey, 1992).) All air-sensitive materials were handled

in a glove box under dry nitrogen atmosphere with oxygen levels < 0.1 ppm.

ICP-AES measurement: Samples for ICP-AES were prepared by using aqua regia solution (HNO_3:HCl = 3:1) for overnight digestion at r.t. The digested samples were 10 times diluted with deionized water. The measurements were acquired using Optima 8300 in the Microanalysis Laboratory at the School of Chemical Sciences Research and Service Facilities at UIUC.

TEM measurement: Samples for TEM were prepared by dropping them on a TEM grid and drying highly concentrated pure QDs in the mixture of chloroform and toluene. TEM images were acquired using JEOL 2010 LaB6 operating at 200 kV in the Frederick Seitz Materials Research Laboratory Central Research Facilities at UIUC.

Characterization of T_{ind} for each BBN-EH/LB pair and growth of ZnSe (or ZnTe, ZnSe/ZnSe$_{1-x}$Te$_x$ QDs: ZnSe cores (50 nmol) were isolated by repeated precipitations from hexane with acetone. The ZnSe QD cores were redispersed in a minimal amount of hexane and loaded in a solvent mixture of 3 mL of OLAm and 3 mL of ODE. The reaction solution was degassed under vacuum at 100 ˚C for 1 h and dropped to 60 ˚C. To ensure the ZnSe QD core stability, 0.61 μmol of TOPSe was added to the reaction vessel. The amount of each Zn or Se precursor was calculated for growing 5 monolayers (MLs) of ZnSe shell on the ZnSe QD cores. The Zn precursor (0.11 mmol zinc oleate in ODE) and the BBN-EH precursor (0.11 mmol of (BBN)$_2$Se and aniline (or 0.11 mmol of BBN-TeH) in 1 mL of OLAm) were injected into the ZnSe (or ZnTe) core solution sequentially. Each coordinating Lewis base (c-LB) as a chemical initiator (0.11 mmol; dimethylaminopyridine (DMAP), 1-methylpyrolidine, picoline, 3-

chloropyridine (3-ClPy), 4-(trimethylfluoro)-pyridine (4-CF$_3$Py)) was added in the mixture. To determine the T$_{ind}$ by different types of activators, the reaction temperature for the mixture of ZnSe cores and shell precursors was slowly increased by 10 °C over 20 min and maintained for another 20 min. The conversion efficiency of BBN-SeH during ZnSe quantum dot (QD) growth reached 98% (±20%). The standard error for this measurement was calculated by taking into account the size heterogeneity and errors for volumetric measurements.

$$Incorporated\ Se\ atoms = \frac{Increased\ volume\ from\ growth}{Volume/unit\ cell} \times \frac{4\ atoms}{unit\ cell} \times mol\ of\ QDs$$

$$= \frac{(98.96nm^3)}{(0.183nm^3)} \times 4 \times 50\ nmol = 108153\ nmol$$

$$Conversion = \frac{Incorporated\ Se\ atoms}{Input\ Se\ atoms} = \frac{108153\ nmol}{110000\ nmol} = 98\ (\%)$$

For ZnTe QD growth, BBN-TeH was used as a Te precursor on the premade ZnTe QDs. The total amount of each Zn or Te precursor was calculated for growing 5 MLs of ZnTe on the ZnTe QD cores, while the temperature profile, solvent, zinc precursor, and LBs were kept the same as above. For ZnSe/ZnSe$_{1-x}$Te$_x$ QD synthesis, BBN-SeH and BBN-TeH were used as Se and Te precursor. Since these two precursors share the c-LBs, DMAP was chosen for activating both precursors. T$_{ind}$ was determined by BBN-TeH which requires a higher temperature than BBN-SeH for activation. Te precursor amount was calculated to be 0, 2, 3, or 6% of Se atoms in total amount of precursor to grow ZnSe was calculated for growing 2 MLs of ZnSe shells on ZnSe QD cores (0, 3, 4.5, 9% for infusing percentage when ZnSe$_{1-x}$Te$_x$ shell growth). For the high-

temperature growth using TOP-Te and TOP-Se, the reaction temperature was 270°C and increased by 5°C per MLs. The final reaction temperature was 280°C.

ZnSe NPLs synthesis: 0.1 mmol of zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$), 2 mL of OLAm, and 1 mL of octylamine were loaded in the flask and degassed under vacuum at 100°C for 30 minutes. Then the Se precursor solution (0.3 mmol of $(BBN)_2Se$, 0.3 mmol of aniline, and 0.6 mmol of each LB in 2 mL of OLAm was prepared in a glove box) was added in the reaction vessel under nitrogen at 100°C. The reaction vessel temperature was kept at 120~140°C, depending on the T_{ind} of each LB. The reaction was quenched by cooling down the solution to room temperature as quickly as possible. ZnSe NPLs were purified by hexane and ethanol and dispersed in hexane. For ZnSe:Te NPL synthesis, BBN-SeH (in situ formation from $(BBN)_2Se$) and BBN-TeH were used as Se and Te precursors. Since it is hard to calculate the concentration of ZnSe NPLs, we estimate the total amount of Se or Te precursor as 50% of the Se precursor for ZnSe NPL synthesis in the first place. For further ZnSe shell growth on ZnSe:Te NPLs, 50% of the Se precursor for ZnSe NPL synthesis was added.

InP QD synthesis and InP/ZnSe core/shell QD growth: 58 mg of $In(Ac)_3$, 180 mg of OA, and 3 mL of ODE were loaded in the flask and degassed under vacuum at 100°C for 60 minutes. Then, a phosphine precursor (25 mg of $(TMS)_3P$ was dispersed in 0.5 mL of TOP) was added into the reaction vessel at 30°C under nitrogen. The reaction vessel temperature was slowly heated up (1°C

/ min). Once the reaction temperature was reached to 260ºC, the reaction vessel was kept at the temperature for 20 minutes. InP QD cores (40 nmol) were isolated by repeated precipitations from hexane with acetone. The purified InP QD cores were redispersed in a minimal amount of hexane and loaded in a mixture of the Zn precursor (0.13 mmol zinc stearate), 1 mL of TOP, 2 mL of OLAm, and 3 mL of ODE. The amount of each Zn or Se precursor was calculated for growing 4 MLs of ZnSe shell on the InP QD cores. The reaction vessel was degassed under vacuum at 100 ˚C for 1 h. The Se precursor (0.13 mmol of $(BBN)_2Se$, each chemical initiator (LBs, 0.13 mmol), and 0.13 mmol of aniline in 2 mL of OLAm) were injected into the InP QD core solution slowly (1 mL/hr). The temperature was increased to 130~190 ˚C depending on the InP QD core. The reaction temperature was maintained for 10 min, then increased by 5ºC every 5 minutes up to 160~220ºC (T_{growth}: 130~160 ºC with DMAP, 140~170ºC with 1-methylpyrolidine, 190~220ºC with 3-ClPy). The reaction temperature was kept at the highest T_{growth} for another 80 min. After the 2 hr precursor injection, the reaction vessel was cooled down to r.t.