Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Continuous Production of Ultrathin Organic-Inorganic Ruddlesden-Popper Perovskite Nanoplatelets via a Flow Reactor

Gill M. Biesold,[a] Shuang Liang,[a,b] Brent Wagner,[c] Zhitao Kang,[a,c] and Zhiqun Lin*[a]*

a. School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

b. School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

c. Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

* Corresponding authors, E-mail: Zhitao.Kang@gtri.gatech.edu and zhiqun.lin@mse.gatech.edu

Experimental Section

Materials

All materials were used as received. Toluene (ACS, VWR), dichloromethane (ACS, VWR), chlorobenzene (ACS, Beantown Chemical), anhydrous dimethylformamide (DMF, Millipore), lead bromide (99.99%, TCI), lead iodide (99.9985%, Alfa Aesar), phenylethylamine (99%, Alfa Aesar), hydrobromic acid (48 wt%, Alfa Aesar), hydroiodic acid (57 wt%, Beantown Chemical), 1-octylamine (99%, Alfa Aesar), diethyl ether (ACS, Millipore Sigma), ethanol (200 proof, Koptec), phenylethylammonium bromide, phenylethylammonium iodide (synthesis details follow)

Phenylethylammonium halide (PEAX) was synthesized in a previously-reported method.[1] In short, excess halide acids were dropped into an ethanol/phenylethylamine mixture at 0 C. The mixture was then washed with diethyl ether three times, recrystallized with ethanol, and dried in a vacuum oven before use.

Flow reactor setup

To create the flow reactor, 1.6 mm inner diameter PTFE tubing (from SCAT Europe) was cut to the desired reactor tube length (15, 30, or 60 cm). It was then fitted onto one end of a polypropylene/polyethylene tapered connector (orifice size 3mm, VWR). Two pieces of PTFE tubing (inner diameter 1.6 mm) with one end adapted to female Luer Lock fitting (Hamilton Company) were then attached to the other two ends of the tapered connector. The female Luer Lock fittings allowed for facile connection to BD syringes that contained the precursor and crystallization solvents, which were dispersed by the Single Syringe Pump (Fisherbrand). A schematic diagram of the flow reactor can be seen in **Figure 1c**.

The same precursor solution was used for all trials except for those testing concentration effect of the precursor solution (described below). The general precursor solution was created by dissolving 0.4 mmol PbX_2 (X= Br, I), 0.8 mmol PEAX, and 12 uL octylamine in 10 mL DMF. The small amount of octylamine was added to passivate any surface defects on the NPLs. The concentration effect precursor solution was made by dissolving 0.8 mmol PbX_2, 1.6 mmol PEAX, and 24 uL octylamine in 10 mL DMF.

Investigation of each parameter

The synthesis of perovskite nanoplatelets in the flow reactor was optimized.

Antisolvent: To isolate the effect of antisolvent, a 15 cm reactor tube and two Luer Lock fitted tubes were connected to the Y adaptor. One syringe was filled with precursor solution (described above) and the other syringe was filled with the antisolvent (either toluene, dichloromethane, or chlorobenzene). The precursor solution was then allowed to flow at 30 mL/hr until it reached the Y connector, at which point the antisolvent was introduced to flow at 1200 mL/hr. The final solution was collected from the end of the 15 cm reactor tube. The antisolvent syringe was removed and the reactor was rinsed with 10 mL of the antisolvent. This procedure was repeated two times for $Q_{precursor}$ =30 mL/hr. Each other $Q_{precursor}$ (5, 10, 15, 20, 25, and 30 mL/hr) was then tested 3 times. This entire procedure was followed for each antisolvent (chlorobenzene, dichloromethane, and toluene)

Reactor tube length: To elucidate the effect of reactor tube length, a 15 cm reactor tube and two Luer Lock fitted tubes were connected to the Y adaptor. One syringe was filled with precursor solution (described above) and the other syringe was filled with the toluene (antisolvent). The precursor solution was then allowed to flow at 30 mL/hr until it reached the Y connector, at which point the antisolvent was allowed to flow at 1200 mL/hr. The final solution was collected from the end of the 15 cm reactor tube. The antisolvent syringe was removed and the reactor was rinsed with 10 mL of the antisolvent. This procedure was repeated two times for $Q_{precursor}$ =30 mL/hr. Each other $Q_{precursor}$ (5, 10, 15, 20, 25, and 30 mL/hr) was then tested 3 times. The entire procedure was then repeated after the reactor was replaced with a 30 and 60 cm tube.

Antisolvent flowrate: To investigate the effect of antisolvent flowrate, a 15 cm reactor tube and two Luer Lock fitted tubes were connected to the Y adaptor. One syringe was filled with precursor solution (described above) and the other syringe was filled with toluene (antisolvent). The precursor solution was then enabled to flow at 5 mL/hr until it reached the Y connector, at which point the antisolvent was flowed at 1200 mL/hr. The final solution was collected from the end of the 15 cm reactor tube. The antisolvent syringe was removed and the reactor was rinsed with 10 mL of the antisolvent. This procedure was repeated three times for each Q_{tol} (1200, 900, 720, 600, 514 mL/hr).

Precursor concentration:
To isolate the effect of precursor solution concentration, a 15 cm reactor tube and two Luer Lock fitted tubes were connected to the Y adaptor. One syringe was filled with the concentrated precursor solution (described above) and the other syringe was filled with toluene. The precursor solution was then allowed to flow at 30 mL/hr until it reached the Y connector, at which point the toluene was introduced to flow at 1200 mL/hr. The final solution was collected from the end of the 15 cm reactor tube. The toluene syringe was removed and the reactor was rinsed with 10 mL of toluene. This procedure was repeated two times for $Q_{precursor}$ =30 mL/hr. Each other $Q_{precursor}$ (5, 10, 15, 20, 25, and 30 mL/hr) was then tested 3 times.

Characterization

The photoluminescence (PL) spectra of each 2D RP perovskite NPL was obtained by a PerkinElmer LS 55 fluorescence spectrometer with a 365nm excitation light. The absolute photoluminescence quantum yield (PLQY) was measured with a Hamamatsu Quantaurus QY Plus with an excitation wavelength of 365 nm. The absorbance of the NPLs was examined by 800-300 nm with a Shimadzu UV-2600. The morphologies of the as-prepared NPLs were investigated with a JEOL CX-II transmission electron microscope (TEM) operated at 100 keV. Atomic force microscopy was conducted with a Bruker Dimension Icon; operated in tapping mode. Samples for AFM were made by drop casting NPL solution onto a silicon substrate. We note that x-ray diffraction studies were not conducted because the monolayer structure of n=1 perovskites lacks sufficient periodicity to yield relevant results.[1]

Estimation of batch synthesis production rate

Precursor solution composition:
0.8 mmol PEABr = 0.1617 g
0.4 mmol $PbBr_2$ = 0.1468 g
10 mL DMF
Total weight per volume = 0.3085 g / 10 mL = 0.03085 g/mL

LARP synthesis ratio: 10 mL toluene: 10 uL precursor solution (10 uL= 0.010 mL)
Weight per batch: 0.010 mL * 0.03085 g/mL = 0.0003 g
*Assume 1 batch takes 60 seconds *
0.0003 g / 60 s * (60 s / min) * (60 min / hr) = **0.0185 g/hr**

Calculation of production rate of continuous flow reactor

Precursor solution composition:
0.8 mmol PEABr = 0.1617 g
0.4 mmol $PbBr_2$ = 0.1468 g
10 mL DMF
Total weight per volume = 0.3085 g / 10 mL = 0.03085 g/mL
Optimized Precursor Solution Injection Rate: 5 mL/hr
Therefore, half mass is distributed per hour, yield would be **0.1542 g/hr**

Figures and Figure Captions

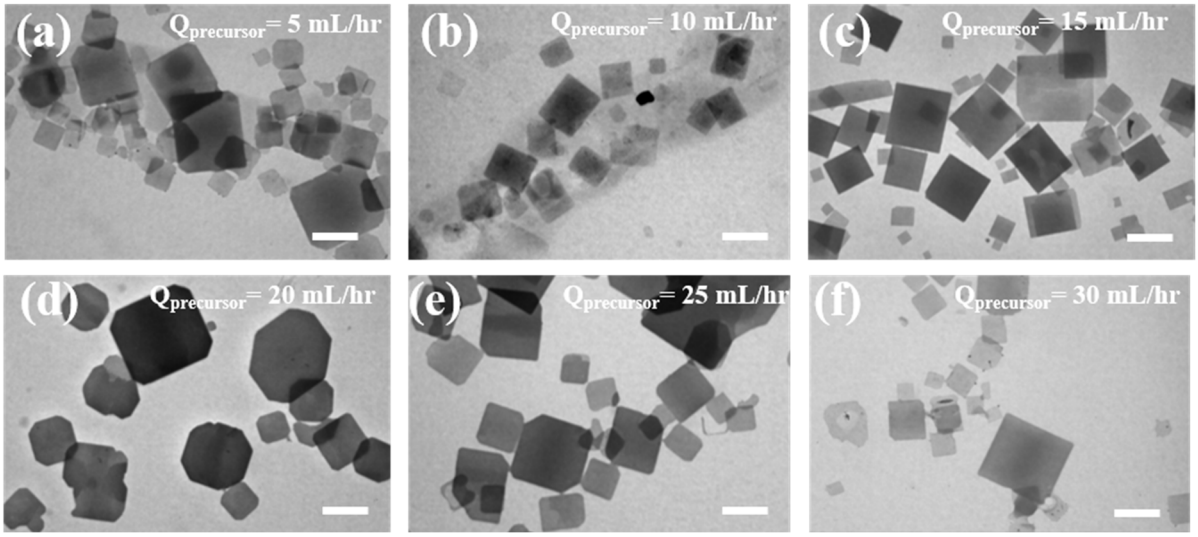

Figure S1. TEM images of $(PEA)_2PbBr_4$ NPLs produced in a 15cm reactor with chlorobenzene as the antisolvent at a constant flowrate of 1200 mL/hr and precursor injection rates ranging from 5-30 mL/hr, that is, (a) 5 mL/hr, (b) 10 mL/hr, (c) 15 mL/hr, (d) 20mL/hr, (e) 25 mL/hr, and (f) 30 mL/hr, respectively.

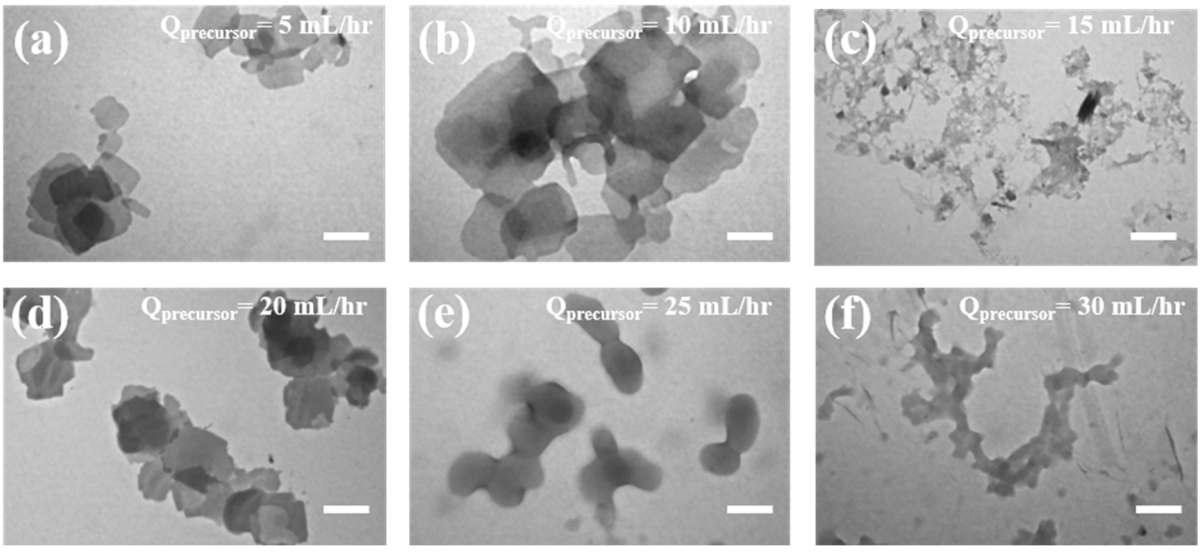

Figure S2. TEM images of $(PEA)_2PbBr_4$ NPLs made in a 15cm reactor with dichloromethane as the antisolvent at a constant flowrate of 1200 mL/hr and precursor injection rates ranging from 5-30 mL/hr, that is, (a) 5 mL/hr, (b) 10 mL/hr, (c) 15 mL/hr, (d) 20mL/hr, (e) 25 mL/hr, and (f) 30 mL/hr, respectively.

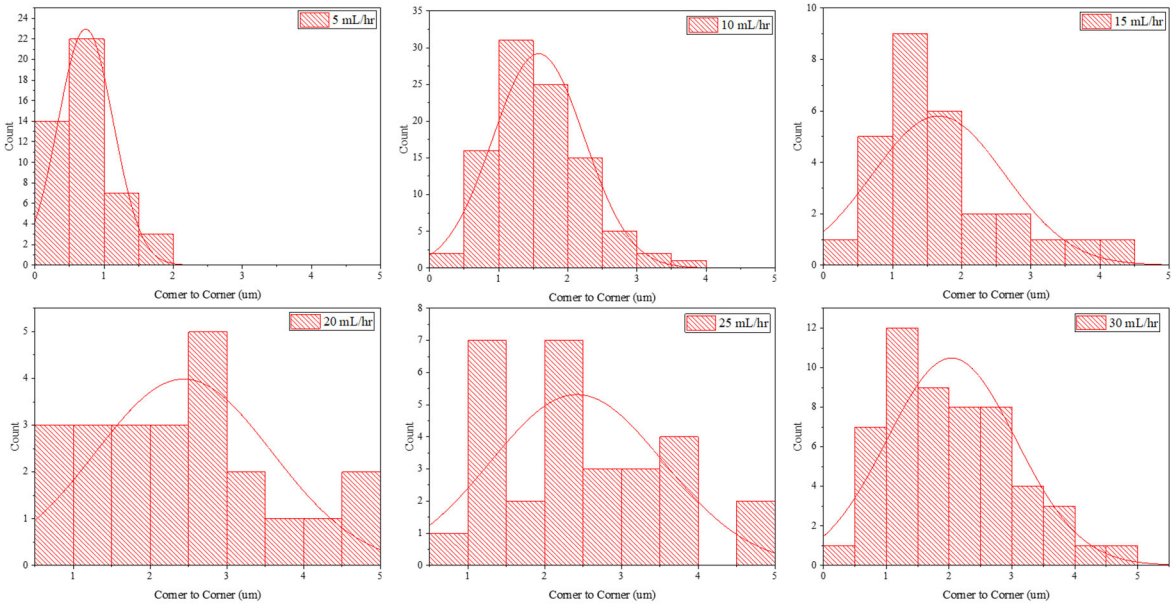

Figure S3. Particle size distribution of $(PEA)_2PbBr_4$ NPLs made in 15cm reactor tube with $Q_{toluene}$=1200 mL/hr at various $Q_{precursor}$.

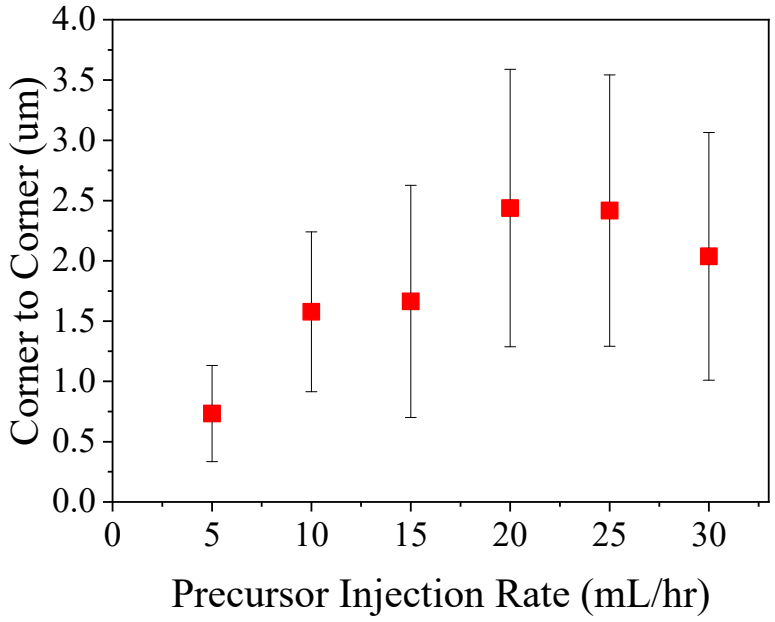

Figure S4. Average corner to corner length and deviation of $(PEA)_2PbBr_4$ NPLs made in 15cm reactor tube with $Q_{toluene}$=1200 mL/hr at various $Q_{precursor}$.

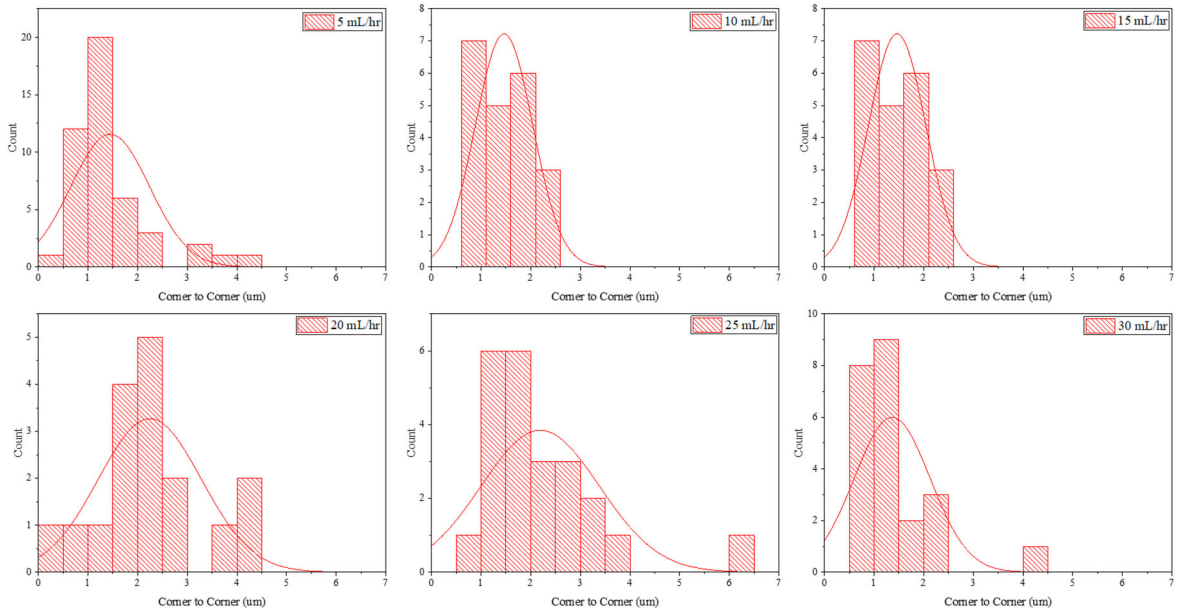

Figure S5. Particle size distribution of $(PEA)_2PbBr_4$ NPLs made in 15cm reactor tube with $Q_{chlorobenzene}$=1200 mL/hr at various $Q_{precursor}$.

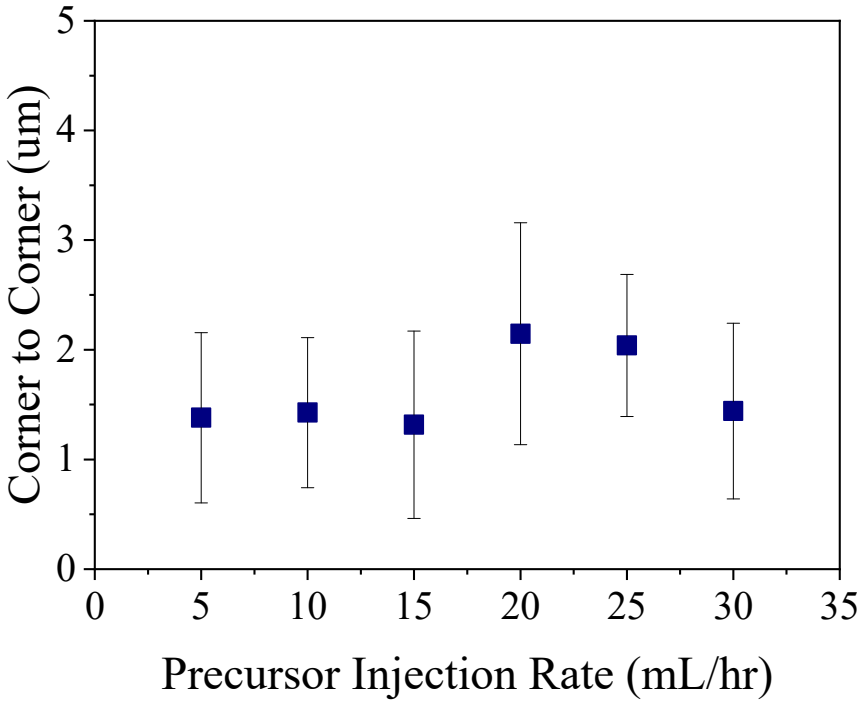

Figure S6. Average corner to corner length and deviation of $(PEA)_2PbBr_4$ NPLs made in 15cm reactor tube with $Q_{chlorobenzene}$=1200 mL/hr at various $Q_{precursor}$.

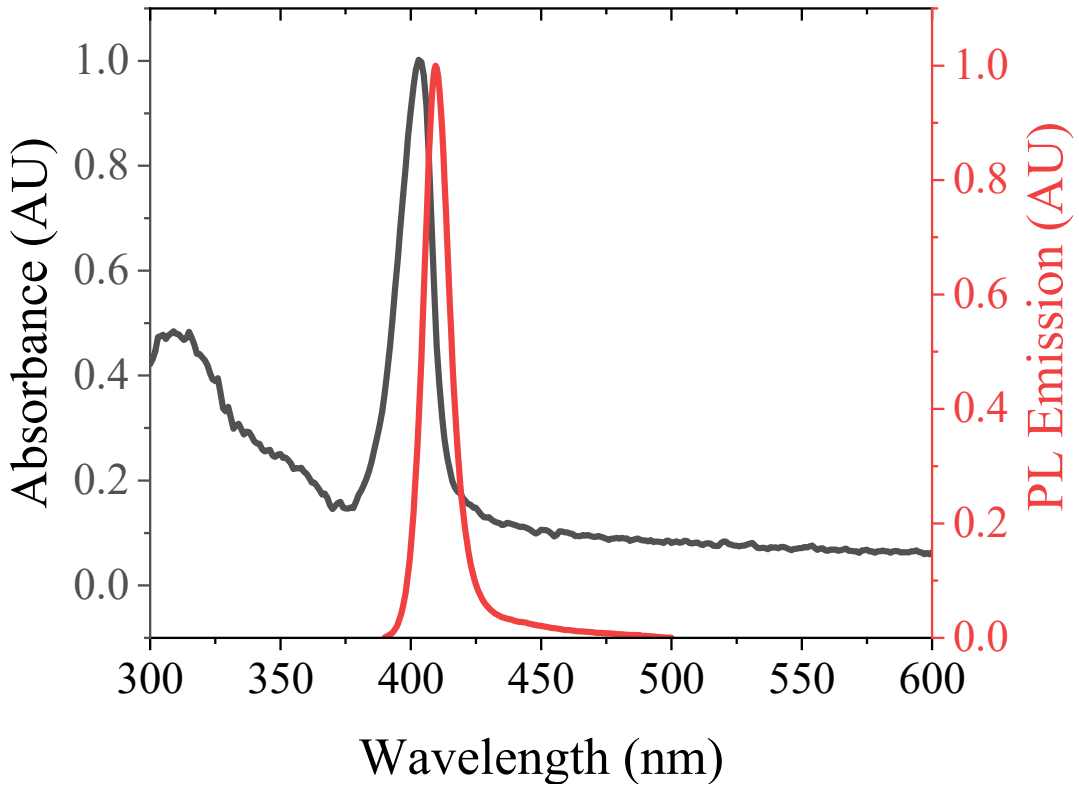

Figure S7. UV-vis absorbance and PL emission of $(PEA)_2PbBr_4$ NPLs produced in 15 cm reactor with 1200 mL/hr flow of toluene antisolvent and 5 mL/hr precursor injection rate.

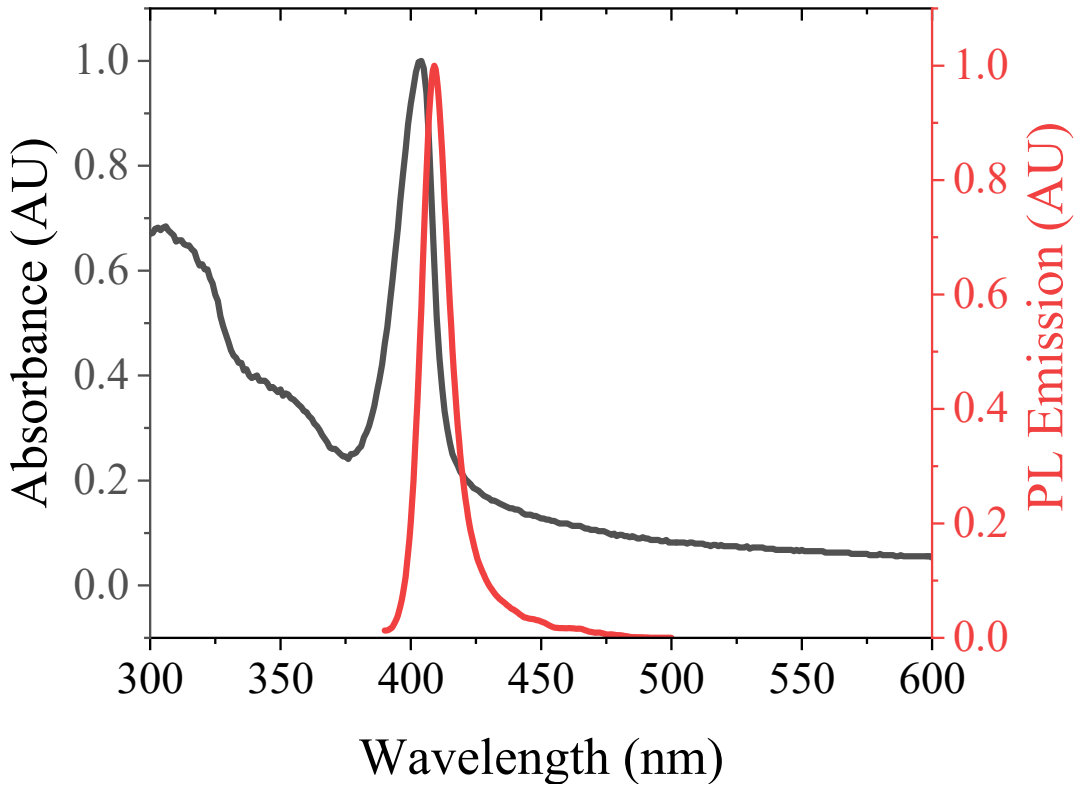

Figure S8. UV-vis absorbance and PL emission of $(PEA)_2PbBr_4$ NPLs produced in 15 cm reactor with 1200 mL/hr flow of chlorobenzene antisolvent and 5 mL/hr precursor injection rate.

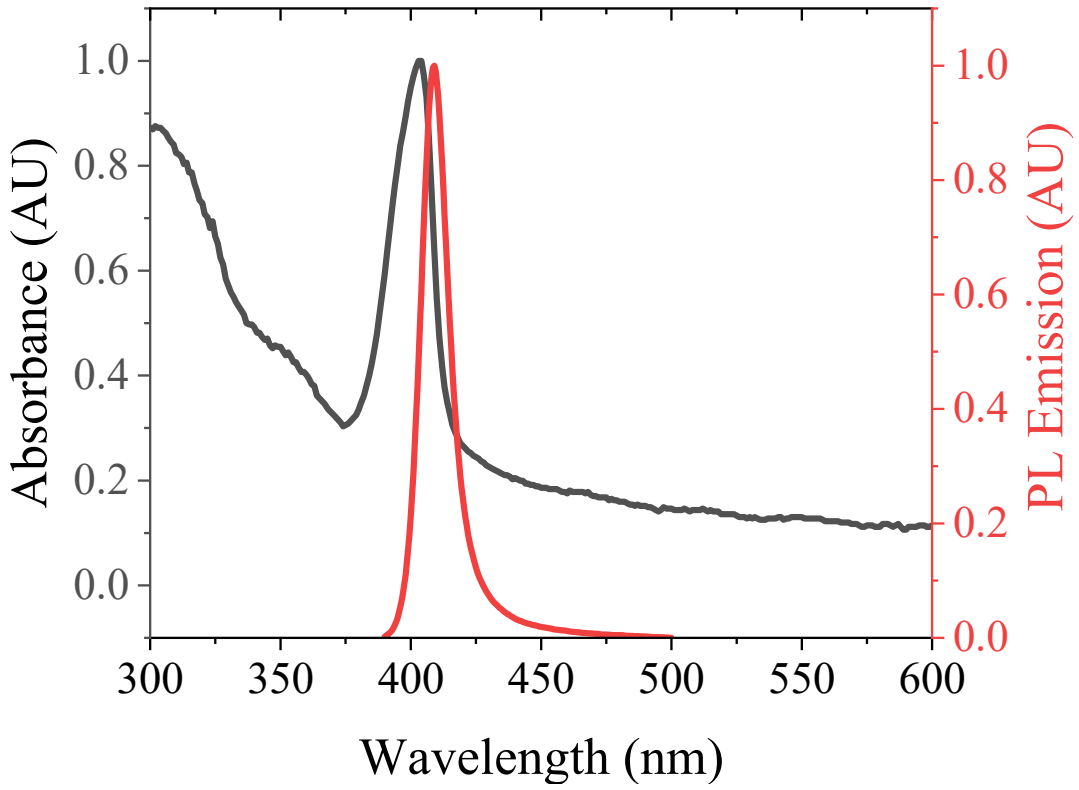

Figure S9. UV-vis absorbance and PL emission of $(PEA)_2PbBr_4$ NPLs produced in 15 cm reactor with 1200 mL/hr flow of dichloromethane antisolvent and 5 mL/hr precursor injection rate.

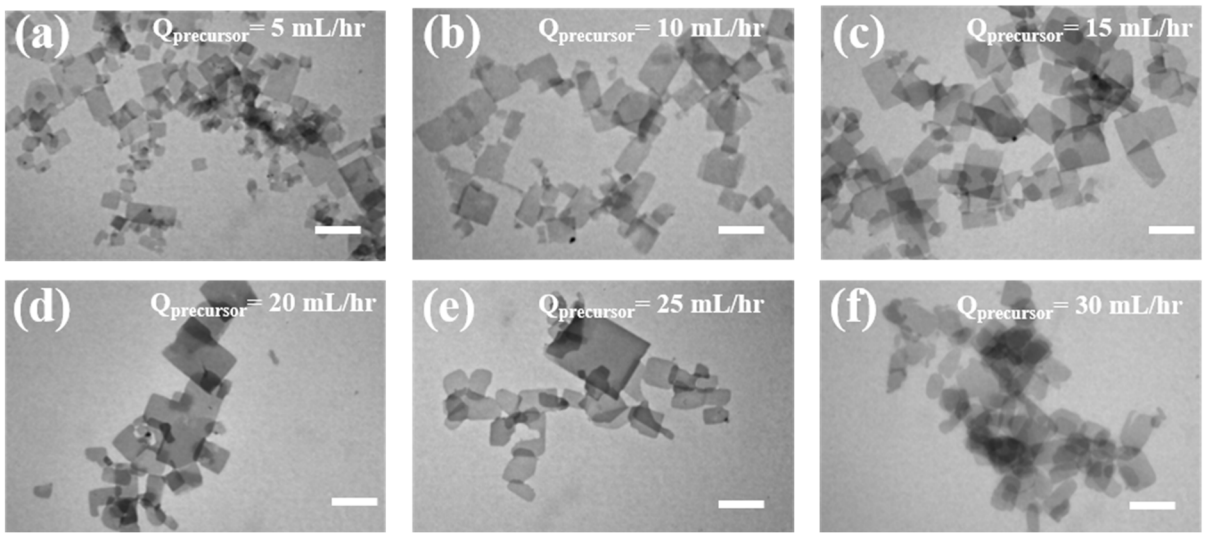

Figure S10. TEM images of $(PEA)_2PbBr_4$ NPLs produced in a 30cm reactor with toluene as the antisolvent at a constant flowrate of 1200 mL/hr and precursor injection rates ranging from 5-30 mL/hr, that is, (a) 5 mL/hr, (b) 10 mL/hr, (c) 15 mL/hr, (d) 20mL/hr, (e) 25 mL/hr, and (f) 30 mL/hr, respectively.

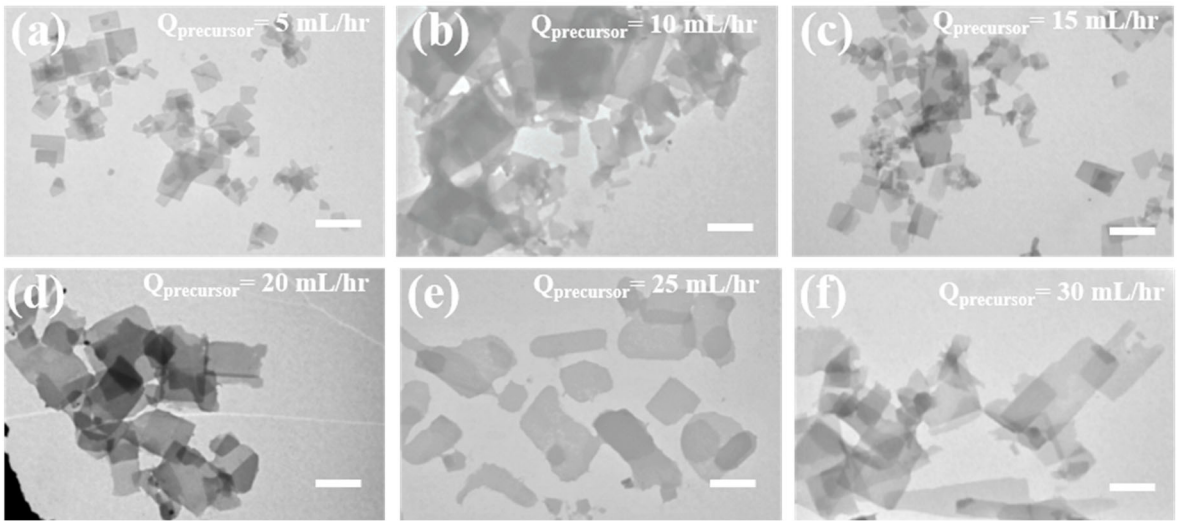

Figure S11. TEM images of $(PEA)_2PbBr_4$ NPLs produced in a 60cm reactor with toluene as the antisolvent at a constant flowrate of 1200 mL/hr and precursor injection rates ranging from 5-30 mL/hr, that is, (a) 5 mL/hr, (b) 10 mL/hr, (c) 15 mL/hr, (d) 20mL/hr, (e) 25 mL/hr, and (f) 30 mL/hr, respectively.

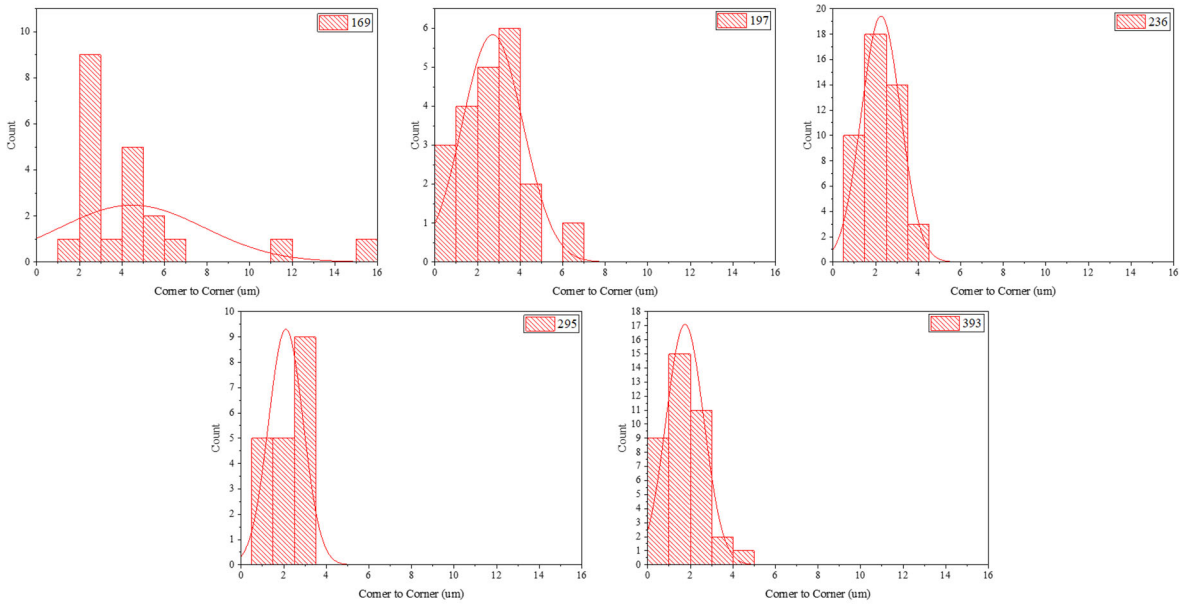

Figure S12. Particle size distribution of $(PEA)_2PbBr_4$ NPLs made in 15 cm reactor tubes with $Q_{precursor}$= 5mL/hr at varied toluene injection.

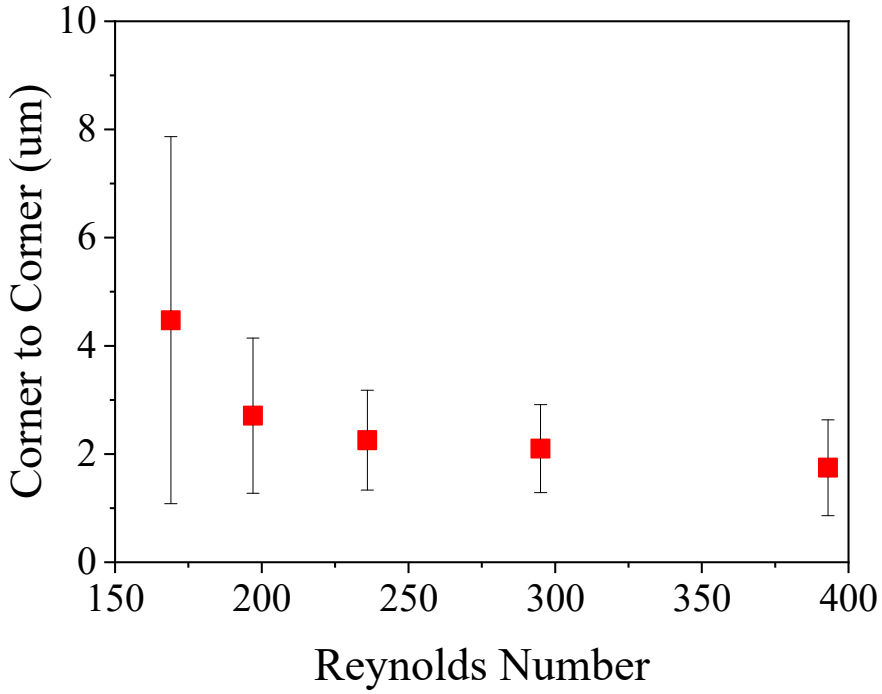

Figure S13. Average corner to corner length and distribution of $(PEA)_2PbBr_4$ NPLs made in 15 cm reactor tubes with $Q_{precursor}$= 5mL/hr at varied toluene injection.

Table S1: Reynolds Number Calculation

$$Re = \frac{\rho Q D}{\mu A}$$

ρ = Density of fluid [kg/m^3]

μ = Dynamic viscosity of liquid [Pa*s]

Q = Flowrate [m^3/s]

A = Cross sectional area of tube [m^2]

D = Inner diameter of tube [m]

Constants

ρ = **870 kg/m^3**

μ = **5.60E-4 Pa s**

D = **0.0016 m**

A = π(D/2)^2= π(0.0008)^2=**2.01E-6 m^2**

Variable Flowrates:

1205 mL/hr = **3.35E-7 m^3/s**

605 mL/hr = 1.68E-7 m^3/s

905 mL/hr = 2.54E-7 m^3/s

519 mL/hr = 1.44E-7 m^3/s

725 mL/hr = 2.01E-7 m^3/s

Determination of Re for total flowrate of 1205 mL/hr

Re= (**870 kg/m^3**)(**3.35E-7 m^3/s**)(**0.0016 m**)/(**5.60E-4 Pa*s**)(**2.01E-6 m^2**) = **393**

The Reynolds number for all flowrates was calculated using the above equation. The results are provided in the table below.

Total Flow [mL/hr]	Re
1205	393
905	295
725	236
605	197
519	169

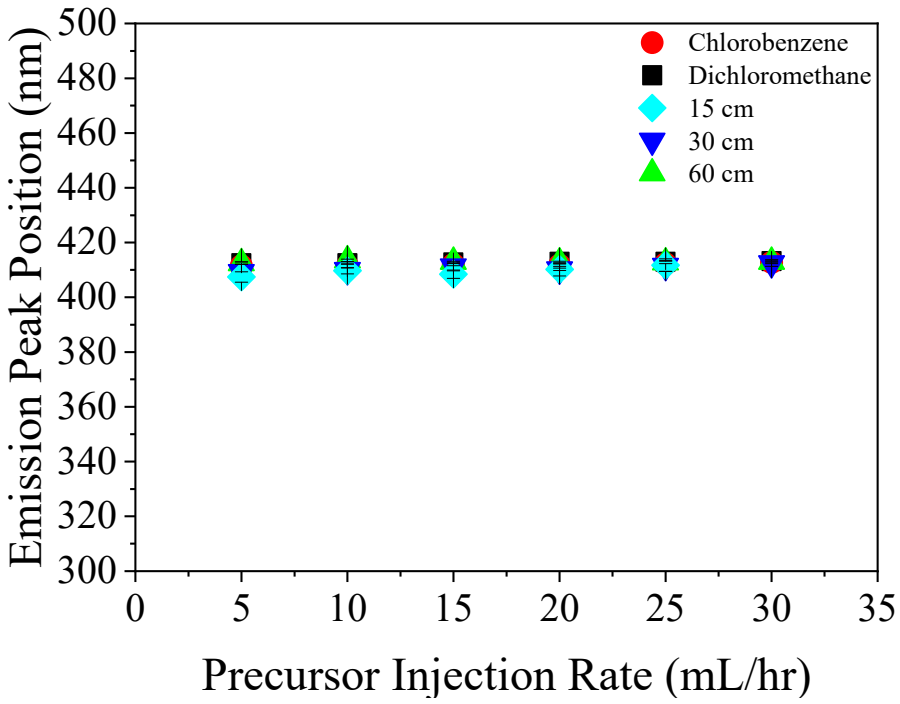

Figure S14. Comparison of emission peak position of a variety of trials. Chlorobenzene and dichloromethane samples were created with Q_{anti} held constant at 1200 mL/hr and 15 cm reactor tube lengths. The variable tube length trials were conducted with toluene as the antisolvent and Q_{tol} was a constant 1200 mL/hr.

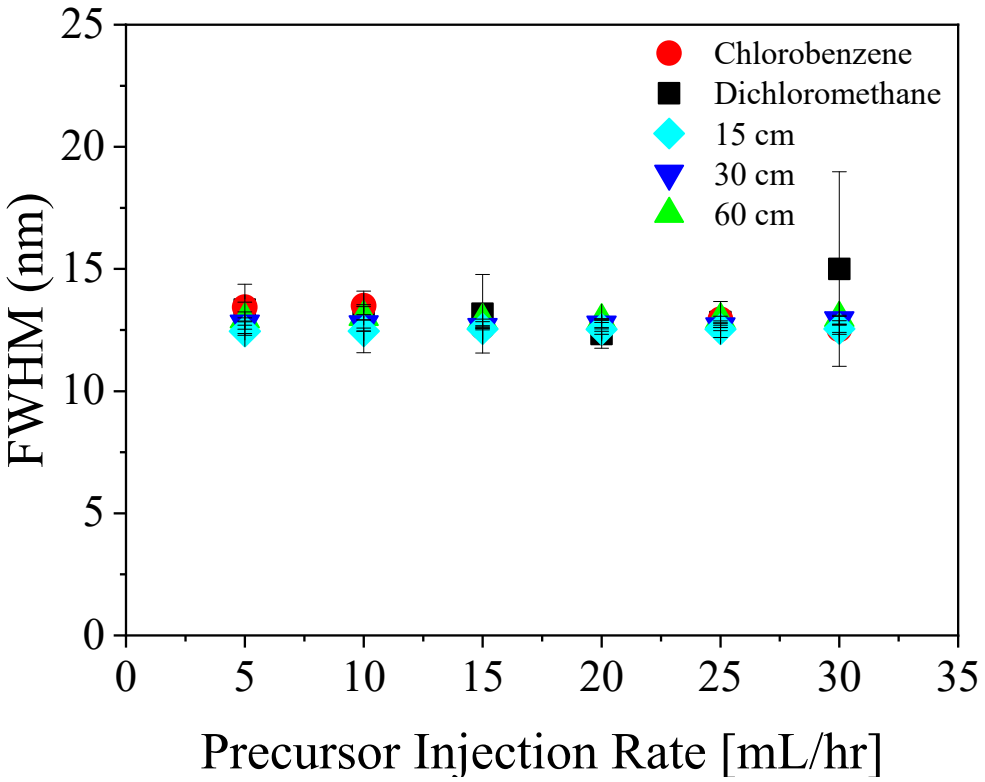

Figure S15. Comparison of FWHM of emission of a variety of trials. Chlorobenzene and dichloromethane samples were created with Q_{anti} held constant at 1200 mL/hr and 15 cm reactor tube lengths. The variable tube length trials were conducted with toluene as the antisolvent and Q_{tol} was a constant 1200 mL/hr.

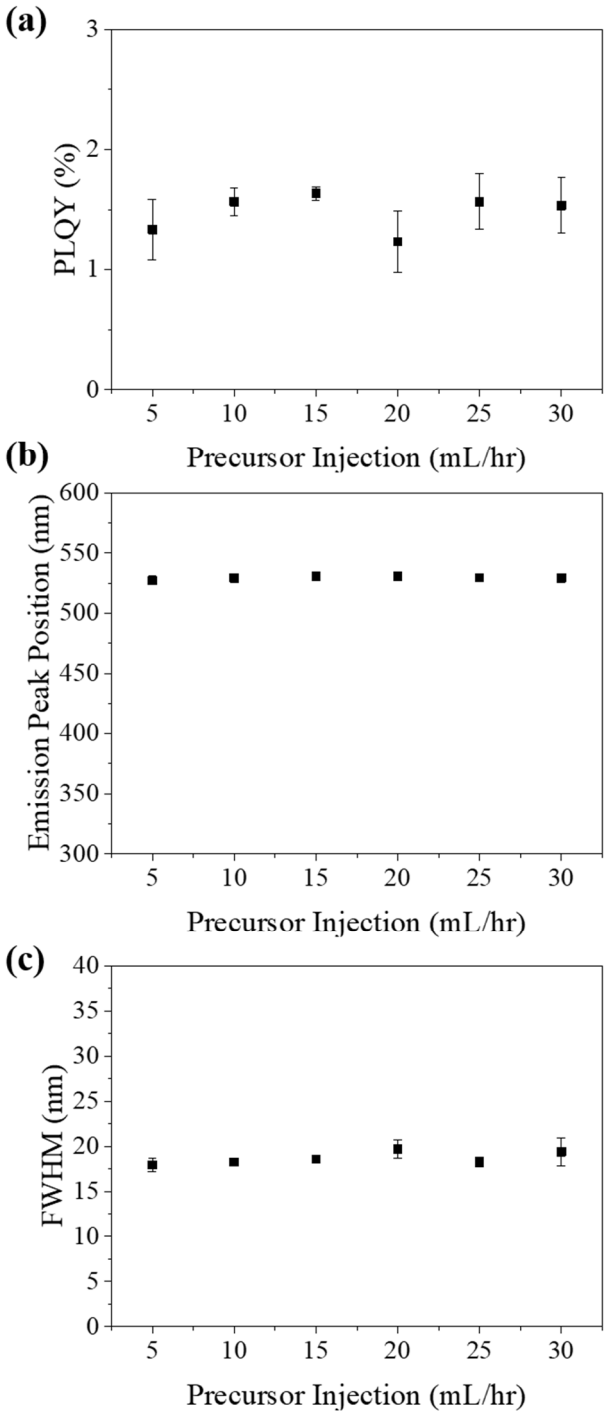

Figure S16. (a) PLQY, (b) emission peak position, and (c) FWHM of $(PEA)_2PbI_4$ NPLs produced in 15 cm reactor tube with a constant 1200 mL/hr toluene (antisolvent) flowrate and precursor solution flowrates ranging from 5-30 mL/hr (see x axis).

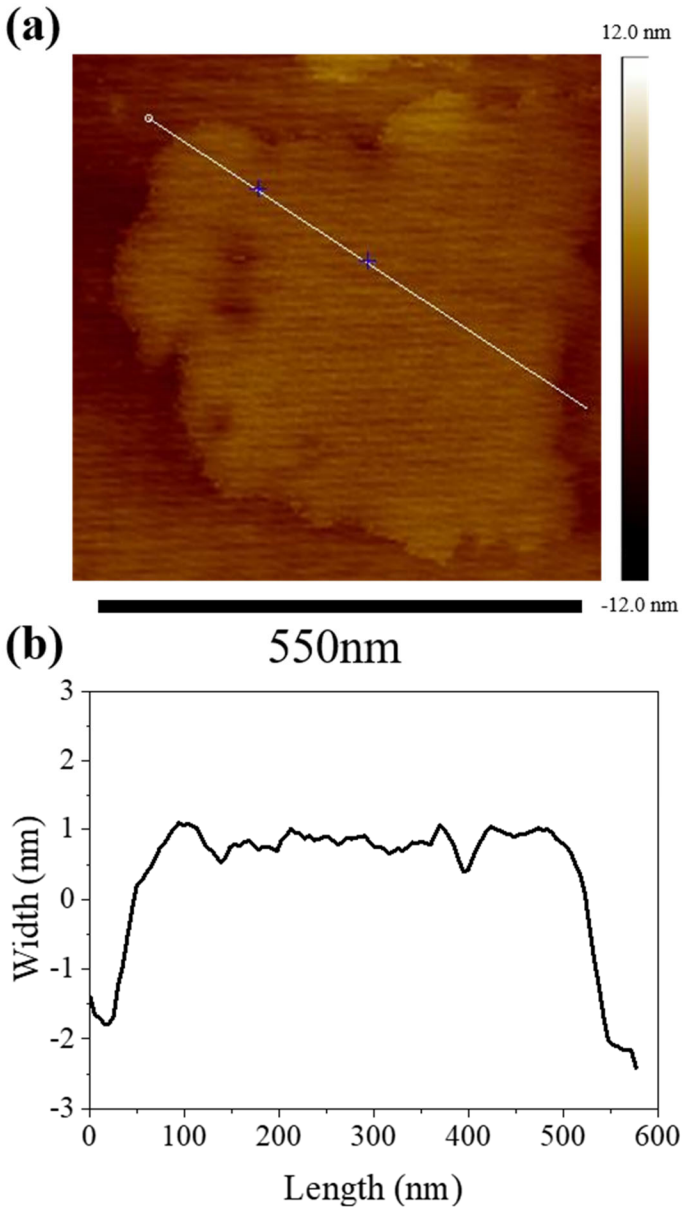

Figure S17. (a) AFM image of $(PEA)_2PbBr_4$ NPL made in a 15cm reactor tube at Q_{tol}=1200 mL/hr and $Q_{precursor}$=5 mL/hr. (b) Cross-sectional analysis of the line indicated in (a).

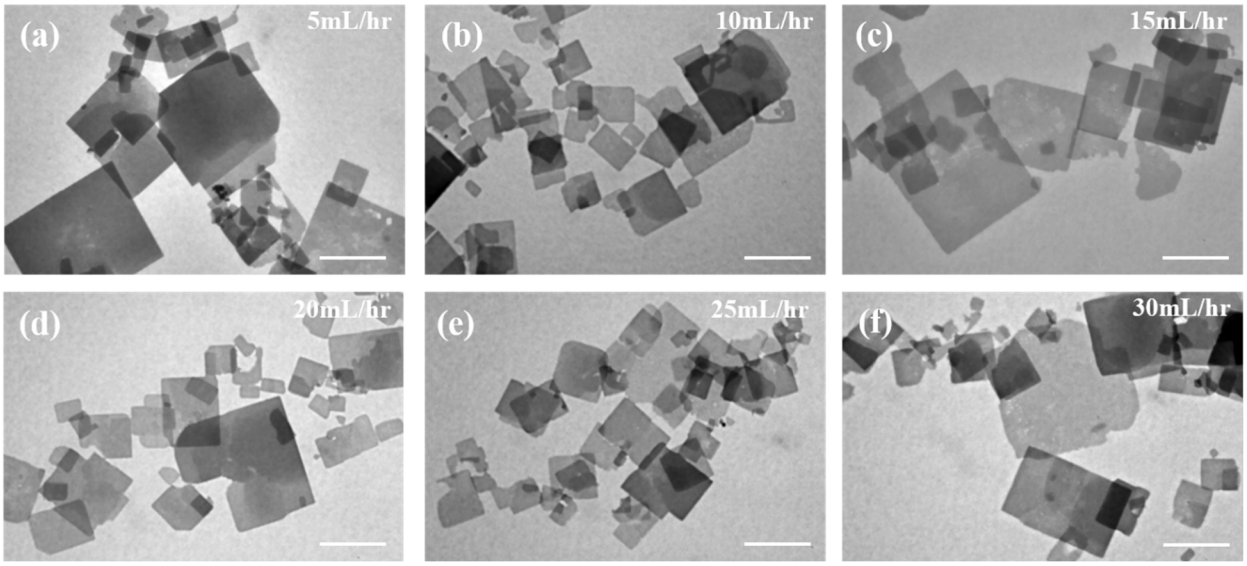

Figure S18. TEM images of $(PEA)_2PbBr_4$ NPLs produced with a precursor solution concentration of 0.04M $PbBr_2$ and 0.08M PEABr (double concentration in DMF) in a 15cm reactor with toluene as the antisolvent at a constant flowrate of 1200 mL/hr and precursor injection rates ranging from 5-30 mL/hr, that is, (a) 5 mL/hr, (b) 10 mL/hr, (c) 15 mL/hr, (d) 20mL/hr, (e) 25 mL/hr, and (f) 30 mL/hr, respectively.

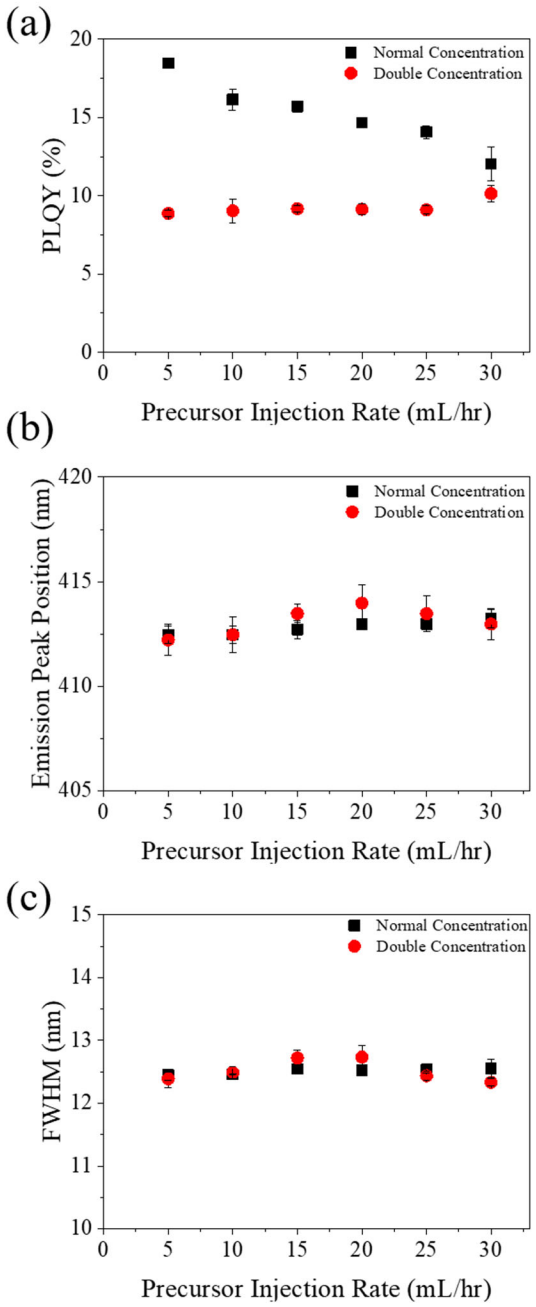

Figure S19. (a) PLQY, (b) emission peak position, and (c) FWHM of $(PEA)_2PbI_4$ NPLs produced with precursor solutions of 0.02M $PbBr_2$ and 0.04 PEABr (normal concentration in DMF) and 0.04M $PbBr_2$ and 0.08M PEABr (double concentration in DMF) in a 15 cm reactor tube with a constant 1200 mL/hr toluene (antisolvent) flowrate and precursor solution flowrates ranging from 5-30 mL/hr (see x axis).

Reference

1. Weidman, M. C.; Seitz, M.; Stranks, S. D.; Tisdale, W. A., Highly tunable colloidal perovskite nanoplatelets through variable cation, metal, and halide composition. *Acs Nano* **2016,** *10* (8), 7830-7839.