

Supporting Information

Surface ligation stage revealed through polarity-dependent fluorescence during perovskite nanocrystal growth

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Experimental Details:

Materials:

All reagents were used as received: lead iodide (99.999%, trace metals basis, Sigma-Aldrich), methylammonium iodide (MAI, $\geq 99\%$, anhydrous, Sigma-Aldrich), octylamine (99%, Sigma-Aldrich), oleic acid (90%, technical grade, Sigma-Aldrich), and hexane ($\geq 95\%$, laboratory reagent grade, Sigma-Aldrich).

Synthesis:

350 mg of PbI₂ and 95 mg of MAI were combined with 40 mL of hexane in a glass test tube and suspended in an ultrasonication bath to provide constant mixing of the precursors. The reaction was initiated with the addition of 100 μ L octylamine and 200 μ L oleic acid. A recirculating chiller in a closed-loop configuration with an aluminum block was used to maintain a temperature of 22 °C in the ultrasonication bath.

Sampling and characterization:

HDPE syringes were used to withdraw two separate 0.6 mL aliquots of reaction mixture at discrete time points. One of each aliquot was filtered through a 0.45 μ m syringe filter (VWR) with either a polytetrafluoroethylene (PTFE) or nylon membrane and into a 1 mm path length quartz cuvette (Starna Cells, 1-Q-1). Following the 25 minute mark a 1.0 μ m PTFE pre-filter (Whatman Resist) was used in conjunction with the 0.45 μ m filter. Following 60 minutes an additional 5.0 μ m filter (Whatman Resist) was also added. 2 mL of reaction mixture was used for these aliquots.

TEM images were obtained with an FEI Titan 80-300 kV STEM equipped with a C_s image corrector operating at 300 kV. NCs were grown for 120 minutes and then filtered through either PTFE or nylon filters into HDPE centrifuge tubes for transport. Sample preparation involved diluting by a factor of 2x with hexane before being immediately drop-cast onto lacey carbon TEM grids with an ultrathin carbon support film. No additional sample preparation was used prior to imaging. 540 particles were counted and used for statistics on PTFE-filtered NCs, while 592 particles were counted for nylon-filtered NCs.

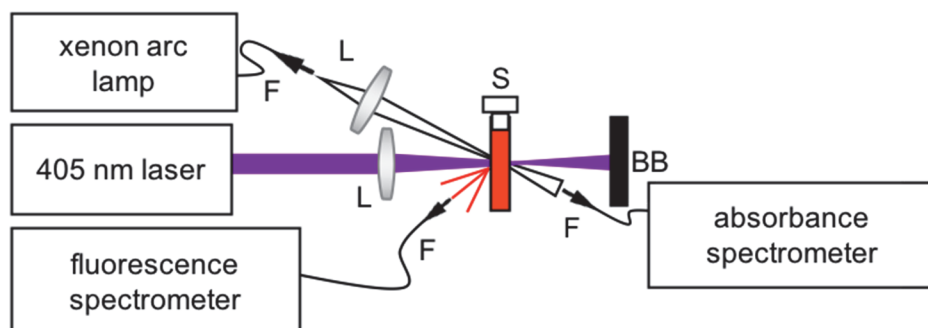


Figure S1: Apparatus used to measure simultaneous absorbance and fluorescence. Light from a xenon arc lamp was directed to the sample (S) using a fiber optic cable (F) (Thorlabs, BFY600HS02) and lens (L). Transmitted light was collected with a fiber optic cable (Thorlabs, M92L01). A 405 nm laser (Thorlabs, CPS405) was used as the excitation source for fluorescence, with the transmitted beam blocked (BB). Fluorescence was collected with a fiber optic cable (Thorlabs, M28L01) off the front face of the cuvette to minimize inner filter effects. Spectra were recorded using two Ocean Optics Flame-T-UV-VIS spectrometers and a homebuilt interface software developed in python.

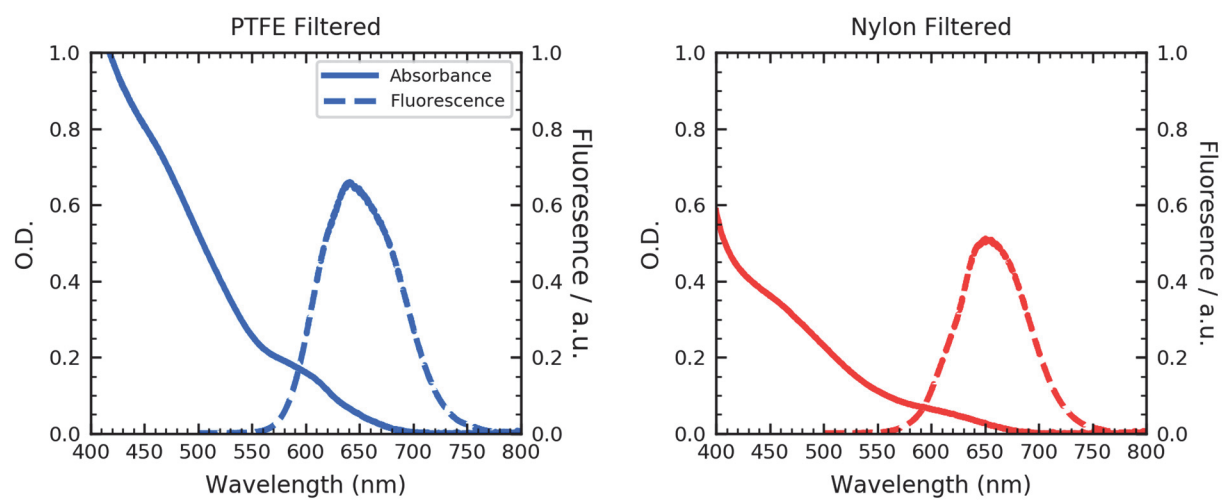


Figure S2: Absorbance (solid) and fluorescence (dashed) of NCs grown for 120 minutes and analyzed with TEM.

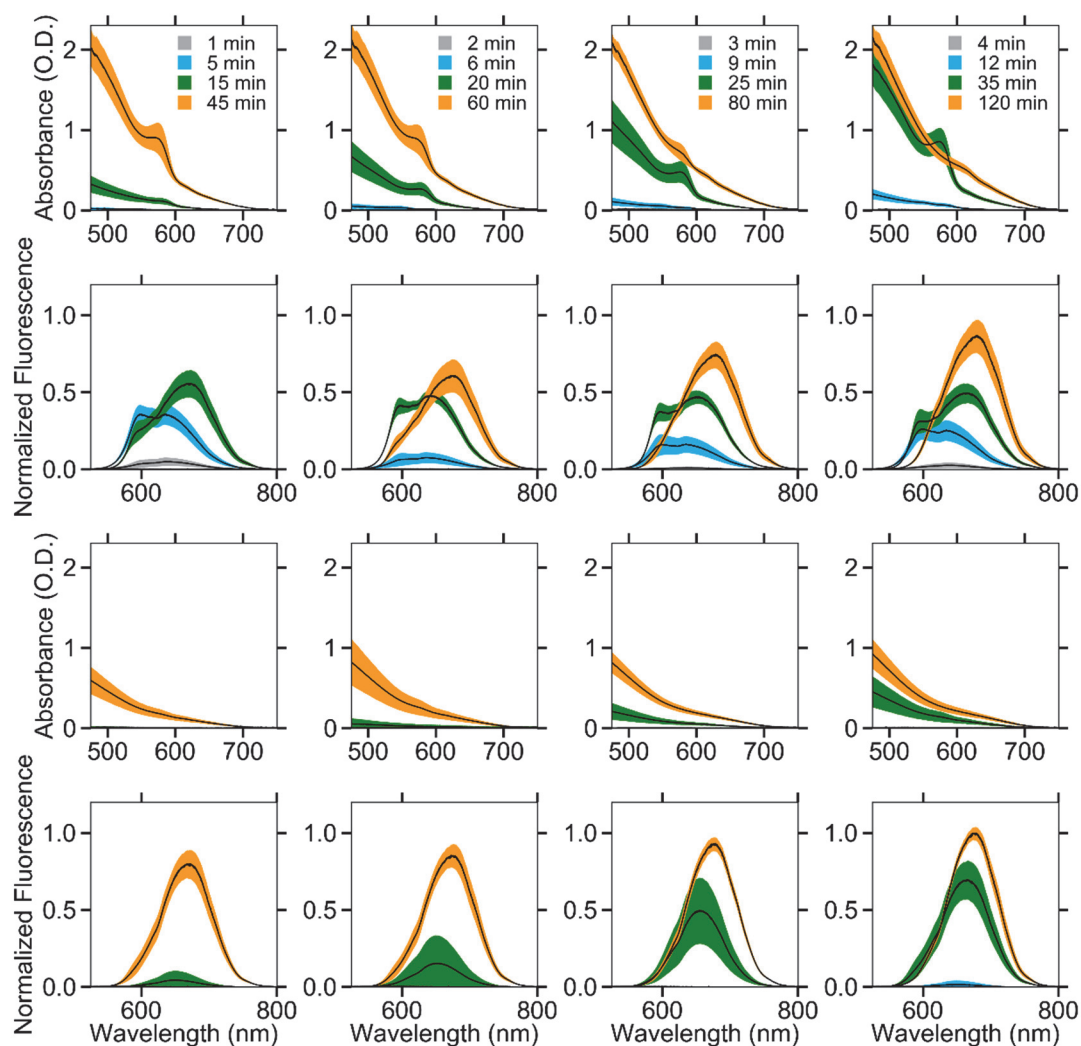


Figure S3: Average absorbance and fluorescence of five syntheses (lines) and their standard deviations (shaded), analogous to Figure 2. Absorbance and fluorescence of PTFE-filtered NCs shown in rows 1 and 2, respectively, absorbance and fluorescence of nylon-filtered NCs shown in rows 3 and 4, respectively.

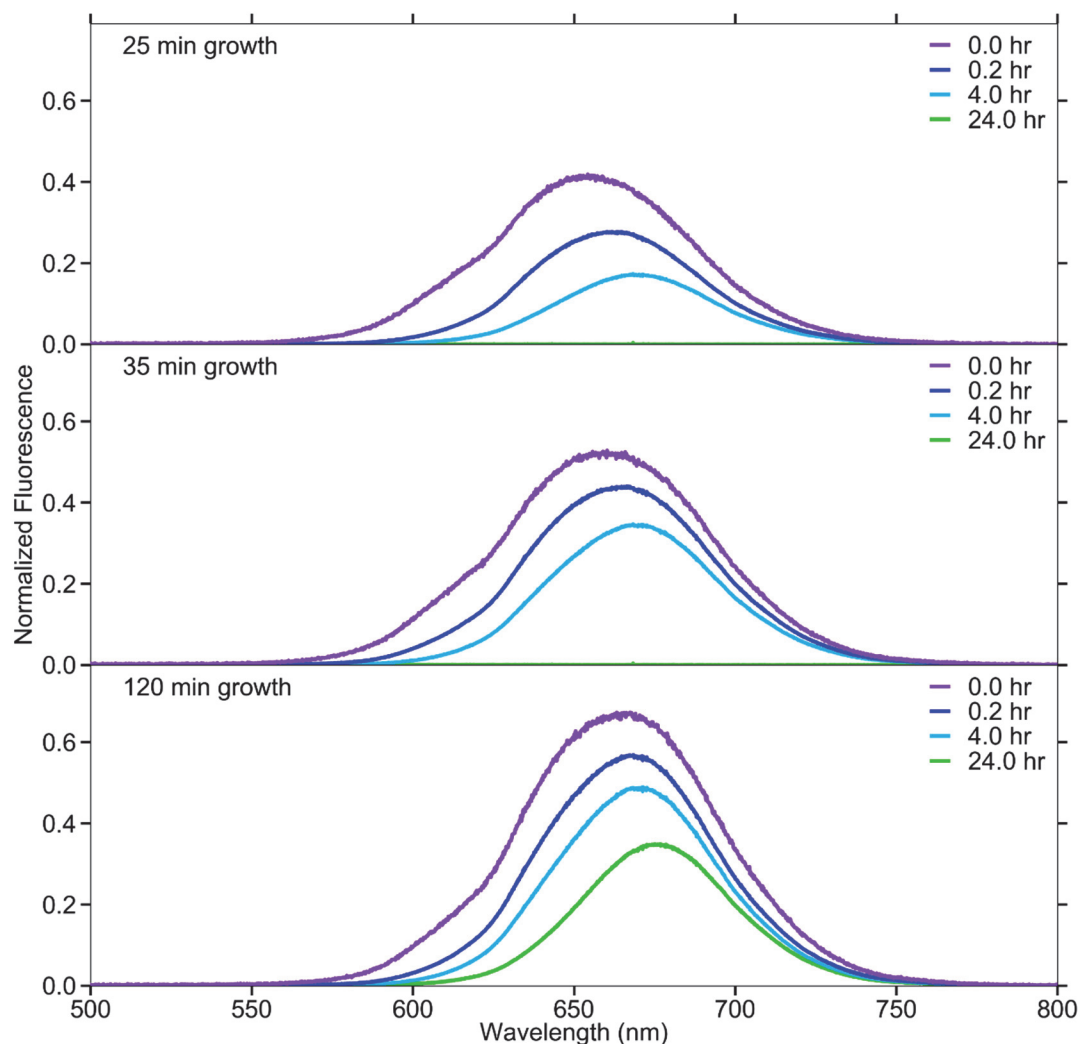


Figure S4: Fluorescence spectra measured during aging of NCs filtered through nylon after 25 minutes (top), 35 minutes (middle), and 120 minutes (bottom) of growth. Unlike NCs filtered through PTFE, all samples filtered through nylon exhibit similar aging regardless of growth time. We attribute this to the polar nylon filter removing significant amounts of free organic ligand, disturbing the equilibrium and causing weakly bound octylamine to detach from the surface over time, destabilizing the NCs.

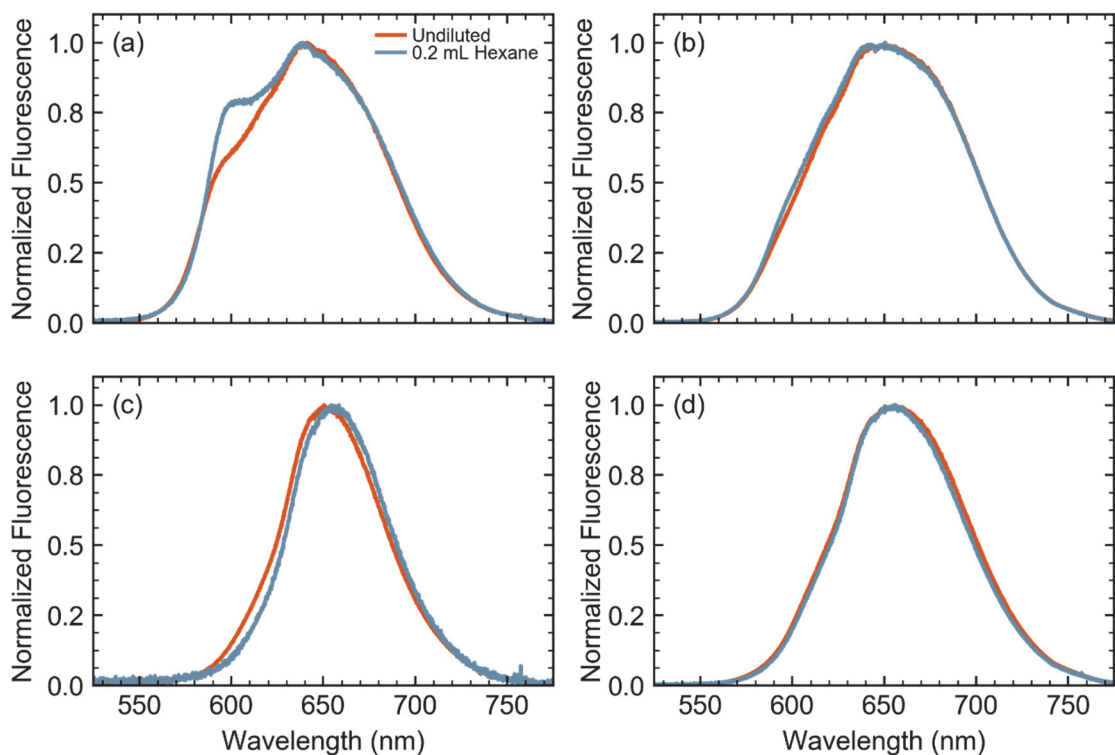


Figure S5: Spectra before (orange) and 1 minute after (blue) diluting 0.07 mL of filtered reaction mixture with 2 mL of hexane. PTFE-filtered NCs grown for 20 minutes (a) and 35 minutes (b) pictured at top. Nylon-filtered NCs grown for the same time points (c,d) shown at bottom. The absence of a feature at 600 nm after dilution of nylon-filtered NCs indicates that the change in rate of fluorescence intensity increase after 20 minutes of growth is not the result of an aggregative nucleation process.