

Supplementary Material for

Automated Microfluidic Platform for Systematic Studies of Colloidal Perovskite Nanocrystals: Towards Continuous Nano-Manufacturing

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S-1 LabVIEW Process Flow Chart

The translation stage, syringe pumps, fiber-coupled light sources, and fiber-coupled miniature photospectrometer are coordinated through automated LabVIEW controls, shown in Figure S1. To begin automated controls, the user specifies the desired inputs including condition flow rates, syringe dimensions, integration times, number of spectra to average (10 by default), flow regime (single- or multi-phase), desired sampling timespan (multi-phase only), and approximate sampling port positions. The system starts operation by first establishing communications with and setting a neutral condition for each of the hardware components. The system then undergoes stabilization and port alignment steps. To conduct these processes first, toluene is manually injected into the reaction tubing. The translation stage then runs eight full passes along the custom-machined aluminum tracks with the embedded Teflon reactor. During the initial 8 passes, the translation stage briefly stops at each sampling port to reduce the setup movement within the newly assembled system during later sampling. The system then detects the precise stage location for optimal sampling at each port. To do this, it turns on the 365 nm LED then samples 20 evenly distributed points across a 1 mm range around the pre-determined approximate port location until a local maximum spectral intensity at 350 nm is found for each port. This position is then saved and used as the specific port location for later sampling. If indicated, the system then collects light and dark references on toluene for each light source at their respective integration times at each port.

After the first flowrate condition is set, based on the user-defined system volume for the furthest sampling port, the system waits for three residence times to reach equilibrium. The translation stage then starts sampling from the port closest to the junction (either T or custom-designed cross) by triggering the light source toggling system at each port location. This process is repeated for each condition until all desired test parameters have been set and sampled. The system then undergoes shut down procedures by halting all syringe pumps and shutting off light sources before ending the script operation.

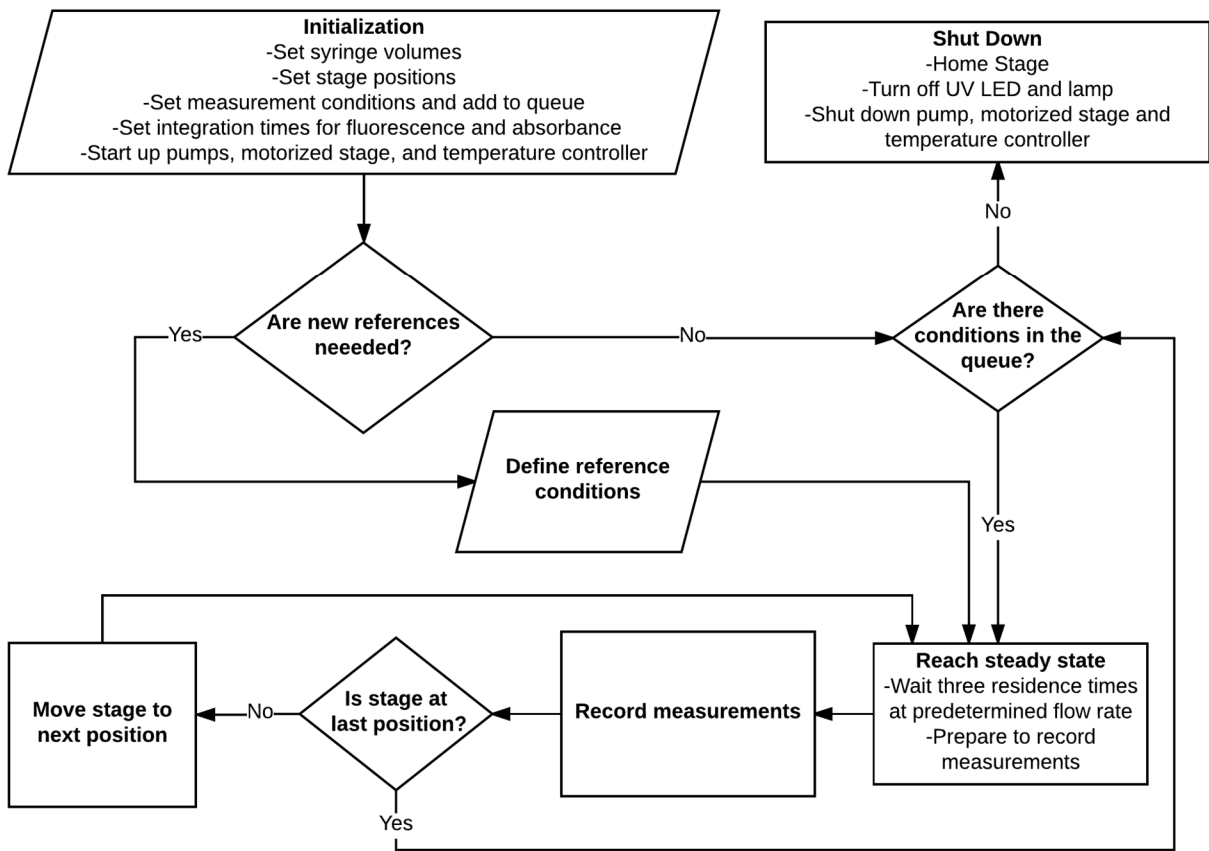


Figure S1. Process logic flow chart for the automated sampling system, run through LabVIEW Virtual Interfaces (VI's). The initialization block also includes an optional eight passes of the translational stage for stabilization followed by the port detection and alignment.

S-2 Port-Flow Cell Alignment over Thirty Stage Passes

The port alignment and sampling process, detailed in S-1, results in precise absorption and PL measurements for at least thirty passes – *i.e.* sampling conditions. Figure S2 shows a characterization of this consistency by sampling the measured light source intensities at each port after the alignment and port detection processes. Furthermore, it demonstrates that scaling these intensities across each of the individual ports results in highly uniform spectral measurements throughout the reaction system. During experiments, port alignment was performed after, at most, every thirty tested sample conditions including toluene references.

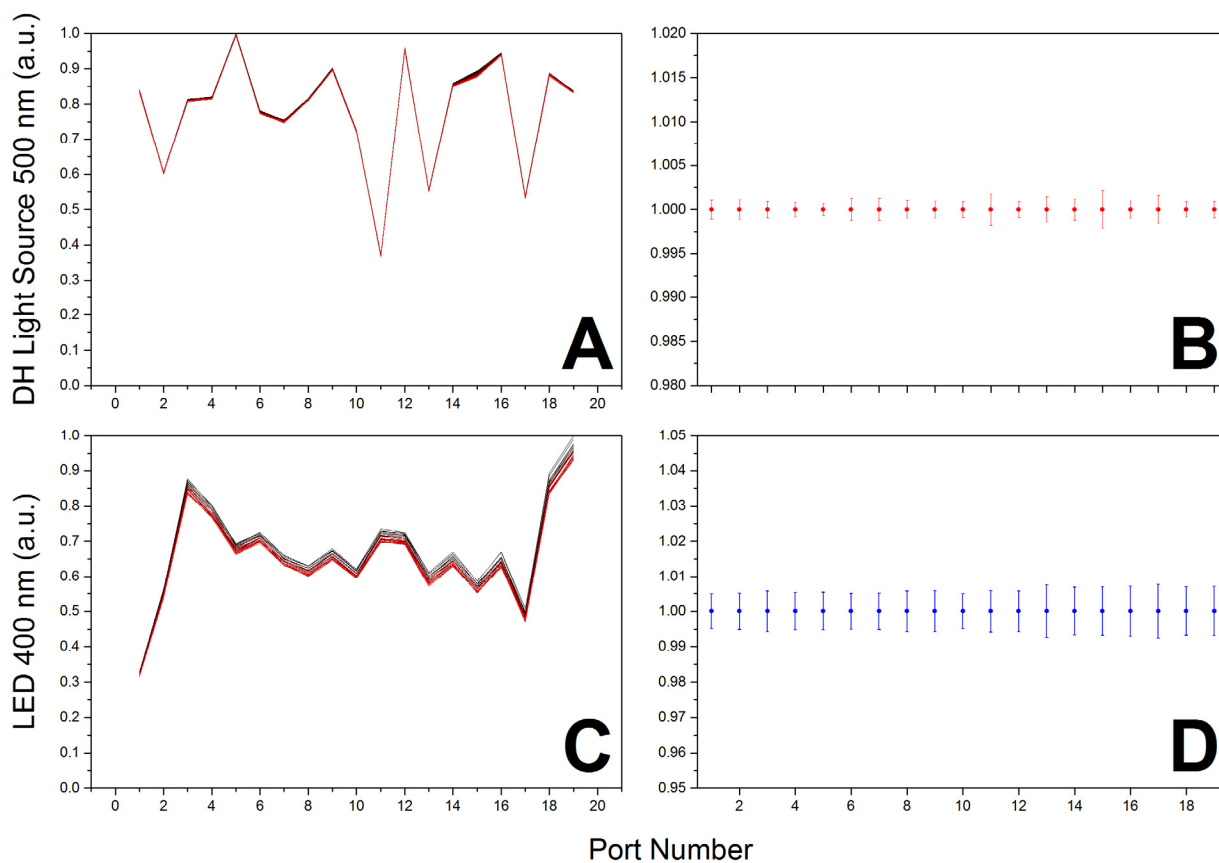


Figure S2. Demonstration of sampling consistency across stage movement. (A) Raw spectral data normalized on the highest measured intensity for the Deuterium-Tungsten light source at 500 nm across all ports and (B) scaled by port over 30 full reactor length passes of the translating flow cell. (C) Raw spectral data normalized on the highest measured intensity for the 400 nm LED at 400 nm across all ports and (D) scaled by port over 30 full reactor length passes of the translating flow cell. Toluene was used as the working fluid within the Teflon microreactor. Error bars indicate a 95 % confidence interval.

S-3 Pathlength Correction by Port

To account for variations in the sampling pathlength at each port location due to factors such as irregular tube placement or minor deformation, pathlength corrections were applied to each port within every alignment cycle. By performing this scaling operation for a synthesized CsPbBr₃ QD sample in toluene across different ports, data collected across the reaction system can be directly compared. Scale factors were determined for base-line corrected PL and absorption curves and applied to experimentally measured absorption and PL spectra processed in a comparable manner. Sample data from the pathlength correction process is shown in Figure S3.

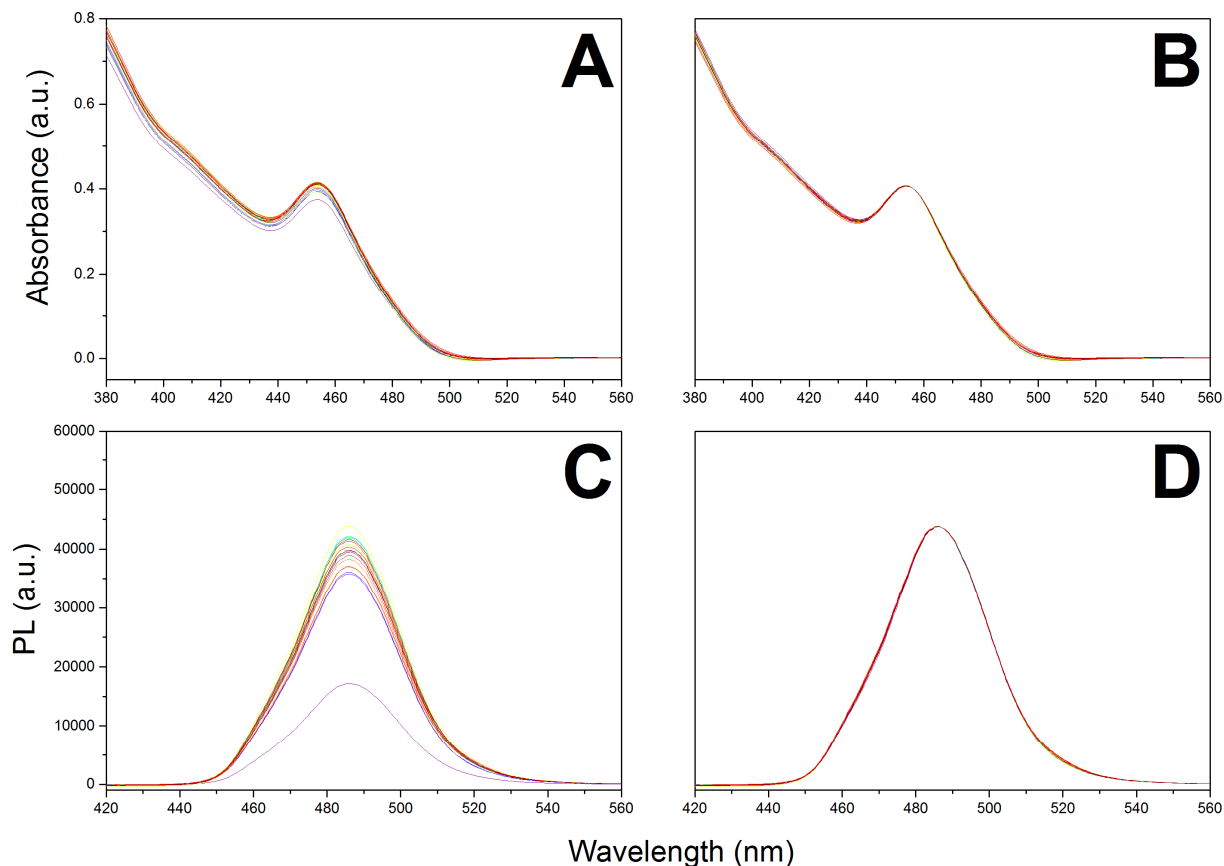


Figure S3. Demonstration of scalar pathlength correction by port location. Absorption spectra of a pre-synthesized CsPbBr₃ QD sample in toluene over all twenty sampling ports (A) without and (B) with the pathlength correction. PL spectra of a pre-synthesized CsPbBr₃ QD sample in toluene over all twenty sampling ports (C) without and (D) with the pathlength correction. The resulting scalar correction values averaged over five replicates were applied to spectra obtained during synthesis tests for each system configuration.

S-4 Plug Detection Methods for Variable Fluid Velocities

Due to the required integration and script execution times (on the order of milliseconds), there is an inherent limitation on the number of spectra that may be obtained within a single moving plug. At average plug velocities higher than 1.1 cm/s, a plug detection method is no longer suitable for sample collection, and instead simply averaging across an evenly distributed set of samples becomes more applicable. Figure S4 shows a sample set of absorption spectra demonstrating the necessity of this distinction. By indiscriminately averaging across a slowly moving plug, the arbitrary point in which sampling is initiated becomes the sole representation of the moving plug, and it does not effectively characterize the bulk solution within the moving liquid plug. In applying the plug detection methods to a quickly moving plug, local variance – see section S-5 – does not meaningfully represent the sample. Therefore, in order to efficiently and accurately perform sampling on multi-phase systems at variable flow rates, a combination of the two approaches is required.

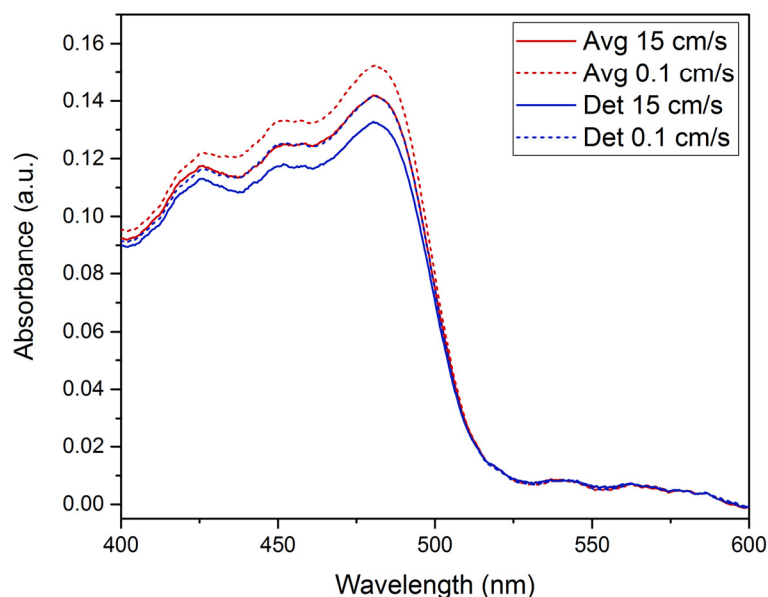


Figure S4. Sample absorption spectra of saturated fluorescein in water obtained with different spectra selection methods and average fluid velocities. Averaged spectra (Avg) were taken across 60 continuously collected samples over ≥ 1 s, and plug detection algorithm spectra (Det) were taken from the ten estimated optimal spectra, as dictated by local variance calculations, within the same 60 samples. Averaged spectra were used to evaluate multi-phase conditions with average fluid velocities > 1.1 cm/s, and the plug detection algorithm was applied to conditions ≤ 1.1 cm/s. An integration time of 15 ms was used for all spectra.

S-5 Plug Detection and Spectra Selection

Figure S5 shows the single intensity spectral data for a microscale multi-phase flow system over time for use in sample selection in the plug detection process. For both absorption (Figure S5A) and PL (Figure S5B) data, the system is characterized by a baseline reading within the gas phase, a sharp peak at the gas-plug interface, and a small plateau region within the plug itself. The plug detection script first discounts extrema associated with the carrier phase and interface, then it finds the ten samples with the lowest local (five point) variance, which are then averaged to obtain each tested condition spectra.

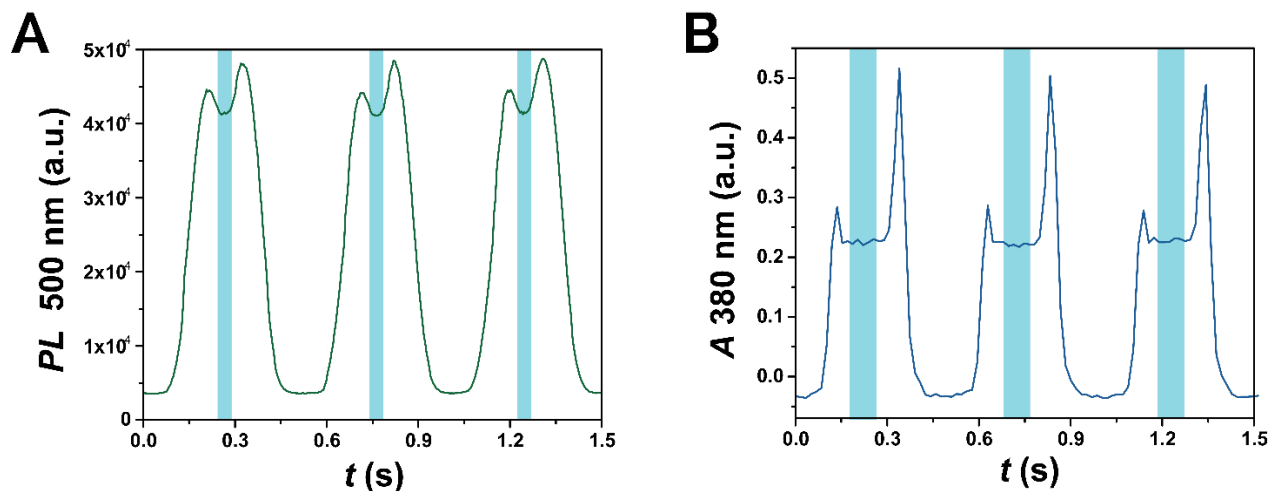


Figure S5. Single wavelength spectra intensities with optimal sample time spans for (A) photoluminescence at 500 nm and (B) absorbance at 380 nm. Spectra were collected at a single sampling port, and conditions correspond to those shown in Fig. 4 (Gas phase: pressurized nitrogen (10 psig) at $Q_G=278 \mu\text{L}/\text{min}$; liquid phase: toluene containing CsPbBr₃ QDs at $Q_L= 185 \mu\text{L}/\text{min}$). Integration times of 4 ms and 15 ms were used for PL and absorption spectra, respectively.

S-6 Sample from Perovskite Synthesis in Flow

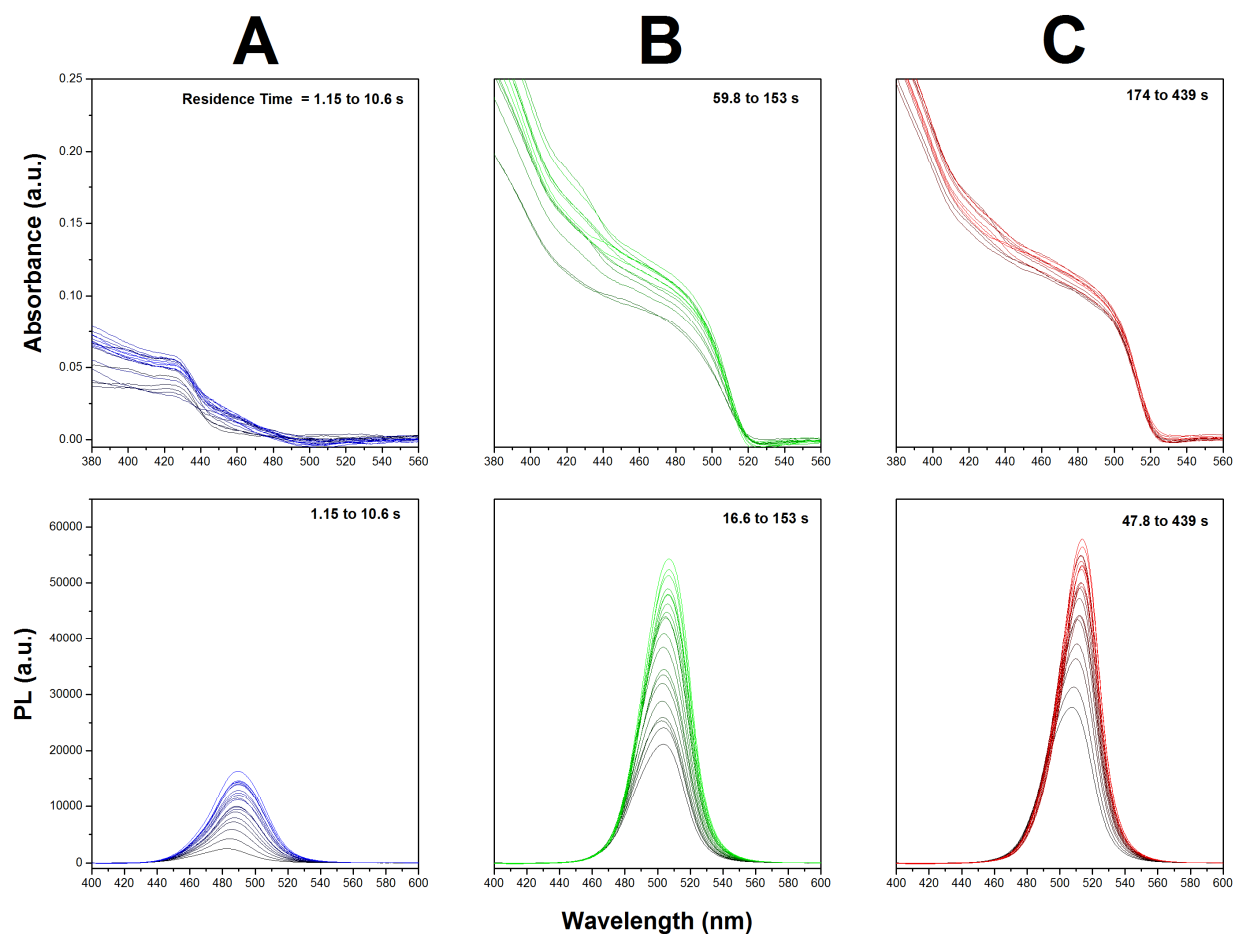


Figure S6 Sample absorption and photoluminescence spectra collected within a single pass of the translating flow cell for total flow rates of (A) 1220, (B) 85, and (C) 29 $\mu\text{L}/\text{min}$ in a multi-phase flow CsPbBr₃ synthesis. Note that absorption spectra below the detection limit are excluded.

S-7 TEM Image of In-Flow Synthesized Perovskite QDs

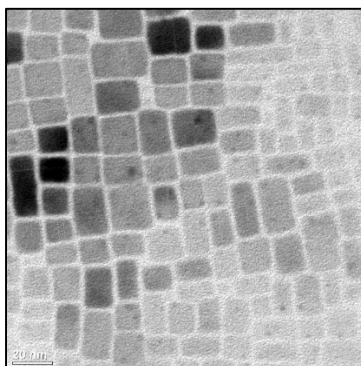


Figure S7 Scanning Transmission Electron Microscopy (STEM) image of a sample of in-flow synthesized CsPbBr₃ QDs using the multi-phase flow format ($Q_G=465$; $Q_1=268$; $Q_2=42$ $\mu\text{L}/\text{min}$) collected on the JEOL 2000FX through the Analytical Instrumentation Facility (AIF) of North Carolina State University. TEM sample was prepared by precipitating the crude perovskite solution with γ -butyrolactone, redispersion in toluene, then drop-casting onto a copper TEM grid (Ted Pella Inc., 200 Mesh Carbon Film).

Supplementary Movie

Movie M-1 Port alignment process. The translation stage positions the flow cell along each of the twenty sampling ports. Using the 365 nm LED, sampling positions over a 1 mm range in 0.05 mm increments are tested for each port, and the optimal position is saved and used for sampling during further studies with the modular microreactor.