

Supporting Information

An Automated Flow Chemistry Platform to Decouple Mixing and Reaction Times

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S.1 – Chemical List

Lead (II) oxide (>99.9% trace metal basis, 211907), tetraoctylammonium bromide (98%, 294136), and oleic acid (technical grade, 90%, 364525) were purchased from *Millipore Sigma*. Cesium hydroxide 50 wt% solution in water (99.9% trace metal basis, AC213601000), toluene (extra dry over molecular sieves, 99.85%, AC364410025), quinine sulfate dihydrate (AC418780050), fluorescein (laser grade, 99%, AC410620010), sodium hydroxide (pellets, S320), and potassium iodide (>95%, S25493) were purchased from *Fisher Scientific*. Sulfuric acid (60%, 098361) was purchased from *Oakwood Chemical*. The toluene used in all synthesis studies was dried further over fresh molecular sieves. All other chemicals were used as received.

S.2 – Quenching Spectra

Fluorescein quenching studies were conducted using the custom three-port optical flow cell connected directly to the 0.25 mm inner diameter (ID) Teflon tubing (fluorinated ethylene propylene, FEP) at different tubing lengths. Fluorescein and potassium iodide solutions were combined at counter current inlets on a 0.50 mm inner diameter (1 μ L dead volume) polyether ether ketone (PEEK) T-junction (P-712, *IDEX-H&S*). All sample spectra were collected by allowing the flow to reach equilibrium (four residence times) then sampling one spectra per second continuously for 20 s. The final sample spectra was selected by averaging these 20 measurements. All quenched and unquenched fluorescein references were retaken each time the flow cell was repositioned. Example spectra are shown in **Fig. S1** with the corresponding intensity measurements used in **Eq. 4** (main text) illustrated for each spectra.

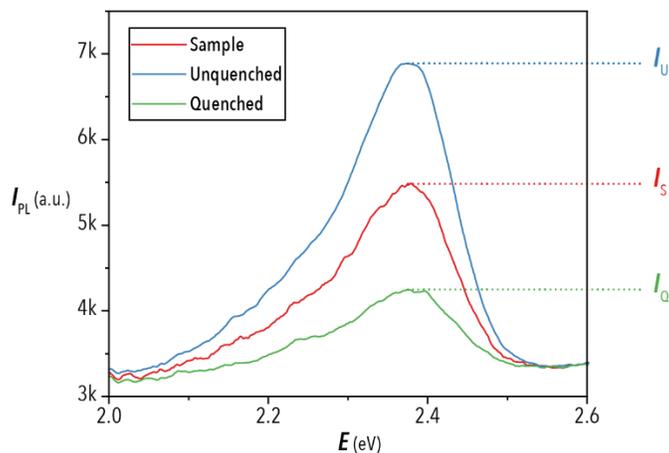


Fig S1. PL spectra of the quenched and unquenched fluorescein references with an example mixing sample measurement spectra, collected on the straight tubing at a residence time of 1.15 s and $Pe=5500$.

S.3 – Synthesis Study Reaction System

For the flow synthesis of perovskite quantum dots (PQDs), four computer-controlled syringe pumps (PHD ULTRA, *Harvard Apparatus* and Fusion 4000, *Chemyx*) were loaded with 20 ml stainless steel syringes for each of the two precursors and two oleic acid (OA) concentrations. Shown in **Fig. S2**, the two OA concentrations of each precursor are combined and mixed in a braided micromixer before entering the primary T-junction referenced throughout the study. To ensure stable flow, the flow ratio at any tee-junction never exceeded 1:5. Sampling and waste lines used a 0.75 mm ID FEP tube.

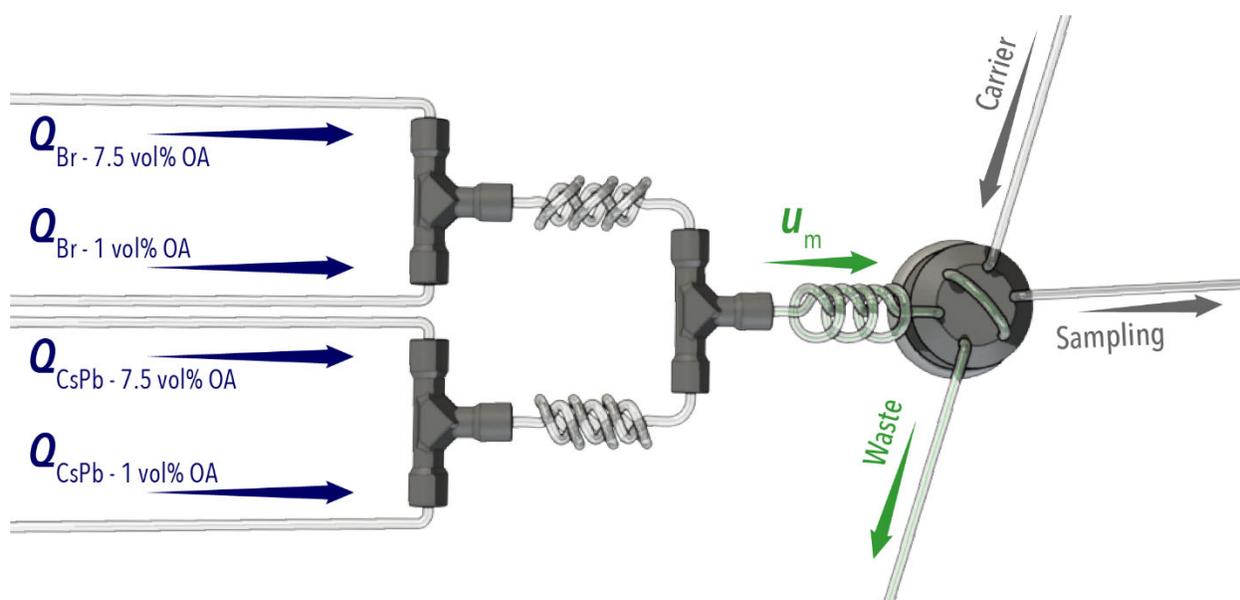


Fig S2. Illustration of the developed automated flow chemistry platform used in PQD synthesis study.

S.4 – PQD Synthesis Reaction Time Estimate

To select a suitable residence time for the PQD synthesis study, the synthesis was conducted at three different Pe values with a constant OA volume fraction of 4.25 vol%. The sampling reactor flow velocity (u_R) was varied to attain four different residence times at each Pe condition. Shown in **Fig. S3**, optical spectra begin to converge as the residence time in the sampling flow reactor (t_R) approaches 1 min. Therefore, all flow experiments were conducted with a t_R of 1 min. Note that these experiments are meant to serve as an approximation of the relevant reaction time and not as a comprehensive kinetic study. Mass-transfer rates will vary in the reactor segment under different u_R values, which could potentially deviate from the measurements of a constant mass-transfer system.

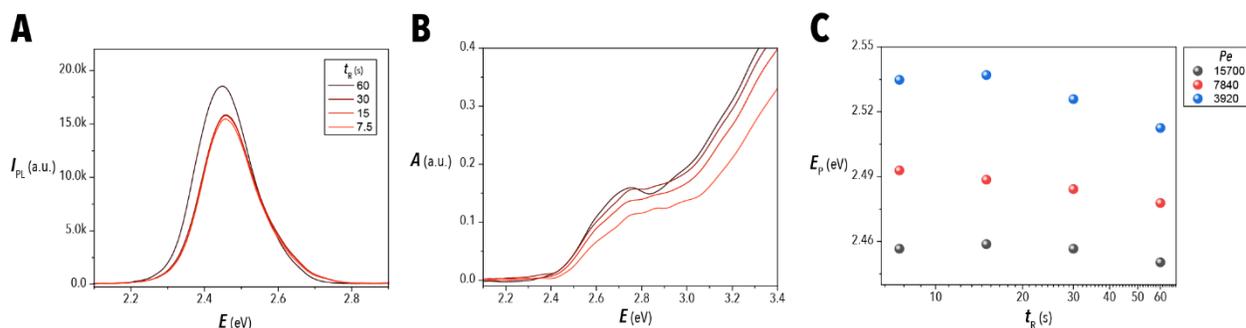


Fig S3. (A) Photoluminescence and (B) absorption spectra of PQDs synthesized in flow using the same Pe at the point of mixing but with varying u_R , corresponding to four different residence times and (C) the subsequently measured E_P with two additional Pe values at the point of mixing for all four residence times.

S.5 – Quantum Yield Calculations

Relative photoluminescence quantum yield (PLQY) of the in-flow synthesized PQDs was calculated using a solution of quinine sulfate in 0.05 M sulphuric acid according to the equation

$$\Phi_{PL} = \frac{\Phi_R I_{Int,S} A_{365nm,R} \eta_S^2}{I_{Int,R} A_{365nm,S} \eta_R^2} \quad (S1)$$

where S and R denote PQD sample and quinine sulfate reference, respectively. Φ is the PLQY, I_{Int} is the integral of the PL emission spectra, A_{365nm} is the absorbance at 365 nm,

and η is the refractive index of the solvents. Property constants of 0.546, 1.337, and 1.506 were used for Φ_R , η_R , and η_S , respectively. [1-3]

S.6 – PQD Nanocrystal and CsPbBr₃ Concentration Calculations

Stoichiometric concentrations of CsPbBr₃ were calculated according to the following relation, as adapted from De Roo *et al.* [4]

$$C_{CsPbBr_3} = \frac{(8.12 \text{ M}) \ln(10) A_{400nm}}{\mu_{400nm} L} \quad (\text{S2})$$

where A_{400nm} is the measured absorption at 400 nm, μ_{400nm} is the intrinsic absorption coefficient of PQDs in toluene at 400 nm ($8.7 \times 10^4 \text{ cm}^{-1}$, Maes *et al.* 2018) and L is the optical path length (0.23 mm). The value 8.12 M is a constant derived from the originally reported equations. The optical path length was estimated by comparing the absorption spectra of a known concentration of quinine sulfate in a 1 cm by 1 cm cuvette to that of the flow cell. Nanocrystal concentrations of PQDs were calculated using the molar extinction coefficient equation adapted from Maes *et al.* [5] in combination with the Beer-Lambert Law

$$C_{PQD} = \frac{A_{400nm}}{(2.42 \times 10^{-2} \text{ cm}^{-1} \mu\text{M}^{-1}) d^3 L} \quad (\text{S3})$$

where the nanocrystal edge length (d) is estimated from its relation to the peak emission energy according to the correlations detailed in Protesescu *et al.* [6] and as adapted below

$$d = \sqrt{\frac{\hbar^2 \pi^2}{(E_P - E_{bulk}) m^*}} \quad (\text{S4})$$

where \hbar is the reduced Planck constant, E_{bulk} is the theoretical emission energy of bulk CsPbBr₃ (2.34 eV) [6], and m^* is the reduced carrier mass ($6.5969 \times 10^{-32} \text{ kg}$) [6].

Supporting Information References

- [1] D. F. Eaton. “Reference Materials for Fluorescence Measurement”, *Pure & Appl. Chem.* 60, 1107-1114 (1988).
- [2] S. Kedenburg, M. Vieweg, T. Gissibl, and H. Giessen. “Linear refractive index and absorption measurements of nonlinear optical liquids in the visible and near-infrared spectral region”, *Opt. Mat. Express* 2, 1588-1611 (2012).
- [3] G. M. Hale and M. R. Querry. “Optical constants of water in the 200-nm to 200- μ m wavelength region”, *Appl. Opt.* 12, 555-563 (1973).
- [4] J. De Roo, M. Ibáñez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, et al. “Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals”, *ACS Nano* 10, 2071-2081 (2016).
- [5] J. Maes, L. Balcaen, E. Drijvers, Q. Zhao, J. De Roo, A. Vantomme, et al. “Light Absorption Coefficient of CsPbBr₃ Perovskite Nanocrystals”, *J. Phys. Chem. Lett.* 9, 3093–3097 (2018).
- [6] L. Protesescu, S. Yakunin, M.I. Bodnarchuk, F. Krieg, R. Caputo, C.H. Hendon, et al. “Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut”, *Nano Lett.* 15, 3692-3696 (2018).