Supporting Information

Continuous Biphasic Chemical Processes in a Four-Phase Segmented Flow Reactor

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S.1 – Droplet Length and Velocity Calculation

Droplet velocity (**Figure S.1**) and length were calculated using the *in situ* measured absorption intensity at 290 nm over time along with the setpoint volumetric flow rates. First, the ratio of gas to liquid flowing through the channel (R_{GL}) is measured by isolating all complete gas-liquid unit cells in the absorption data and measuring the passing time for both the gas and the liquid phase. Assuming the liquid phase is non-compressible, the total liquid flow rate in the channel (Q_L) is set equal to the sum of the setpoint flow rates:

$$Q_L = Q_T + Q_F + Q_O$$

where Q_T, Q_F, and Q_O, are the setpoint volumetric flow rates of toluene, formamide, and perfluorinated oil, respectively. The gas to liquid ratio in the microreactor may then be defined as:

$$R_{GL} = \frac{Q_{Ar} + \Delta Q_{Ar}}{Q_L}$$

where Q_{Ar} and ΔQ_{Ar} are the setpoint flow rate of argon and the difference between the setpoint flow rate and its actual flow rate in the microreactor (compressibility), respectively. By solving for ΔQ_{Ar} the total volumetric flow rate may be used to calculate the droplet velocity (u_D):

$$u_D = \frac{Q_L + Q_{Ar} + \Delta Q_{Ar}}{\pi r_C^2}$$

where r_C is the diameter of the microchannel (0.015 in). The droplet length is then calculated using the velocity and the liquid phase passing time extracted from absorption data.

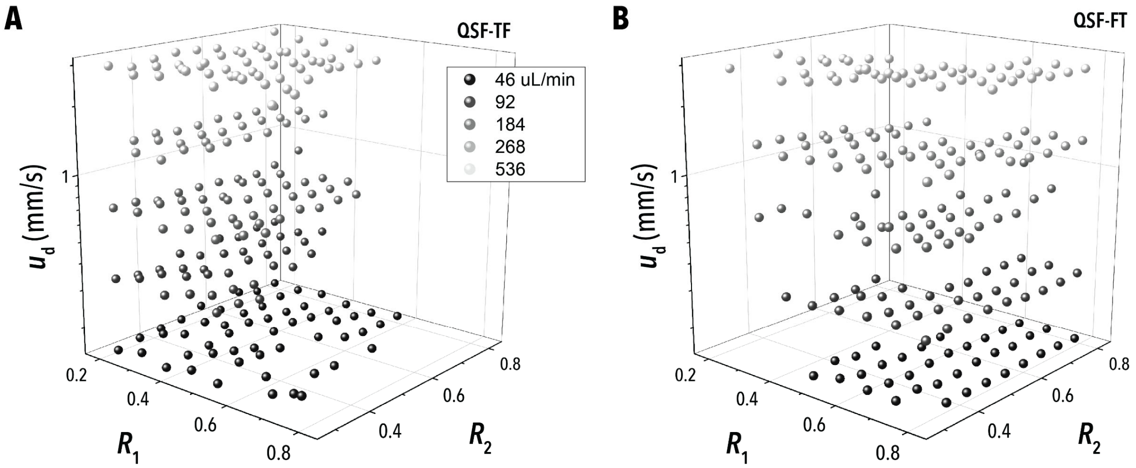

Figure S1. *Measured droplet velocity across five total volumetric flow rates over a grid of R_1 and R_2 values ranging from 0.2 to 0.8 and 0.3 to 0.8 respectively for the (A) QSF-TF and (B) QSF-FT flow configurations. Velocities are calculated from the absorption data, and unviable conditions are excluded.*

S.2 – Gas Passing Time for QSF-TF

Similar to the data shown in main text **Figure 3E**, the gas passing time as a function of the injection flow rate for the QSF-TF system is shown in **Figure S2**. Gas passing time is calculated through *in situ* obtained absorption intensity data at 290 nm collected continuously over time. Sampling rates were varied from 6 ms to 30 ms per sample depending on the total flow rate, and the sampling window was varied to capture at least three full gas-liquid unit cells per condition.

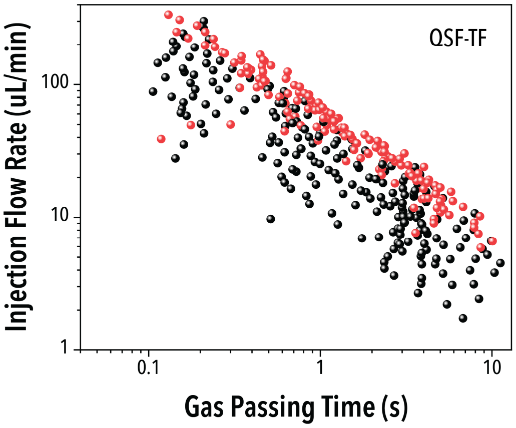

Figure S2. *Four-phase flow secondary injection species flow rate as a function of absorption measured gas phase passing time for configuration QSF-TF where conditions measured as stable are black and unstable are red.*

S.3 – Adjustable Length Spiral Microreactor

Rapid prototyping and analysis of flow reaction systems requires integration of adaptable, modular components. The spiral tubing mount implemented in this work was used to enable uniform UV illumination of the entire reaction system over a range of microreactor lengths, shown in **Figure S3**. The microchannel length is adjusted by selecting among the different paths through the spiral. It should be noted that the QSF systems used throughout the study required a constriction of the tubing immediately after the cross junction. This was achieved by tightly securing the cross junction at an angle 90 degrees to the surface and connecting tubing.

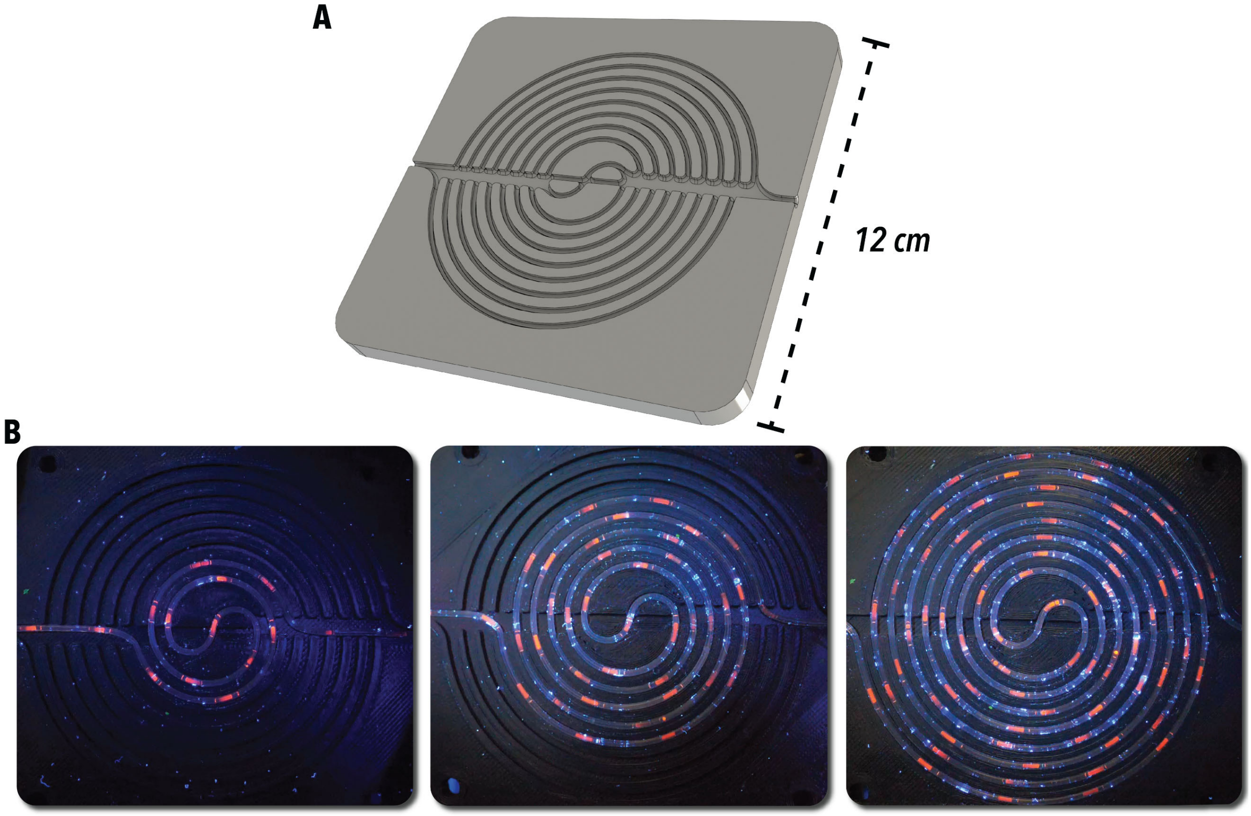

Figure S3. *(A) Illustration of the adjustable length spiral microreactor plate with (B) images of biphasic ligand exchange reactions conducted in flow under UV illumination at three sample microreactor lengths.*

S.4 – Biphasic Ligand Exchange Photoluminescence Spectra

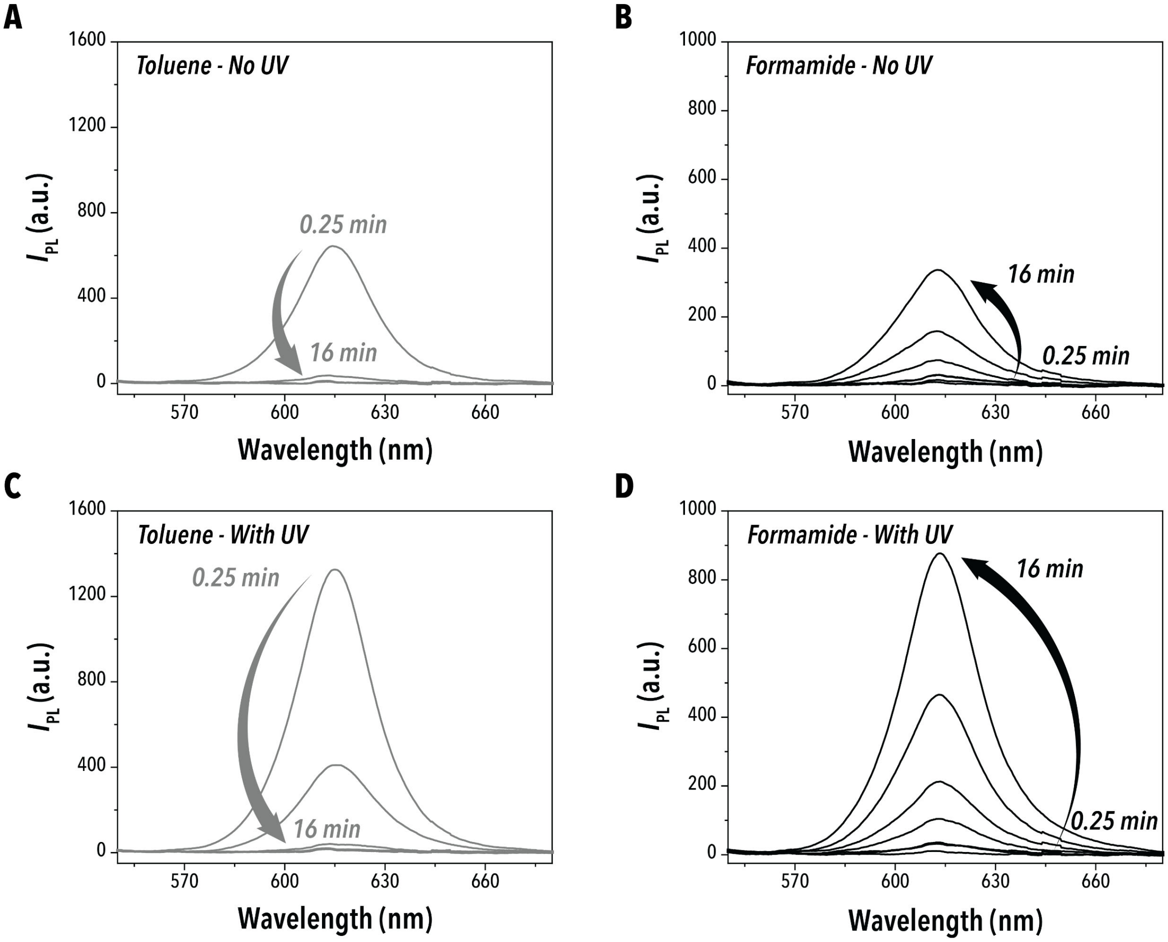

Figure S4. *Photoluminescence spectra of cadmium selenide (CdSe) quantum dots during the continuous biphasic ligand exchange in (A) the starting toluene phase and (B) the final formamide phase without UV exposure and (C, D) with UV exposure. Measured reaction times are 0.25, 0.5, 1, 2, 4, 8, and 16 min. It should be noted that the toluene solution is injected at half the flow ratio of the formamide solution, resulting in a higher CdSe concentration in the toluene phase.*

S.5 – Synthesis of Starting CdSe QDs

The initial CdSe synthesis procedure is adapted from Knauf *et al.*[1] 300 mg cadmium oxide (CdO) was converted to $Cd(OA)_2$ by heating under inert conditions to 280 °C in 10 mL of 1-octadecene (ODE) and 2 mL of oleic acid (OA). Conversion is monitored qualitatively by a change from a brown/red dispersion to a clear, colorless solution. Once converted, the solution is cooled to approximately 130 °C and kept at temperature until needed. In a triple neck flask, equipped with a thermometer and reflux condenser with an N_2 adapter under flowing N_2, 10 mL ODE and 100 mg Se^0 metal are mixed and heated slowly to 300 °C. The reaction solution turns to a yellow/orange color at ~180 °C and complete conversion is observed at 300 °C. After the Se is completely dissolved in the ODE, the reaction temperature is set to 240 °C. At this time, 12 mL of the $Cd(OA)_2$/ODE stock solution is injected into the flask via a syringe. The reaction proceeds for 8 min at the set growth temperature, monitoring temperature fluctuations. After the growth period is completed, the reaction is quenched by injecting 40 mL of chilled toluene and allowed to cool to room temperature before washing.

The as synthesized CdSe QDs were washed using centrifugation in five stages at 4300 rpm. In the first stage, acetone was added to the reaction mixture in a 1:1.5 volumetric ratio of acetone to the crude reaction solution to precipitate excess reactants, *i.e.*, $Cd(OA)_2$ or Se^0. After discarding the solid precipitate from stage one, the second stage is collected through precipitation of the CdSe QDs that remain in the stage 1 supernatant by addition of methanol in a 1:10 volumetric ratio of methanol to QD solution. The third stage is a series of dispersions followed by precipitation. The solid CdSe QDs is dispersed in toluene, then methanol is injected to precipitate the CdSe QDs in a 1:10 volumetric ratio, respectively. This process is repeated 5 times. The fourth stage is flocculation of the NPs via a 1:10 mixture of toluene to ethanol (toluene to disperse, ethanol to flocculate/precipitate). This is also repeated 5 times. The final stage is the addition of toluene to redisperse the CdSe QDs and acetone to precipitate in a 1:10 volumetric ratio, respectively. This is repeated 5 times and upon completion a solid pellet of CdSe QDs is formed. The pellet is then dried in air before being stored as a powder for later use.

[1] R. R. Knauf, J. C. Lennox, and J. L. Dempsey, "Quantifying ligand exchange reactions at CdSe nanocrystal surfaces," *Chem. Mater.*, 2016, 28 (13), 4762–4770.