Electronic Supplementary Material (ESI) for Lab on a Chip

Supporting information for:

Photoreversible Fragmentation of a Liquid Interface for Micro-Droplet Generation by Light Actuation

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1. Experimental Section

Microfluidic device fabrication. Devices were prepared by standard soft lithography fabrication. Fabrication of master mold was performed by spin-coating a 50 µm layer of negative SU8 photoresist (Clariant) on a silicon wafer (Siltronix), UV exposure through a photomask, and development. Polydimethysiloxane (PDMS, RTV 615, GE Toshiba Silicones Co., Ltd.) was poured on the mold, degassed, cured at 80 °C for 2 h, and peeled off from the mold. Inlet and outlet holes were punched in the PDMS block prior to washing by isopropanol. The PDMS part and a microscopy glass slide (Menzel-Gläser) were assembled after exposition to air plasma at 500 mTorr for 3 min (Plasma Cleaner, Harricks). Just before experiment, devices were baked on a hot plate at 150 °C for 1 h to render them hydrophobic.

Contact angle measurements. A 10 mM AzoTAB solution droplet deposited on the solid substrate in an oleic acid bath was inflated and deflated at a constant flow rate (3 µL min^{-1}) using a syringe pump (Harvard Apparatus) to measure advancing and receding contact angles, respectively. Pictures were recorded with a digital viewer (GE-5, Aigo, China) and analyzed using a tangent method with ImageJ software. 10 measurements were performed for each value, which provided a ± 2° precision.

Microfluidic experiments. Two syringe pumps, KDS-100-CE (KDScientific, USA) for AzoTAB solution (10 mM in water) and TS2-60 (Longer Precision Pumps, China) for oleic acid were used to inject solutions into the microfluidic device. Observations and illuminations were performed using an Axioobserver D1 inverted microscope (Zeiss), equipped with a 10× objective lense and a 365 ± 40 nm bandpass filter (Zeiss) for UV illumination. For Device 1, illumination was applied on an area larger than the observation field around the flow focusing junction. For Device 2, illumination was performed through a ~2 mm wide slit made between two UV-cutting plastic filters and placed in close contact to the bottom part of the device. Pictures and movies were acquired by using an EM-CCD camera (Photonmax 512B, Princeton Scientific) and Micro-Manager 1.3 software.

2. Movie Legends

Movie S1. UV-induced "Drop → Drop" transition. A photosensitive aqueous solution (AzoTAB, 10 mM in water) is injected at a rate 0.5 μL min^{-1} in a flow of oleic acid (0.5 μL min^{-1}) using the microfluidic Device 1**.** The movie shows the flow focusing junction part. At the beginning, UV illumination is first turned off and droplets are formed. When UV illumination is turned on (365 nm), droplets of a larger diameter are formed at a lower frequency. When UV illumination is turned off again, droplets are formed with the initial size and frequency. The movie is displayed at the acquisition rate (10 fps), which is much smaller than the droplet generation frequency. The acquisition time per frame is 1 ms. The frame size is 768 μm × 768 μm.

Movie S2. UV-induced "Tube → Drop" transition. A photosensitive aqueous solution (AzoTAB, 10 mM in water) is injected at a rate 3 μL min^{-1} in a flow of oleic acid (2 μL min^{-1}) using the microfluidic Device 1. The movie shows the flow focusing junction part. At the beginning, UV illumination is first turned off and a stable tube is formed. When UV illumination is turned on (365 nm), monodisperse droplets are formed. When UV illumination is turned off again, a stable tube similar to the initial one is formed. The movie is displayed at the acquisition rate (10 fps), which is much smaller than the droplet generation frequency. The acquisition time per frame is 1 ms. The frame size is 768 μm × 768 μm.

Movie S3. UV-induced "Tube → Tube" transition. A photosensitive aqueous solution (AzoTAB, 10 mM in water) is injected at a rate 8 μL min^{-1} in a flow of oleic acid (2 μL min^{-1}) using the microfluidic Device 1**.** The movie shows the flow focusing junction part. At the beginning, UV illumination is first turned off and a stable tube is formed. When UV illumination is turned on (365 nm), a stable tube with a slightly larger apparent diameter. When UV illumination is turned off again, a stable tube similar to the initial one is formed. The movie is displayed at the acquisition rate (10 fps). The acquisition time per frame is 1 ms. The frame size is 768 μm × 768 μm.

Movie S4. Reversible liquid fragmentation by UV light. A photosensitive aqueous solution (AzoTAB, 10 mM in water) is injected at a rate 3 μL min^{-1} in a flow of oleic acid (2 μL min^{-1}) using the microfluidic Device 1. The movie shows the flow focusing junction part. Cycles of 'tube → drop → tube' are observed by successively switching on and off UV illumination (365 nm). The movie is displayed at the acquisition rate (10 fps), which is much smaller than the droplet generation frequency. The acquisition time per frame is 1 ms. The frame size is 768 μm × 768 μm.

Movie S5. Spatio-selective fragmentation of a two-phase flow by UV light. A photosensitive aqueous solution (AzoTAB, 10 mM in water) is injected at a rate 1.5 µL min^{-1} in a flow of oleic acid (2.4 µL min^{-1}) using the flow focusing microfluidic Device 2. UV light (365 nm) is applied through a photomask to selectively illuminate the microchannel on a desired area. First, we observe that droplets are formed in the UV-exposed area. When the observation field is moved just before the UV-exposed area (upstream), we observe that the flow is forming a stable tube. When the observation field is moved back to the UV-exposed area, we observe the destabilization of the tube into droplets. When the observation field is moved after the UV-exposed are (downstream), we observe a flow of stable droplets. The movie is displayed at the acquisition rate (10 fps), which is smaller than the droplet generation frequency. The acquisition time per frame is 1 ms. The frame size is 768 µm × 768 µm.

3) Phase diagram for [AzoTAB] = 2 mM

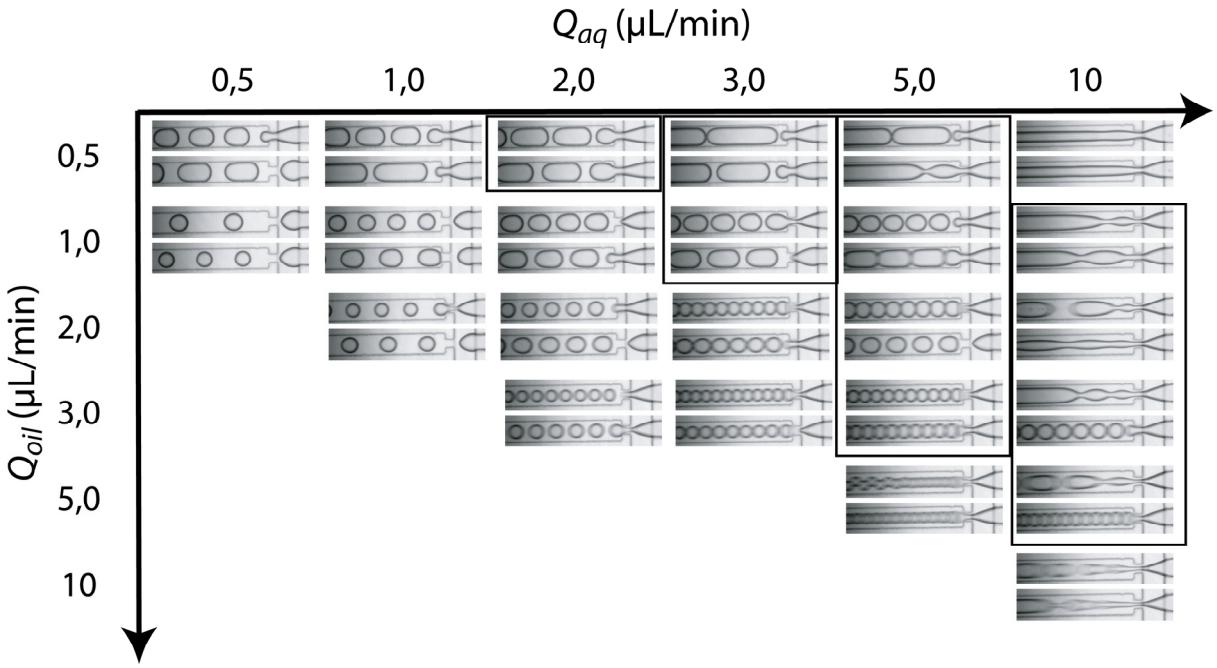

Figure S1. A solution of *trans*-AzoTAB (2 mM) injected at various aqueous flow rates Q_{aq} in oleic acid at various flow rates Q_{oil} using the microfluidic Device 1. For each flow rate condition, upper and lower images corresponds to the regime observed before and after UV illumination (365 nm), respectively. Square black boxes indicate unstable flow regimes.

4) Effect of blue light on cis-AzoTAB solution

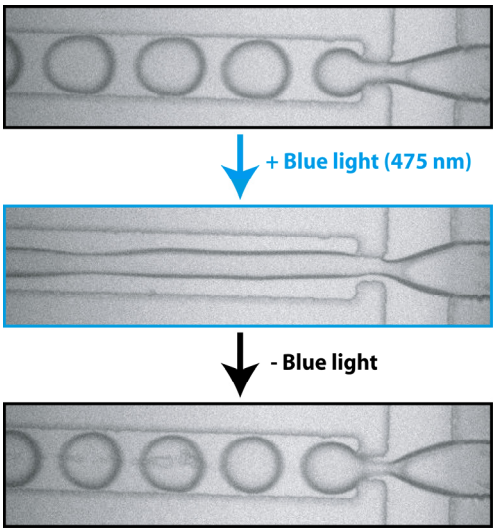

Figure S2. A solution of *cis*-AzoTAB (10 mM), obtained by illumination of *trans*-AzoTAB with UV (365 nm) for 1 h, is injected at a rate 2 µL min^{-1} in a flow of oleic acid (2 µL min^{-1}) using the microfluidic Device 1. The system is initially in a stable droplet regime. The illumination by blue light (475 nm) induces the conversion of *trans*- to *cis*-AzoTAB and a transition to a stable tube regime. After stopping the illumination, the systems goes back to a stable droplet regime.