Supporting Information for:

Microfluidic mixing triggered by an external LED illumination

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1. Experimental Section

Materials:

Nile Red was from Sigma. MilliQ water (Millipore) was used for all experiments.

AzoTAB synthesis:

Azobenzene trimethylammonium bromide (AzoTAB) synthesis was adapted from the method that was described by Hayashita et al.[1] More details can be found in the protocols describing the synthesis of AzoTAB homologs.[2] Briefly, the azocoupling of p-ethoxyaniline with phenol was carried out to give AzoOH. Alkylation of the phenol was then performed by dripping a solution of AzoOH in an excess of dibromoethane, leading to AzoBr. Finally bubbling trimethylamine gas gave the quaternized surfactant, AzoTAB. The purity of the final product was checked by 250 MHz ^{1}H and ^{13}C NMR spectroscopy.

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) previously coated with OmniCoat. UV exposure was carried out through a photomask, and the resist was then developed and treated with trimethylsilyl chloride. Polydimethysiloxane (PDMS, RTV 615, GE Toshiba Silicones Co., Ltd.) was poured on the mold, degassed, cured at 80 °C overnight, and peeled off from the mold. Inlet

and outlet holes were punched in the PDMS block prior to washing by isopropanol and drying with pressurized air. The PDMS chip and a microscopy glass slide (Menzel-Gläser), also washed with isopropanol and air-dried, 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 make the surfaces hydrophobic.

Microfluidic experiments:

Three syringe pumps, Pump 11 Elite (Harvard Apparatus), were used to inject the 3 solutions into the microfluidic device: an AzoTAB solution (8 mM in water), pure oleic acid and oleic acid + Nile Red (at 85 µM). Observations and illuminations were performed using an Axioobserver D1 inverted microscope (Zeiss), equipped with a 10× objective lens and a 545/25 nm bandpass filter (Zeiss) to follow the intensity of the fluorescent oil phase. Pictures and movies were acquired by using an EM-CCD camera (Photonmask 512, Princeton Scientific) and Micro-Manager software.

Illumination set-up:

Illumination at 365 nm was obtained with a light-emitting diode (LED) from pE-1 excitation system (CoolLED). Illumination was applied through a liquid light guide (CoolLED) on an area around the flow-focusing junction, with the tip placed 1 cm above the top of a device.

Yield of oil recovery after the droplet separation unit:

A mixing experiment was carried out with flow rates set at 0.5 µL min^{-1} for the oil phases and at 3 µL min^{-1} for the aqueous phase. By weighing the oil obtained at the output for a 1 hour experiment, we calculated an average output flow rate of 90 $nL.min^{-1}$, which corresponds to a 9% yield of oil recovery.

Water content of the mixed oil phases:

Using the deuterated methanol from the same batch, 3 solutions were prepared: i) pure MeOD , ii) 10 µL oleic acid in 500 µL MeOD, iii) 10 µL oil phase after the optofluidic mixer unit in 500 µL MeOD. ^{1}H NMR experiments at 300 MHz gave access to the water content of the deuterated methanol, of the oleic acid prior to injection in the device (1.9 wt%) and finally of the output (2.2 wt%).

2. Supplementary figures

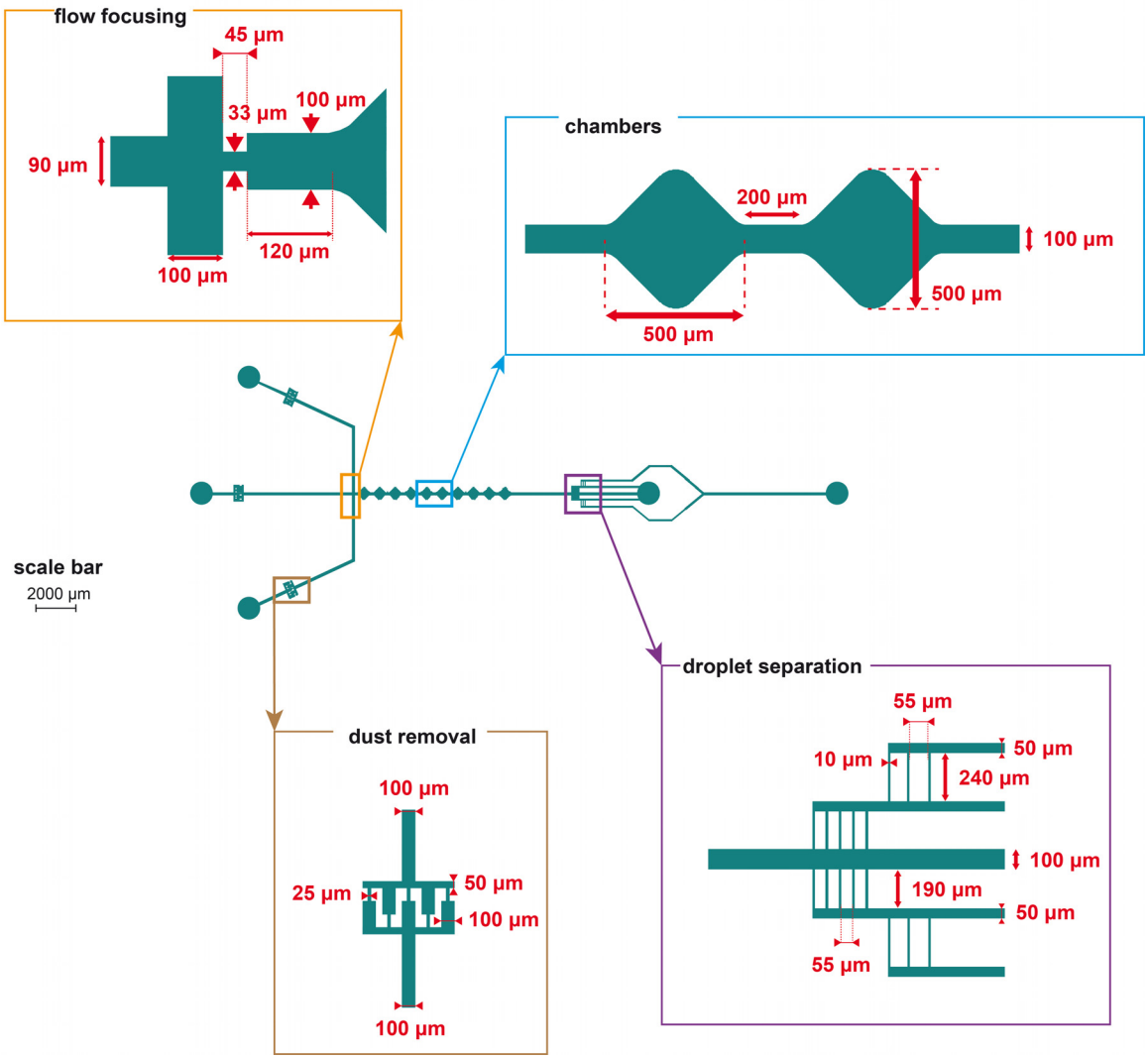

Figure S1. Full design is drawn to scale and the geometric characteristics of noteworthy regions are given.

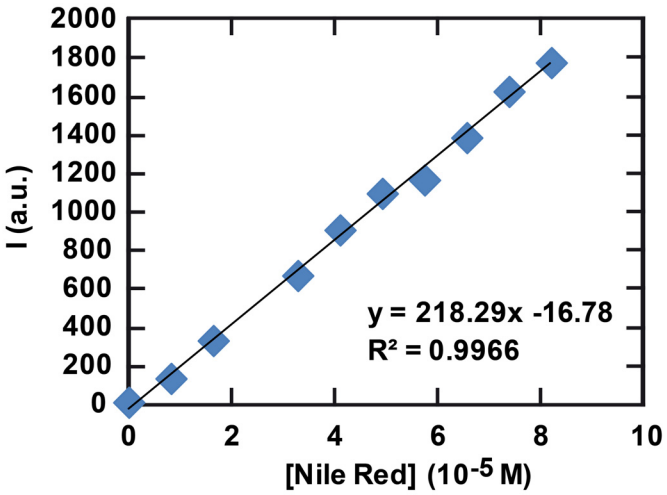

Figure S2. Correlation between the fluorescence intensity measured with fluorescent microscopy in the device and the concentration of Nile Red in oleic acid. Symbols are data points and the solid line is a linear fit.

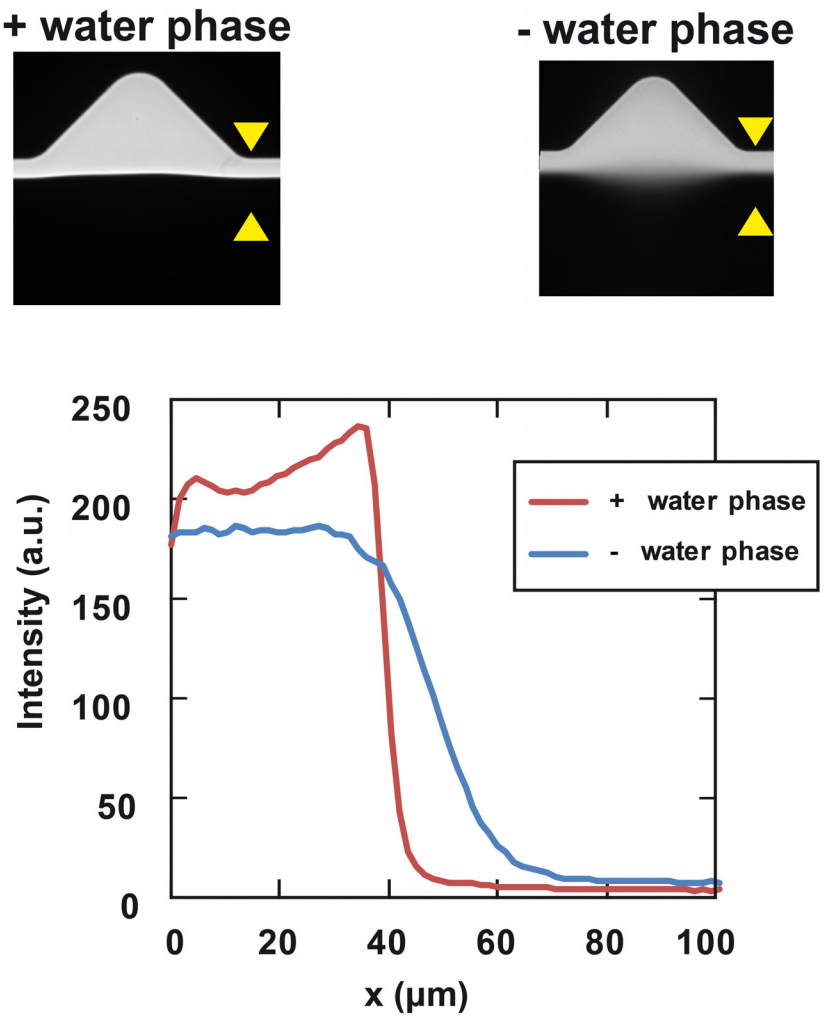

Figure S3. Intensity profile between the yellow arrow heads (top to bottom) for expansion chamber 10 in presence (red curve) and in absence (blue curve) of the water phase. Q_{oil} = 0.5 µL min^{-1}; Q_{water} = 6 µL min^{-1}; acquisition time: 10 ms.

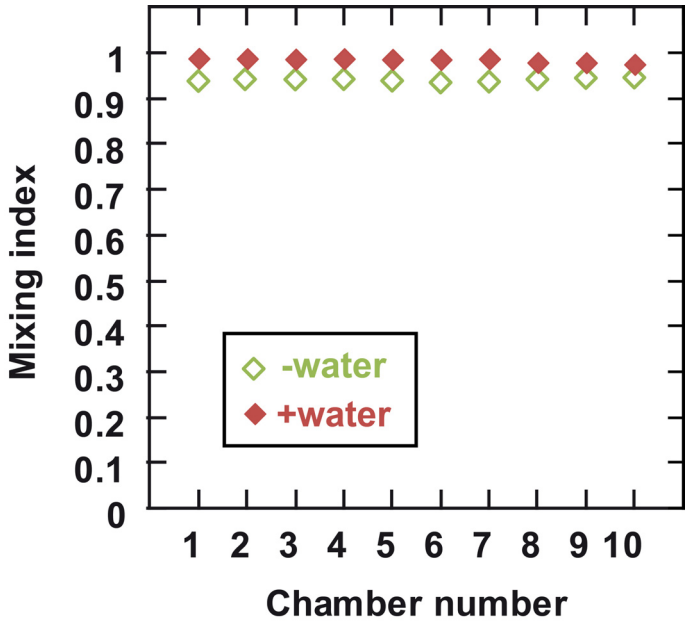

Figure S4. Evolution of the mixing index calculated as shown in figure 2C with or without the water phase. Q_{oil} = 0.5 µL min^{-1}; Q_{water} = 5 µL min^{-1}; acquisition time: 10 ms.

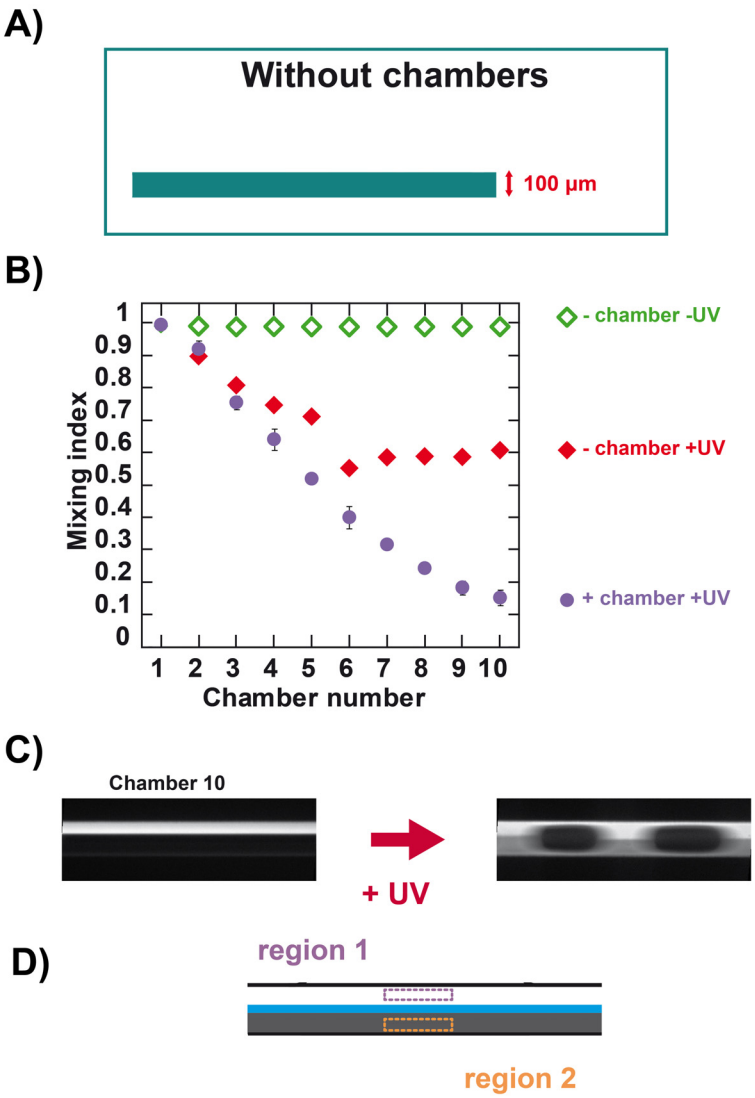

Figure S5. Role of the expansion chambers. **A)** design of the straight channel without chambers. **B)** evolution of the mixing index along the channel, at positions corresponding to chambers of the reference design, compared to the reference (in purple), before (in green, open diamonds) and after (in red, filled diamonds) UV illumination. **C)** Fluorescence microscopy image of the position of chamber 10 before and after UV. **D)** Position of regions 1 and 2 to measure the mixing index in a straight geometry.

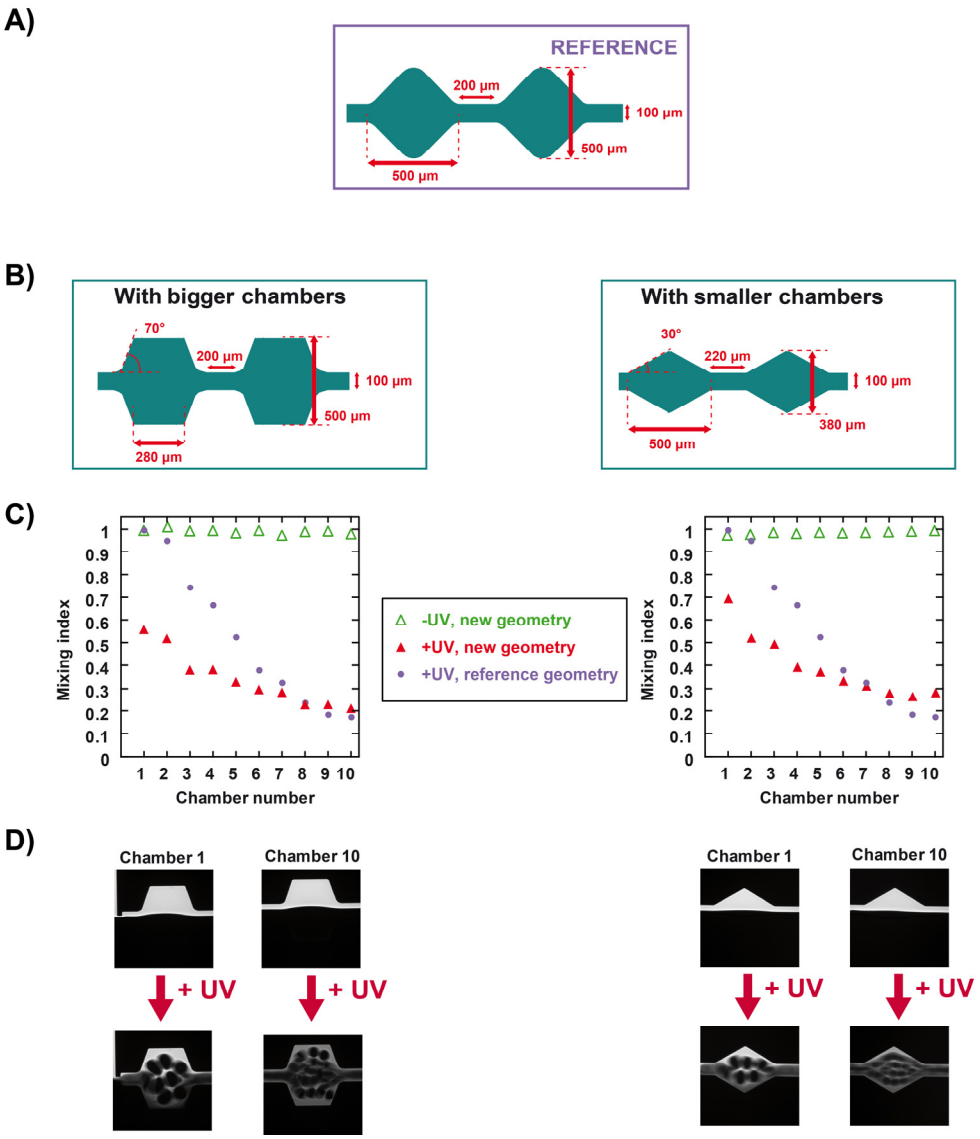

Figure S6. Examples of other geometries investigated. **A)** Reference geometry. **B)** Other types of chambers. **C)** Evolution of the mixing index along the channel for both geometries, compared to the reference (purple dots), before (green, opened triangles) and after (red, filled triangles) UV illumination. **D)** Fluorescence microscopy images of chambers 1 and 10 before and after UV. In all experiments, Q_{oil} = 0.5 µL min^{-1}; Q_{water} = 6 µL min^{-1}; acquisition time: 10 ms.

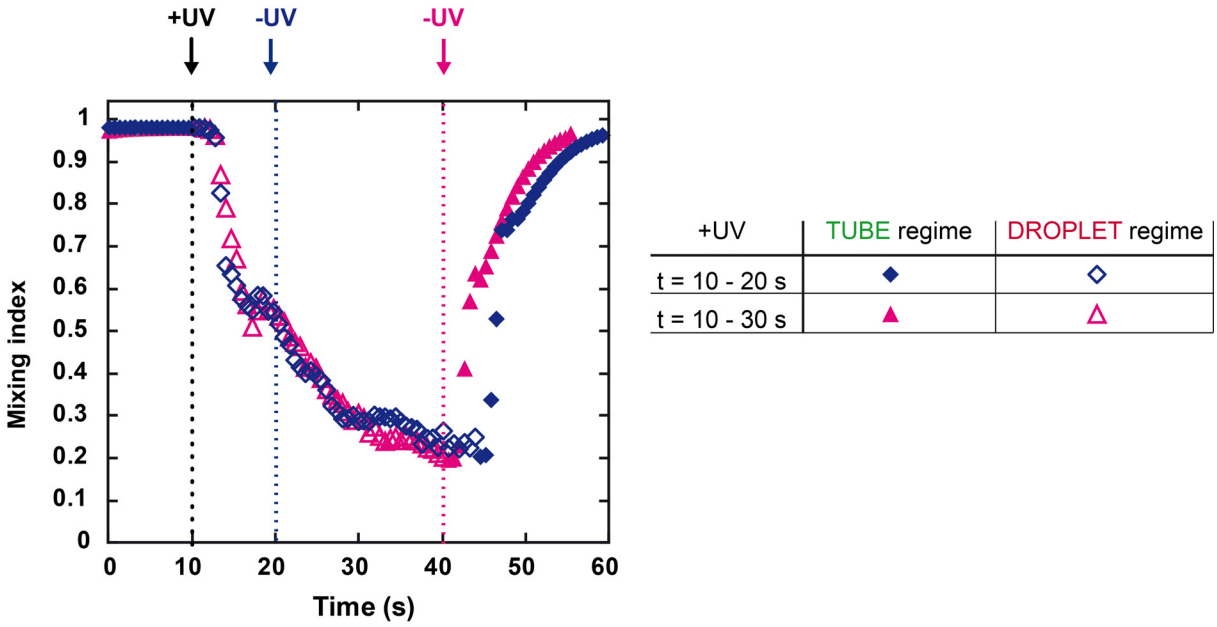

Figure S7. **Mixing index as a function of time for two experiments.** UV is applied at 10 s for all experiments (+UV, black dashed line) and removed at 20 s (blue diamonds) and 40 s (pink triangles) Q_{oil} = 0.5 µL min^{-1} , Q_{water} = 2.5 µL min^{-1} ; acquisition time: 10 ms.

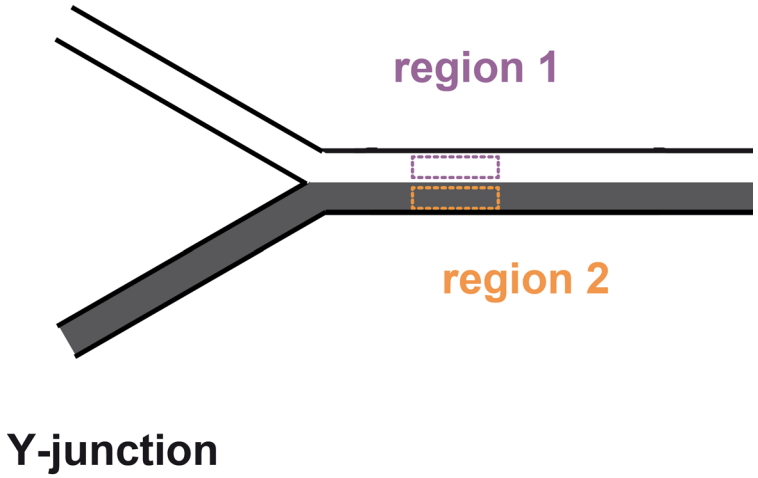

Figure S8. Definition of regions 1 and 2 used to determine the mixing index in the channel after the Y-junction.

3. Movie Legends

Movie S1. Light-triggered mixing. A photosensitive aqueous solution (AzoTAB, 8 mM in water) is injected at a rate 4 µL min^{-1} in a flow of two oil phases, the bottom one is pure oleic acid and the top one is oleic acid with Nile Red (85 µM) at a rate of 0.5 µL min^{-1} using the microfluidic device described in Fig. 1A. The movie shows the various chambers (chamber 1 to chamber 10) before and after UV illumination (365 nm). At the beginning (**-UV**), there is no UV illumination and the water phase forms a continuous flow. Then the UV illumination is turned on and droplets are formed, allowing the mixing of the oil phases (**+UV**). The movie is displayed at real speed. Acquisition rate: 15 fps; exposure time: 10 ms; frame size: 768 µm × 768 µm.

Movie S2. Reversible optofluidic mixing. A photosensitive aqueous solution (AzoTAB, 8 mM in water) is injected at a rate 3 µL min^{-1} in a flow of two oil phases, the bottom one is pure oleic acid and the top one is oleic acid with Nile Red (85 µM) at a rate of 0.5 µL min^{-1} using the microfluidic device described in Fig. 1A. The movie shows the chamber 10, where the illumination is changed every 30 s (indication at the bottom of the video : **-UV** and **+UV**). The movie is displayed at four times the real speed. Acquisition rate: 5 fps; exposure time: 200 ms; frame size: 768 µm × 768 µm.

4. Supplementary references

(1) Hayashita, T.; Kurosawa, T.; Miyata, T.; Tanaka, K.; Igawa, M. *Colloid & Polymer Science* **1994**, *272*, 1611–1619.

(2) Diguet, A.; Mani, N. K.; Geoffroy, M.; Sollogoub, M.; Baigl, D. *Chem.--Eur. J.* **2010**, *16*, 11890–11896.