(1) Device design

Monodisperse o/w microdroplets were generated by injecting oil and water phases into a microfluidic device with a channel height of 25 μm. The chip design is shown in Fig. S1.

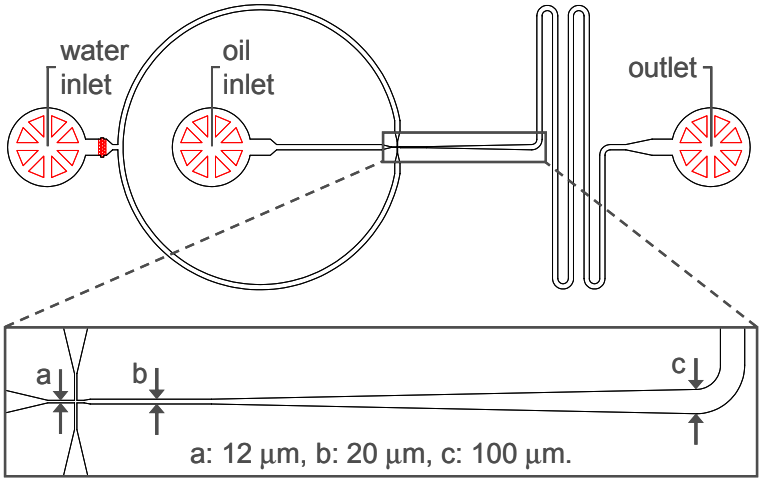

Fig. S1 Design of the device used for the controlled formation of o/w microdroplets as shown in Fig. 2(a) and Fig. 2(b).

(2) Movies

(a) M1 – Formation of functional o/w droplets

This movie depicted in Fig. 2(a) shows the formation of dodecane-in-water droplets stabilized by a pH responsive MAA/PEGMA surfactant at an oil flow rate of 100 μl h^{-1} and a water flow rate of 300 μl h^{-1}.

(b) M2 – Injection of the emulsion sample into basic water

In this movie depicted in Fig. 2(e) the injection of the emulsion sample into an open reservoir containing basic water (pH 10) at a constant flow rate of 70 μl h^{-1} is illustrated. Due to the absence of inter-droplet hydrogen bonding a dispersion of non-interacting droplets is generated.

(c) M3 – Injection of the emulsion sample into acidic water

The injection of the emulsion sample into an open reservoir containing acidic water (pH 2) at a constant flow rate of 70 μl h^{-1}, as depicted in Fig. 2(f), is shown in this movie. As inter-droplet hydrogen bonding occurs a droplet aggregate is formed at the end of the tubing.

(d) M4 – Quantitative analysis of droplet-droplet interactions via optical tweezers

This movie illustrates the computer-controlled 3D manipulation of a droplet pair using optical tweezers. While the left microdroplet is kept quasi-stationary the right droplet is slowly

retracted. Within 120 s the trap distance is steadily increased from 20 μm to 25 μm. Displacements of the left droplet are measured and used to quantify droplet-droplet adhesion. Pictures taken from the movie are displayed in Fig. 4(a).