Supplementary Material (ESI) for Lab on a Chip

Supplementary Information

Controlling the contents of microdroplets by exploiting the permeability of PDMS

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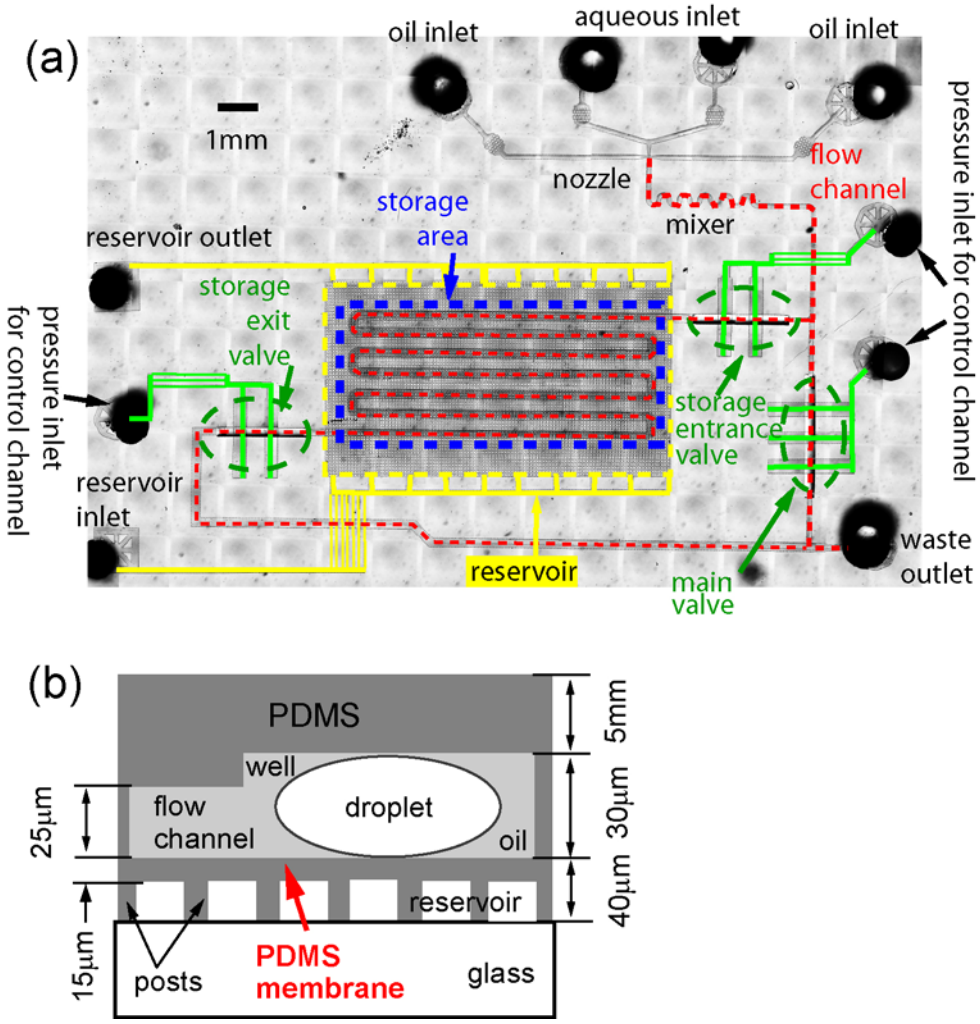
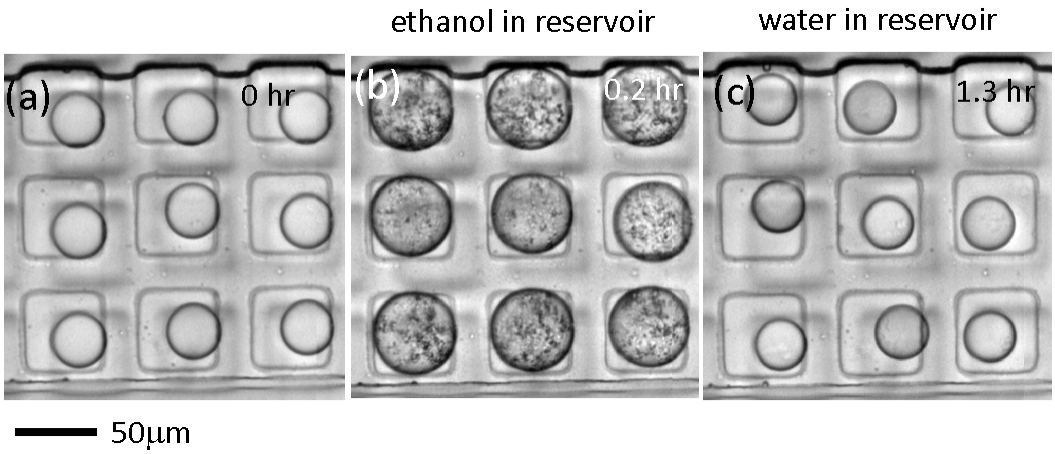
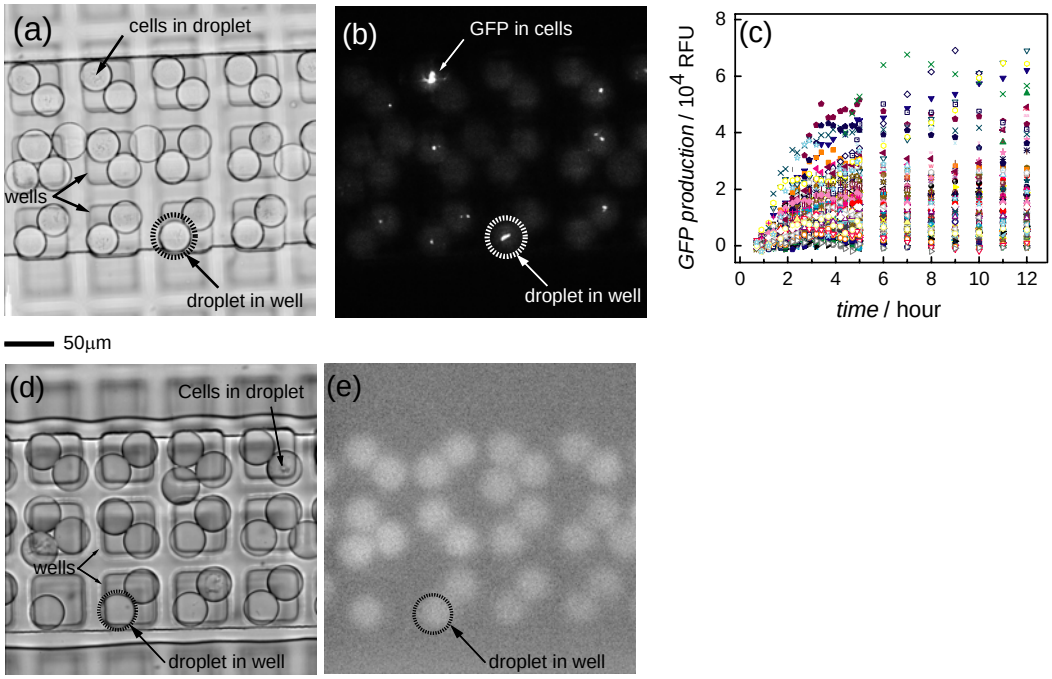


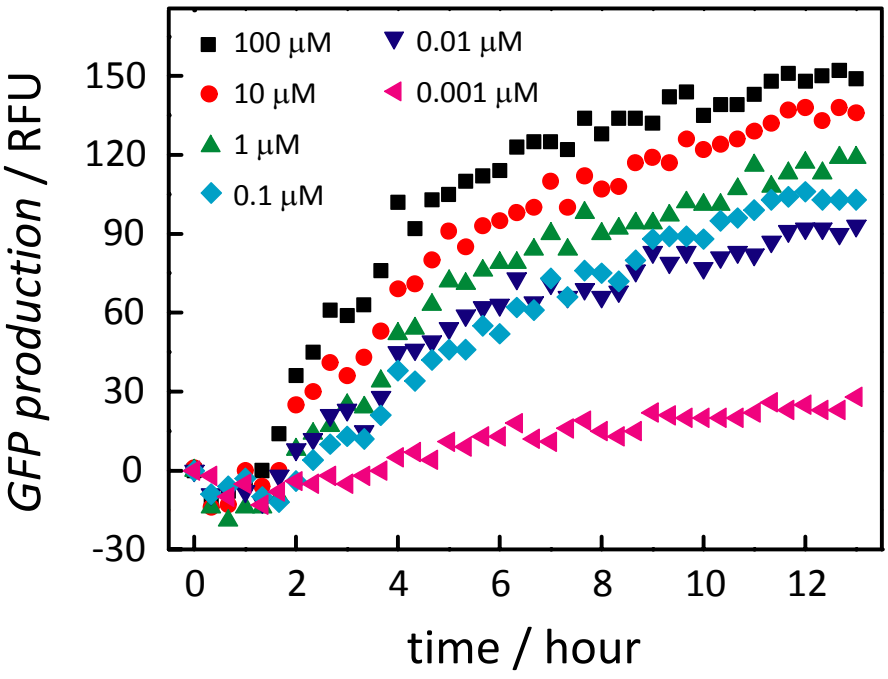
SI-Fig.1 (a) A global view of the device. It has four injection holes to introduce fluids into the device; the outer two for oil and the inner two for the aqueous solution. The winding channel, the mixer, generates chaotic advection, thus uniformly blending the multiple solutes of droplets.[1] There is a storage region in which the device can store the droplets. The storage region has an entrance and an exit valve to control the stream of drops that flow into the area. When these valves are open to guide the stream into the storage region, the main valve have to be closed otherwise all droplets will flow out through the waste outlet because of the lower flow resistance that is linearly proportional to the length of the channel. Once the storage region is filled with droplets, the region is isolated by closing valves. (b) A schematic diagram of a vertical cut through the storage wells in the multi-layer PDMS device used. The upper, thicker layer (5 mm) contains flow channels and storage wells. The lower, thinner layer (40 μm) contains a reservoir (used for small molecule delivery) sealed by a 15 μm thick PDMS membrane, through which molecules were diffused.



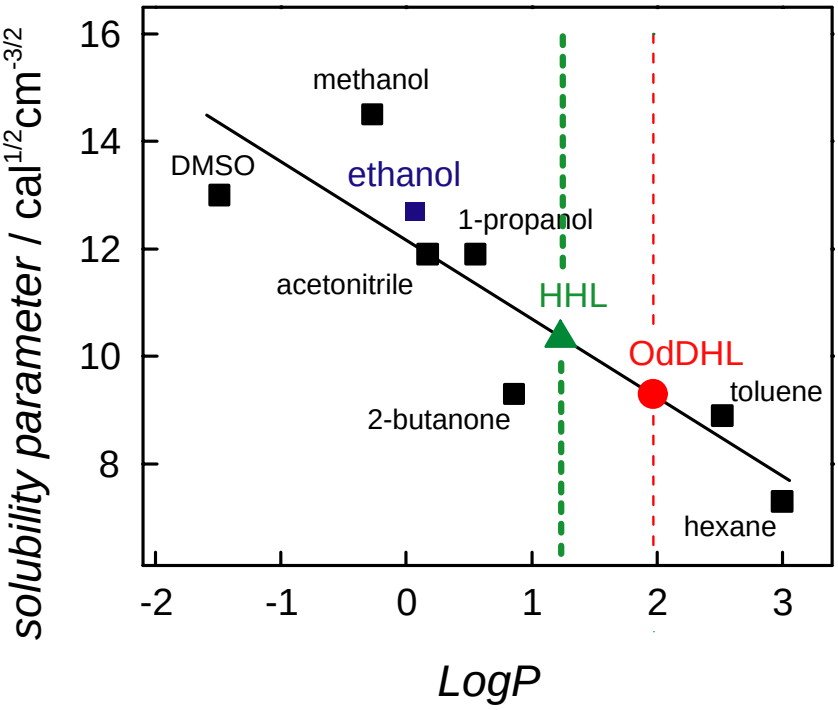
SI-Fig.2 (a) A stable protein solution of lysozyme stored in wells at the beginning of the experiment. (b) Protein precipitation occurred at 12 minutes after the reservoir was filled with ethanol. Ethanol transported from reservoir to droplets, increasing ethanol contents in droplets thus lowering the protein solubility. (c) After the reservoir channel was filled with pure water, ethanol kept evaporating from droplets into the bulk PDMS and was replaced with water thus the solubility of the protein in the microdroplets increased and the precipitate dissolved.



SI-Fig.3 (a)-(c) A positive control experiment. (a) Microdroplets encapsulating cells were stored in the storage wells. 10 μM of OdDHL dissolved in water was introduced into reservoir. (b) A fluorescence image shows GFP production in cells encapsulated after 10 hour since storage. Bright spots are cells expressing the fluorescent protein. (c) GFP productions in microdroplets were monitored as a function of time. Each symbol represents each microdroplet. (d)-(e) A negative control experiment. Cells were encapsulated and stored in the microfluidic device without OdDHL. Water was introduced in reservoir to maintain the chemical condition in microdroplets. No GFP was observed for more than 20 hours.



SI-Fig.4 Time course of GFP expression as given OdDHL concentrations measured by a 96 plate reader. Cells and various concentrations of OdDHL were mixed and the fluorescence was monitored as a function of time. The numbers in the graph represent concentrations. Its dependence on OdDHL concentrations is similar to the microdroplet experiment (Fig. 3c).



SI-Fig.5 Comparison of known solubility parameters of various organic molecules in PDMS[2] and their partition coefficient (LogP value) calculated by ChemDraw (CambridgeSoft). The solubility parameter is a physical parameter indicating the relative solvation behaviour of a specific solvent. A smaller value of this solubility parameter represents higher solubility of a specific molecule. As two physical parameters have an inverse linear proportionality, the solubility of OdDHL and HHL in PDMS can be determined by determining their LogP values and using the linear relationship to estimate the solubility parameter of these molecules. The LogP of OdDHL and HHL are 1.97 (thin dashed line) and 1.15 (thick dashed line), respectively, giving a solubility parameter of 9.3 ($cal^{1/2}cm^{-3/2}$, circle) and 10.5 ($cal^{1/2}cm^{-3/2}$, triagle) based on the linear extrapolation (solid line) approximated from other known organic molecules (squares). This analysis shows that OdDHL solubility in PDMS is slightly lower than that of toluene.

References

1. H. Song, J. D. Tice and R. F. Ismagilov, *Angew. Chem., Int. Ed.*, 2003, **42**, 768-772.
2. J. N. Lee, C. Park and G. M. Whitesides, *Anal. Chem.*, 2003, **75**, 6544-6554.