Molecular Confinement in Femtoliter scale aqueous Compartments

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Molecular confinement is known to lead to acceleration of molecular dynamics along with surface interaction. Nature employs confinement in molecularly crowded, heterogeneous and, specialized femtoliter (fL) compartments inside living cells for spontaneously achieving higher reaction efficiency and spatial-programming of composite, multi-step biochemical processes (1). We here show the facile production of aqueous fL droplets for studying molecular confinement on a biochip. We prepare fL aqueous droplets in oil drops on solid substrates by a "field-free"- no external electric fields and electrolytes (2) - piezoelectric inkjet printing in which a novel actuating waveform is employed by picoliter sized nozzles (Fig 1.a). The droplets form an almost-regular circular pattern at the border of mineral oil drops (3), (Fig 1.b) and Alexa 647 molecules, at 10-0.01 μM concentrations, form ring patterns at the surfactant/oil interface (Fig.1c) as predicted by numerical adsorption general models (4). At the single droplet level, we show that molecular confinement leads to modify solute-solvent and solvent driven solute-solute interactions. Confinement effects are tested by using Fluorescence lifetime imaging which reveals different characteristic lifetimes of specific molecules in confined volumes with respect to macroscopic solutions. The same method using the signal of a molecular rotor- i.e. 9-(2-Carboxy-2-cyanovinyl)julolidine - did not reveal changes in solution viscosity due to confinement. We exploit the possibility of analyzing molecules "in action" in fL volume solutions to study the behavior of molecular machines in confined environments. At these volume scales, by employing a model DNA beacon machine, we highlight that DNA-machines/ target interaction is favored in confined conditions with respect to microliter/macroscopic volumes.

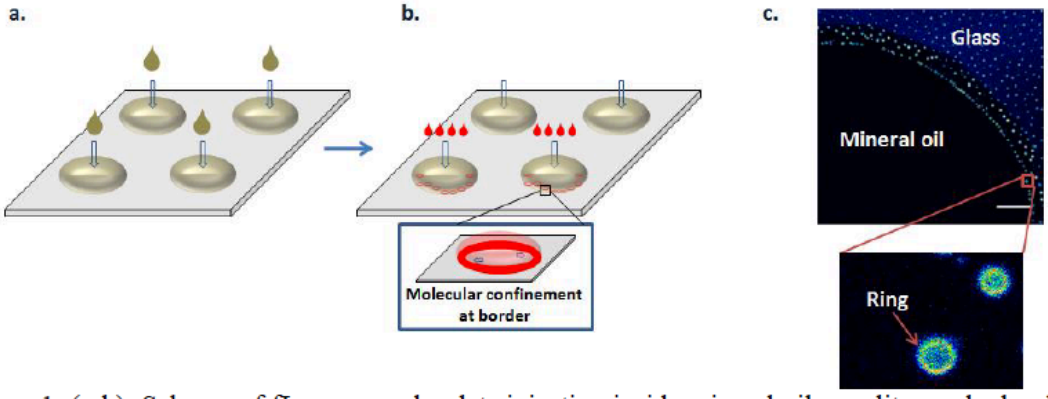

Figure 1. (a-b) Scheme of fL aqueous droplets injection inside mineral oil nanoliter scale droplets. (c) Fluorescence confocal images show the molecular confinement at the border of the droplets (Alexa 647 dye, 10 μM).

References: 1. Maike M. K. Hansen et al., Nature Nanotechnology 2016, 11, 191 2. Jang-Ung Park et al., Nature Materials 2007, 6, 782. 3. G. Arrabito, F. Cavaleri et al. Lab Chip, 2016,16, 46664.Staszak, Maciej, Journal of Surfactants and Detergents, 2016, 19, 297.