Supporting information

Supporting text and figures

Characterizing the detachment of DNA from the interface at constant electric field

In this section we describe how the detachment of DNA from liquid-liquid interface occurring at a constant electric field has been examined. The corresponding ATPSs have been prepared with different ionic strength ranging from 5 to 20 mM. The phases are extracted, and λ -DNA is dissolved in dextran at a concentration of 6.6 pg μ l⁻¹. After that, the two liquids are introduced into the microfluidic device and the flow is stopped, with each phase occupying half of the compartment. A constant electric field is applied and the fluorescence at the liquid-liquid interface is followed as depicted in Supplementary Figure 1. Usually, the maximum intensity corresponds to the time when a spontaneous detachment of DNA is triggered, termed the maximum accumulation time.

The maximum accumulation time shows a distinct correlation with the Debye length of the double layer at the interface. The Debye length is calculated from

$$\lambda_{D} = \sqrt{\frac{k_{B}T\varepsilon_{0}\varepsilon_{r}}{e^{2}\sum_{j=1}^{N}c_{j}z_{j}^{2}}}$$
(1)

using a dielectric constant $\varepsilon_r = 78$ and absolute temperature T = 293 K, where k_B denotes the Boltzmann constant, ε_0 the permittivity of the vacuum, *e* the elementary charge, c_j the concentration of ion species *j*, and z_j its charge number.



Supplementary Figure 1: Interfacial fluorescence as a function of time at a constant electric field of 122 V m⁻¹. The sudden decrease of fluorescence intensity coincides with the spontaneous detachment of λ -DNA from the liquid-liquid interface. Data for different values of the ionic strength in the ATPS have been taken.

Determination of the escape time

The experiments for determining the escape time have been performed with 100 bp and 150 bp DNA. Either of the two molecular samples is accumulated for 100 s at the liquid-liquid interface applying 150 V m^{-1} . The electric field is increased to a specific value to trigger the detachment. The exponential decay in interfacial fluorescence is followed (Supplementary Figure 2). The procedure is repeated for different electric fields while the decay of the interfacial fluorescence intensity is described by

$$f(t) = A \exp\left(-\frac{t}{\tau_b}\right)$$
(2)

where A is the initial intensity, τ_b the escape time and t the progressed time. The data is used to determine the dependence of the escape time on the electric field strength shown in Figure 2b of the main text.



Supplementary Figure 2: Fluorescence at the interface as a function of time. The symbols represent the measurements, the curve an exponential fit to the data. The graph illustrates the detachment of 150 bp DNA at 465 V m⁻¹, where a dextran lamella of 300 μ m width is sandwiched between two equal PEG phases.