Pickering Emulsions Stabilized with Oligoglycine-Functionalized Nanodiamond and Their Application in Ocular Drug Delivery

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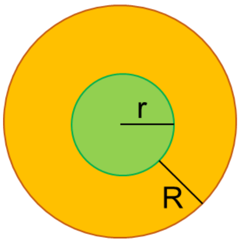
S1. Calculation of the Surface Coverage of 2T on ND-2T Nanoparticles



Assumption: The 2T molecules are extended with only *one* tail attached to the ND surface.

Given that ρ_{ND} is the density of a ND particle, the mass is $\mathrm{m} = \rho_{ND} \times \frac{4}{3}\pi r^3$

The mass of 2T in an ND-2T particle is $M = \rho_{Gly} \times \frac{4}{3}\pi[(R+r)^3 - r^3]$, where ρ_{Gly} is the density of glycine, which is an approximation for the 2T density.

We use literature values for the density[1] of ND ($\rho_{ND} = 3.1\ g/cm^3$) and the density of glycine[2] ($\rho_{Gly} = 1.6\ g/cm^3$). From TEM analysis, we estimate the radius of ND as $r = 2.5\ nm$. The length of 2T chains is taken from previous molecular modelling[3] to be $R = 4\ nm$.

Therefore, the mass of an ND particle is $m = 2.0 \times 10^{-19}\ g$,

The mass of 2T needed to create a dense shell on an ND particle surface is

$M = 1.1 \times 10^{-18}\ g.$

From the TGA results, we know that the mass fraction of 2T in an ND-2T particle is 0.477.

The estimated mass of a single ND-2T particle, considering the theoretical mass of ND (*m*) and the TGA measurement, is

$$M_{ND-2T} = \frac{\mathrm{m}}{1-0.477} = 3.8 \times 10^{-19}\ g$$

Accordingly, the estimated mass of 2T in a single ND-2T particle is:

$$M_{2T} = M_{ND-2T} \times 0.477 = 1.8 \times 10^{-19}\ g$$

We estimate the coverage of 2T on the ND surface, θ, by comparing this mass to the theoretical mass for a dense 2T shell: $\theta = \frac{M_{2T}}{M} = 0.16$ or 16%.

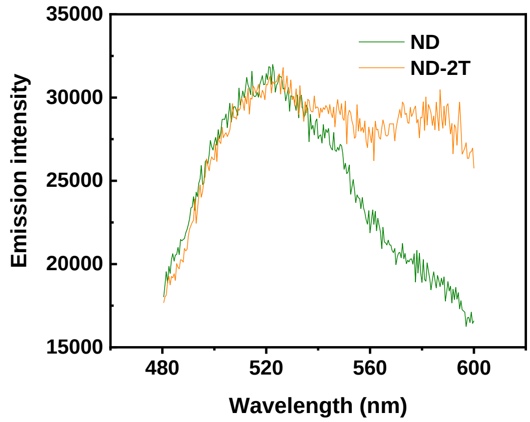


Figure S1. Fluorescence spectrum of 0.8 mg mL^{-1} ND dispersions and 0.8 mg/mL ND-2T dispersions at an excitation wavelength of 460 nm.

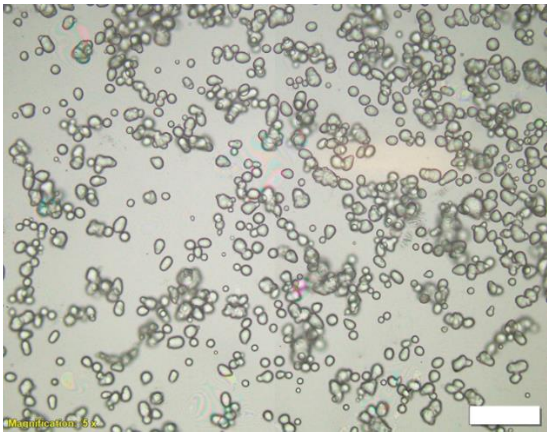


Figure S2. Optical microscope image of 1 mg/mL ND-2T-stabilized Pickering emulsion at an age of three months, which gives a mean size of 34 µm and a coefficient variation of 31%. The scale bar represents 200 µm.

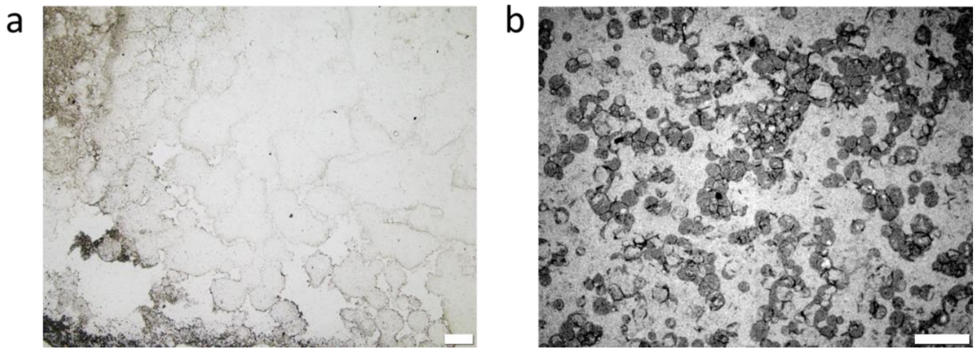


Figure S3. Optical microscope images of dried and toluene-purified (a) ND emulsions and (b) ND-2T emulsions on a glass slide." The scale bars represent 200 µm

Surface Tension Measurements of the Emulsions

A drop shape analyser (Krüss, FTA DSA1000B) was used for pendant drop tensiometry to measure the surface tension of the three emulsions. In this experiment, an emulsion drop with a volume of approximately 4 µL was injected and hung from a 0.52 mm diameter needle in air. Then through analysis of the drop shape using the video camera system on the apparatus (FTA32 software), the surface tension value was compared. The experiments were conducted in a temperature-controlled room with a temperature of 22 +/-1 °C.

The forces that determine the shape of the pendant drop are mainly the balance of surface tension and gravitation. The surface tension seeks to minimize the surface area and make the drop take a spherical shape. The gravitation, on the other hand, stretches the drop from this spherical shape and a typical pear-like shape results. The interfacial tension for a drop with a diameter of D_{eq} at its equator was calculated as:[4]

$$\gamma = \frac{\Delta\rho \cdot g {D_{eq}}^2}{H} \quad (1)$$

where $\Delta\rho$ is the density difference between water and air, g is the acceleration due to gravity (taken as 9.8 m/s^2), and H is a shape factor that is decided by the shape of the drop. Here, the water density was taken to be ρ_w = 0.998 g/cm^3 (obtained from the FTA32 software), and the density of sunflower oil[5] was taken as ρ_o = 0.918 g/cm^3. Therefore, the density of the emulsion is approximated as $\Delta\rho = 0.3\rho_o + 0.7\rho_w$ = 0.974 g/cm^3.

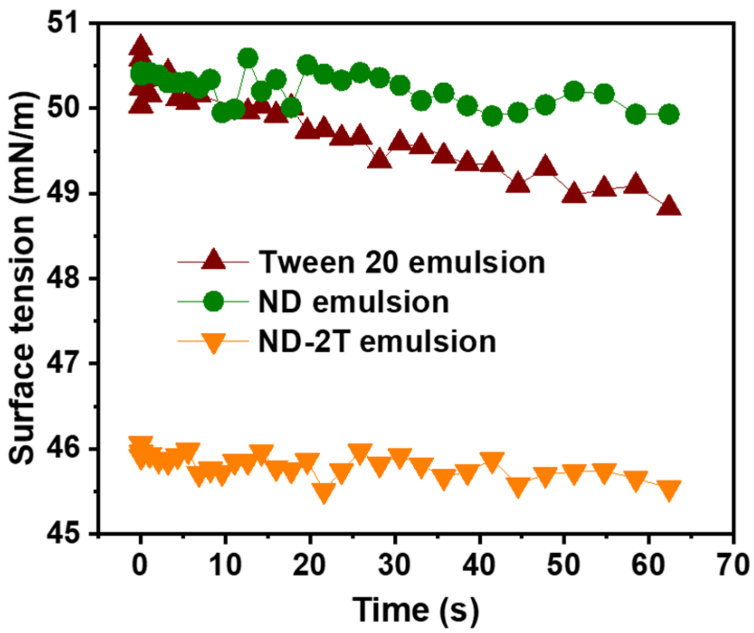


Figure S4. The surface tension of emulsions stabilized with ND-2T, ND, and Tween 20 measured over a period of 62 s.

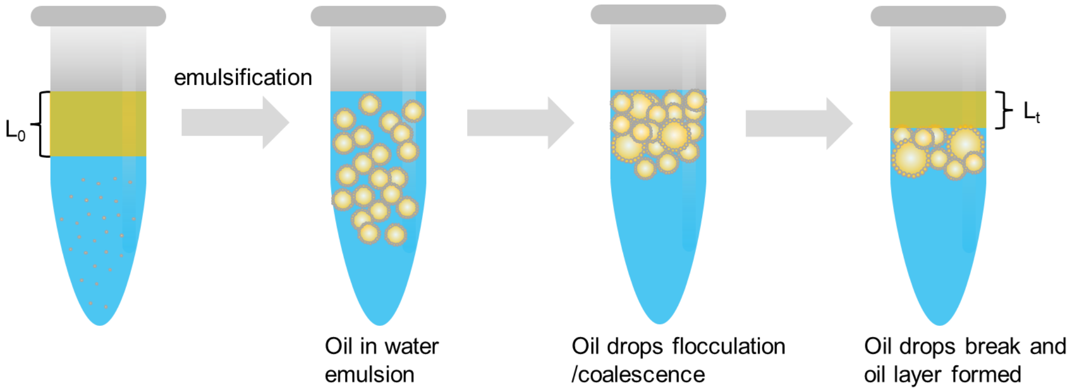


Figure S5. Emulsion stability characterization. The fraction of oil resolved over time is equal to L_t/L_0, where L_0 represents the initial oil layer thickness before emulsification, and L_t is the oil layer thickness after the emulsion was stored for time t.

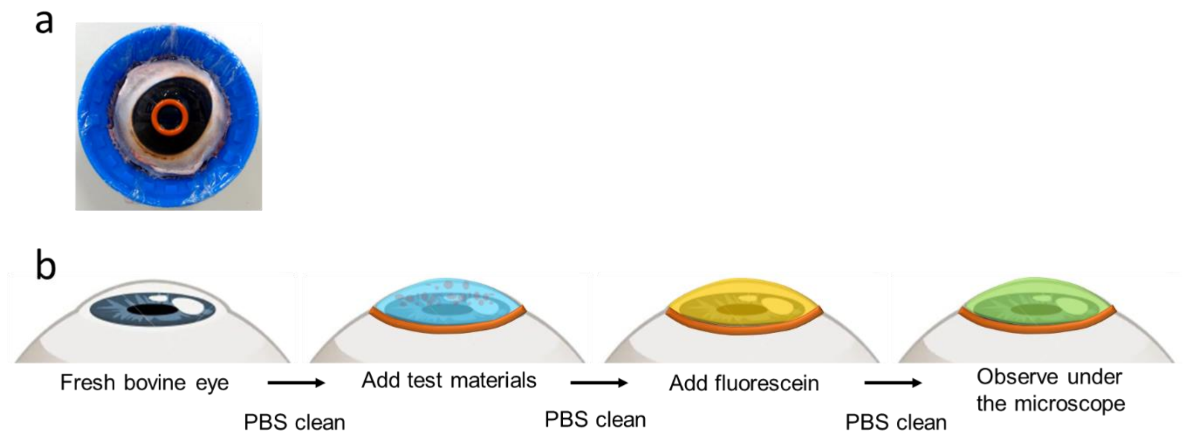


Figure S6. (a) A silicone ring placed on a fresh bovine eye. (b) Schematic diagram demonstrating the BCOP experiment process.

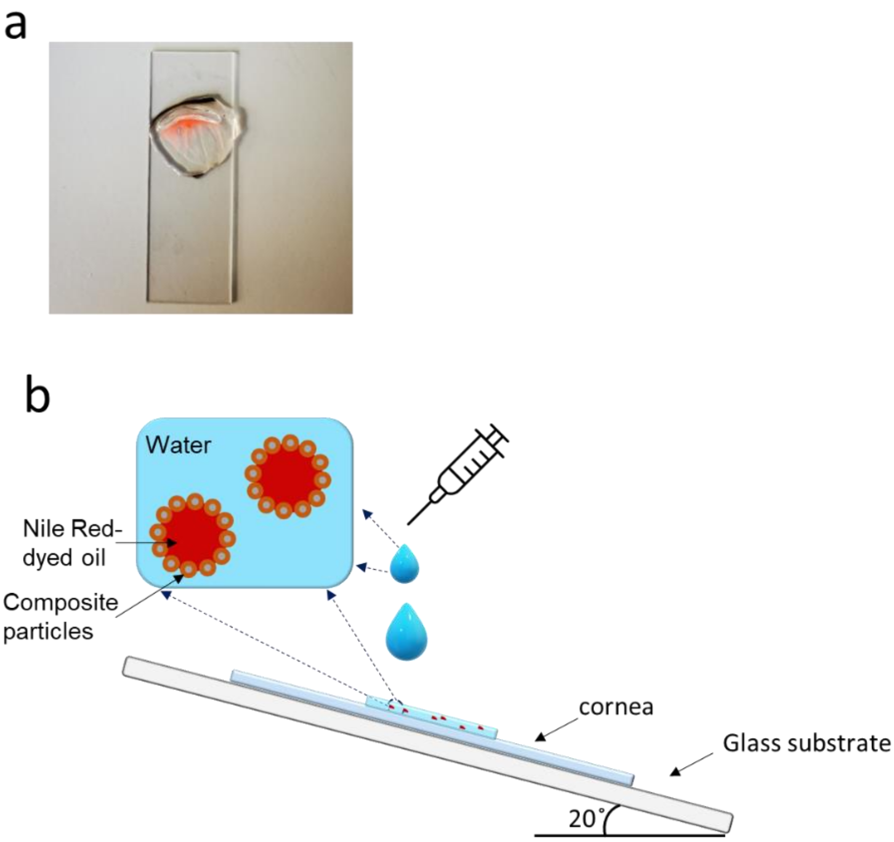


Figure S7. (a) ND-2T emulsions (with oil dyed with 0.5 mg/mL Nile Red) dropped on a bovine eye cornea. (b) A schematic diagram demonstrating the experiment process.

References

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