

Supplementary information

Functionalization of nano-emulsions with amino-silica shell at the oil-water interface

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1. Stability of nano-emulsions in serum (FBS)

Longitudinal size measurements were carried out in serum (FBS), as a function of the incubation time, for different dilutions (1/10, 1/100 and 1/1000), in order to investigate their stability. The data reported in Fig. S1.

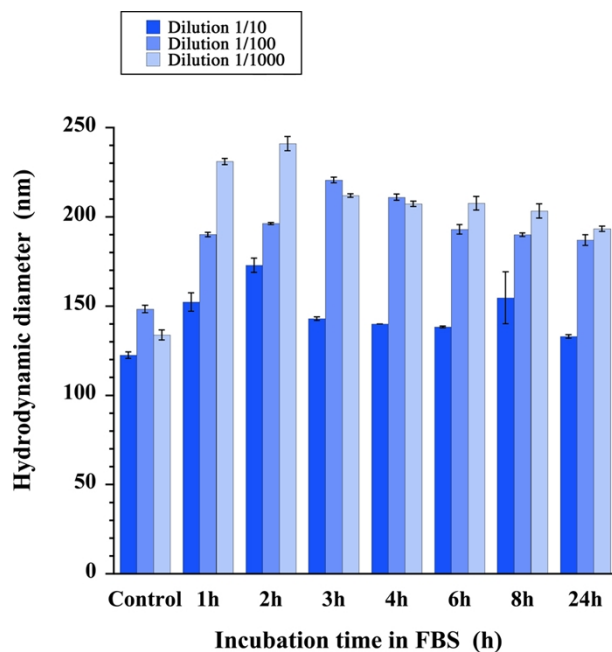


Figure S1: Stability of nano-emulsions in serum (FBS). The sizes of the droplets were determined by DLS for nanocapsules with $[APTES]_{oil} = 0.5$ M, at different dilutions ($n = 3$).

2. Quantification of NH_2 available onto the nanocapsule surface by the fluorescamine method

This section presents how the NH_2 quantification method using fluorescamine has been worked out. First, we used a model amine soluble in water, ethanolamine, in a given range of concentrations, to find the amounts of fluorescamine necessary to react with all the species.

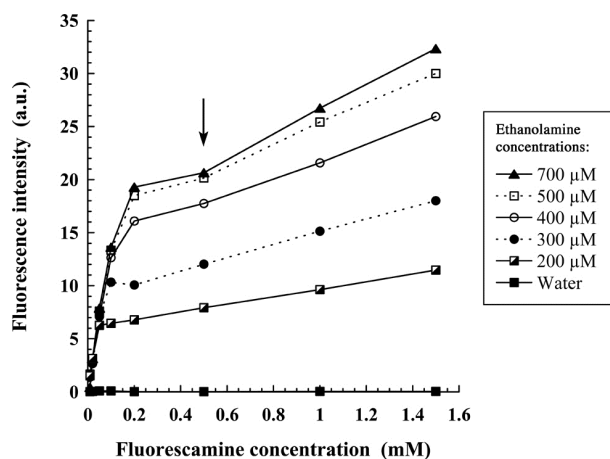


Figure S2: Determination of the fluorescamine concentrations necessary to saturate all NH_2 groups present in solution (see details in the text).

In Fig. S2, the ethanolamine concentrations were varied from 0 to 700 μM , and we measured the fluorescence intensities in the presence of increasing concentrations of fluorescamine. The curves show two distinct regions: (i) a sudden increase of the fluorescence for the lower fluorescamine concentrations, likely indicating that fluorescamine does not saturate the NH_2 sites, and (ii) a second region where fluorescence stabilizes, indicating that fluorescamine saturates all sites. We can note that fluorescence intensity is still slightly increasing in this second region, likely due to the fact that fluorescamine molecules do not actually saturate all NH_2 , and these unreacted sites are gradually accessed as fluorescamine concentration increase. However if we set the fluorescamine concentration this point will not interfere in the quantification. In addition, above an ethanolamine concentration equal to 500 μM , saturation region is reached.

Finally, if we chose $[\text{fluorescamine}] = 500 \mu\text{M}$ inside the fluorescamine excess region (shown by an arrow in Fig. S1), the linearity region is found for ethanolamine in the range $[0 ; 500 \mu\text{M}]$. The corresponding calibration curve, for $[\text{fluorescamine}] = 500 \mu\text{M}$ is thus reported in Fig. S3.

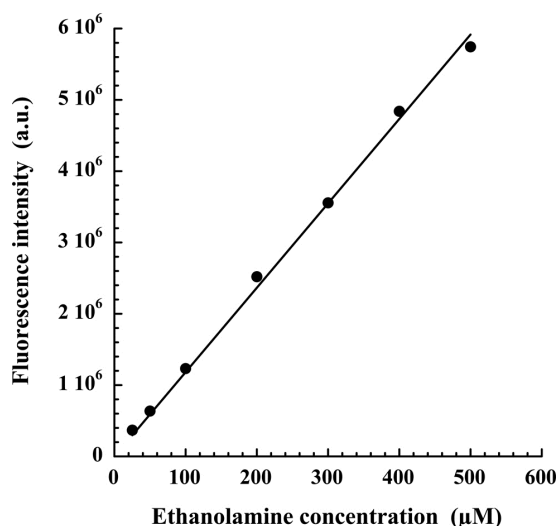


Figure S3: Calibration curve for the determination of the NH_2 concentrations in solution (made up with ethanolamine), at a fixed fluorescamine concentration of 500 μM .

3. Complementary results on the quantification of available NH_2 groups on the nanocapsule surface by the fluorescamine method

Fig. 5 in the main text describes the numbers of NH_2 groups that has reacted with fluorescamine per nanocapsule. Comparison of these numbers with the total numbers of NH_2 functions that were introduced in the formulations indicates that about half of the amines are still entrapped within the droplets (Fig. S4).

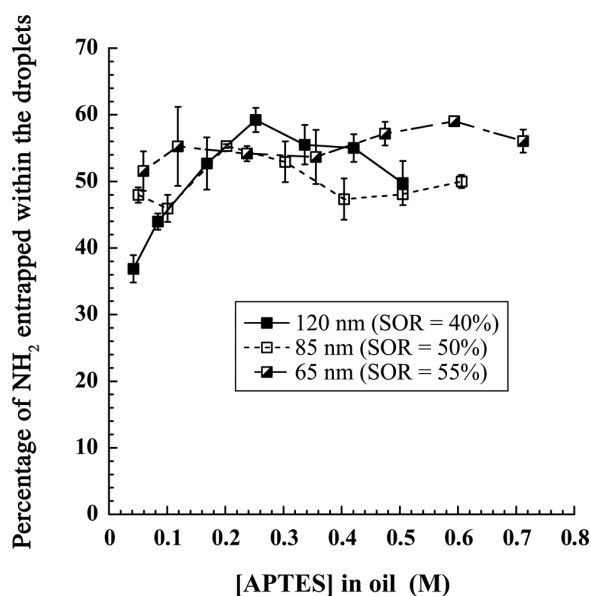


Figure S4: Proportion of NH_2 groups that have not reacted with fluorescamine, and that are thus, entrapped into the nano-emulsion core or within the nano-capsule surface.

4. Excitation and absorption spectra of coumarin blue grafted onto the surface of nanocapsules.

In addition to the emission spectra showing a red-shift of coumarin blue, once it is grafted onto the surface of nano-emulsion droplets, we report in Fig. S5 its absorption and excitation spectra.

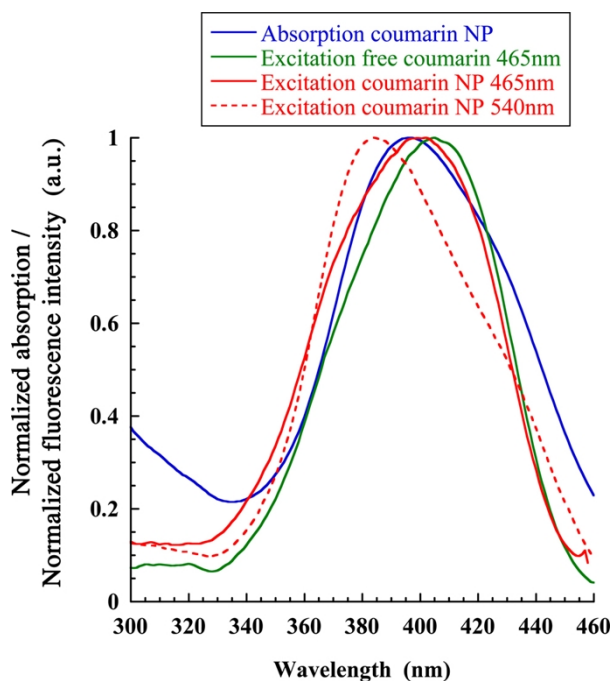


Figure S5: Absorption spectra of coumarin dye grafted onto the nano-emulsion droplets (blue) compared to the excitation spectra of free coumarin (green) and to the excitation spectra of coumarin grafted onto nanoparticles (red).

Excitation spectrum at 465 nm corresponds to free or unreacted dyes, and fit relatively well with the absorption spectrum of the free dye, as expected. On the other hand, the excitation spectrum at 540 nm corresponds to the grafted dyes. Its slightly spread profile and blue-shifted maximum can be explained by an aggregation-like state at the droplet surface.