## **Supporting Information**

#### 1. Methods

# a. Analysis of the Small Angle Scattering (X-ray and Neutron) Measurements on Silica Nanoparticles.

The SAXS data were fitted using a sphere model, where the scattered intensity is expressed as follows:

$$I_{sphere}(q,R) = P^2(q,R,\Delta\eta)$$

Where P is the expression of the form factor for sphere such as:

$$P(q, R, \Delta \eta) = \frac{4}{3}\pi R^3 \Delta \eta \frac{\sin qR - qR \cos qR}{(qR)^3}$$

And:

$$\lim_{q=0} I_{sphere}(q,R) = \left(\frac{4}{3}\pi R^3 \Delta \eta\right)^2$$

Where *R* is the radius of the sphere,  $\Delta \eta$  the scattering contrast and *q* the scattering wave vector.

### b. Cumulant Analysis of the Dynamic Light Scattering Data

DLS measurements involve the analysis of the time autocorrelation function of scattered light as performed by a digital correlator. The normalized time autocorrelation function of the intensity of the scattered light  $g^{(2)}(\tau)$  for a given delay time  $\tau$  is given by:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

where I(t) and  $I(t+\tau)$  are the intensities of the scattered light at times t and  $t+\tau$ , respectively.

The intensity-intensity time autocorrelation function may also be expressed in terms of the field-field time autocorrelation function  $g^{(l)}(\tau)$  as defined by the Siegert Relation:

$$g^{(2)}(\tau) = B + \beta [g^{(1)}(\tau)]^2$$

Where  $\beta$  is a factor that depends on the scattering geometry and B, commonly referred to as the baseline is the long-time value of  $g^{(2)}(\tau)$ .

The analysis of the cumulant expansion of the correlation function is performed here by fitting a polynom up to third order to the function  $ln(g^{(l)}(\tau))$ .

$$\ln[g^{(1)}(\tau)] = -\overline{\Gamma}\tau + \frac{\mu_2}{2}\tau^2 - \frac{\mu_3}{6}\tau^3$$

From this fit the mean apparent hydrodynamic radius  $R_h$  is calculated from the time first to third order fitting and the polydispersity index is calculated from the second moment  $\mu_2$  of second and third order fitting according to the following formulas:

$$R_h = \frac{k_B T}{6\pi\eta\overline{\Gamma}} q^2$$

$$PD.I = \frac{\mu_2}{\overline{\Gamma}^2}$$

Where T is the temperature,  $\eta$  the viscosity, q the scattering wave vector,  $k_B$  the Boltzmann's constant and  $\Gamma$  the mean decay rate.

## 2. Supporting Data

## a. Small Angle X-ray Scattering Measurements on Silica Nanoparticles.



Figure S1: Small Angle X-ray Scattering data of the pure Ludox HS-40 solution (4 wt.%). Fit performed using a sphere model leading to a particle radius of 8.36 nm and a polydispersity index of 0.14.

## b. Polydispersity Index From the Dynamic Light Scattering Data



Figure S2: Evolution of the polydispersity Index obtained by Dynamic Light Scattering measurements on samples containing different ratios [NP]/[Vesicle].



c. Cryo-TEM Images of mixed systems Liposomes/Nanoparticles

*Figure S3: CryoTEM image of a sample with [NP]/[Vesicle] = 18.5 showing the presence of a few free silica nanoparticles.* 



Figure S4: CryoTEM images of giant vesicles observed in instable systems where [NP]/[Vesicle] < 12.

- d. Stability at different pH and ionic strength.
- 1. samples at pH = 10



Figure S5: Photographs of samples with [NP]/[Vesicle] = 0, 4.6, 9.2, and 18.5 (from left to right) at pH = 10 immediately after preparation (A), after 65 h (B), and after 250 h (C). In (D) the hydrodynamic radius as obtained from DLS measurements as a function of time is displayed.

2. samples at pH = 6



Figure S6: Photographs of samples with [NP]/[Vesicle] = 0, 4.6, 9.2, and 18.5 (from left to right) at pH = 6 immediately after preparation (A), after 65 h (B), and after 250 h (C). In (D) the hydrodynamic radius as obtained from DLS measurements as a function of time is displayed.

3. samples in PBS buffer (pH = 7.4)



Figure S7: Photographs of samples with [NP]/[Vesicle] = 0, 4.6, 9.2, and 18.5 (from left to right) in PBS buffer (pH = 7.4) immediately after preparation (A), after 65 h (B), and after 250 h (C). In (D) the hydrodynamic radius as obtained from DLS measurements as a function of time is displayed.