

Electronic Supplementary Material (ESI) for Soft Matter

Deformation and poration of lipid bilayer membranes by cationic nanoparticles

Su Li and Noah Malmstadt

Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, 925 Bloom Walk, HED 216, Los Angeles, CA 90007, USA. Fax: +1 213 740 1056; Tel: +1 213 821 2034; E-mail: malmstad@usc.edu

Varying nanoparticle size and charge

In addition to the 20 nm cationic particles described in detail in the main text, GUVs were also incubated with 20 nm anionic carboxylate-modified polystyrene PNPs, 120 nm cationic amidine-modified polystyrene PNPs, and 25 kDa branched polyethylenimine (PEI) solutions. The zeta potentials of these NPs were 71, -45, 67, and 56 mV respectively for 20 nm cationic PNPs, 20 nm anionic PNPs, 120 nm cationic PNPs, and PEI. Typical results are shown in Figure 7. For the anionic PNPs (orange fluorescence) solution, the GUV membranes (red fluorescence) did not display any morphological changes (Figure S1a). There is in fact no significant accumulation of anionic NPs on the GUV surface, indicating that any interaction of anionic PNPs with the phosphatidylcholine group is weak. The 120 nm cationic NPs (green fluorescence) adhered to the GUVs membrane (red fluorescence) as shown in Figure S1b. There are some structures protruding from the membrane, but these are not as prominent or numerous as in the case of 20 nm cationic PNPs. As PEI (no fluorescence) attached to the

GUV membrane (red fluorescence), the GUV started to shrink and rh-dex (dim orange fluorescence in Figure S1b) leaked out of the GUV. Instead of forming dendritic protrusions, PEI caused membrane budding and collapse.

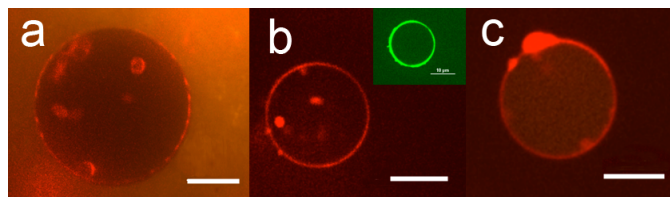


Fig. S1. Confocal images of GUVs interacting with various polymeric nanomaterials. (a) GUV with 20 nm anionic PNPs, (b) GUV membrane with 120 nm cationic PNPs, (c) GUV membrane with PEI. The scale bar is 10 μm in each image.

Fluorescein-dextran (fl-dex) photobleaching control

To demonstrate that intensity changes in fl-dex leakage experiments were caused by the membrane leakage instead of photobleaching, the fluorescent intensity of GUV-encapsulated fl-dex (250 kDa, 500 kDa, 2000 kDa) was monitored in the absence of PNPs over the experimental time frame, using the same illumination conditions and capture rate used in the experiment. No significant photobleaching could be observed.

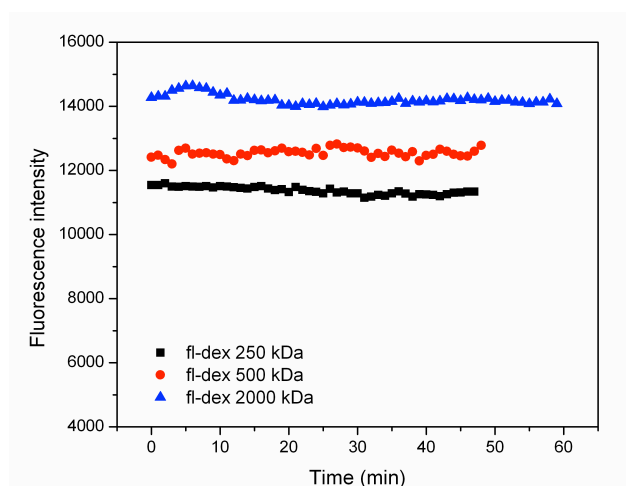


Fig. S2: Fluorescent intensity change of GUV-encapsulated fl-dex (250 kDa, 500 kDa, 2000 kDa) monitored in the absence of PNPs.

Delayed onset of nanoparticle binding is a result of particle diffusion to the GUV

In all time course nanoparticle binding experiments, we observed that there was a delay of 20-40 minutes between nanoparticle injection and initial observable nanoparticle binding to the membrane. This “induction time” is simply a result of the amount of time it takes for the nanoparticles to diffuse from the top of the sample chamber, where they are injected, to the bottom, at which the GUVs are sitting. This is clear if we examine the “background” nanoparticle fluorescence away from a GUV. Figure S3 shows two examples. Notice that these background intensities plateau at a level significantly less than that shown associating with the membrane in Figure 3.

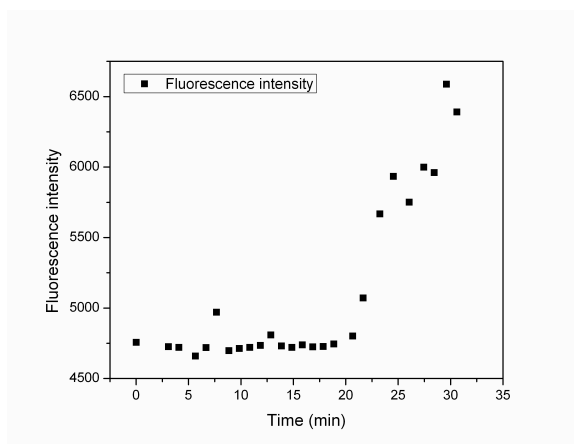


Figure S3: Typical background intensity change for in GUV-nanoparticle binding experiments.

Fraction of 2000 kDa fl-dex retained

We have estimated what fraction of 2000 kDa fl-dex was retained in the vesicle in the experiment shown in Figure 5. Based on the known size of the vesicle and assuming a constant fl-dex concentration and that intensity is linearly proportional to concentration, we have determined a “calculated” intensity, given as the red trace in Figure S4a below.

Notice that the experimental increase in intensity is less than this calculated increase. This means that some of the polymer species is being lost. We have calculated the amount of fl-dex present in the vesicle as a fraction of that expected to be present based on the assumption of no loss. The resulting leakage fraction is shown in Figure S4b. The actual loss of 2000 kDa fl-dex is about 60% on the basis of this analysis. A significant fraction was retained, and what was lost was likely due to fl-dex polydispersity.

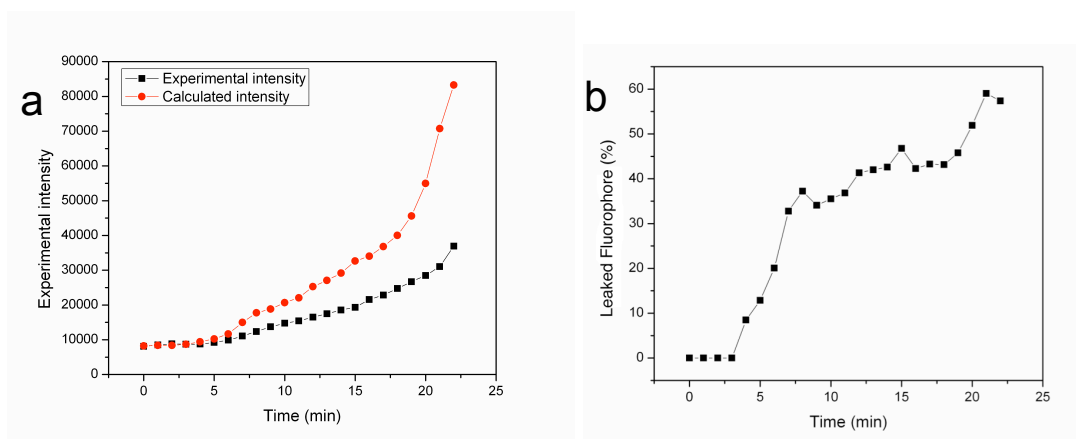


Figure S4: a) Fluorescence intensity changes of fl-dextran 2000k as calculated assuming no fluorophore leakage and as observed experimentally. b) Estimated fluorophore leakage determined by comparing calculated and experimental fluorescence intensities.

Budding of vesicles with bound nanoparticles

As described in the manuscript, we noted several occasions on which nanoparticle binding to GUVs induced vesicle budding. In many of these cases, an accumulation of nanoparticles at the junction between the main body of the vesicle and the budding region was apparent. Representative images showing this phenomenon are reproduced in Figure S5 below.

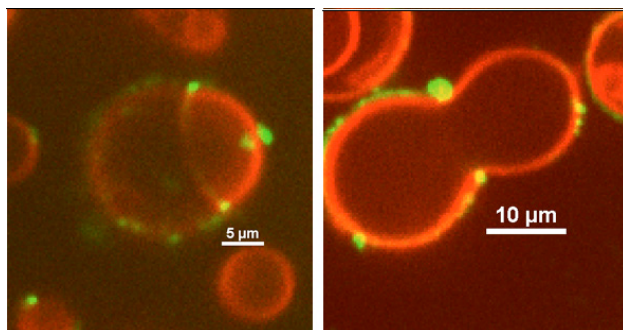


Figure S5: Representative confocal fluorescence micrographs of GUVs budding upon nanoparticle binding. Note particularly the accumulation of (green) nanoparticles at the budding boundary.