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Supporting Information for

Capsules with Hierarchical Shell Structure Assembled by Aminoglycoside and DNA via Kinetic Path

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Experimental Section

Materials: Kanamycin sulfate, salmon DNA (~2000 bp), Rhodamine B, and 1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine (DPPC, purity > 99%), were purchased from Sigma-Aldrich (St Louis, US). Rhodamine B-labeled lipid, 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine-N-(lissamine rhodamine B sulfonyl) (Rh-DPPE, purity > 99%), was purchased from Avanti Polar Lipids, Inc (AL, US). Whatman Nuclepore Track-Etch membrane for extrusion was purchased form GE Healthcare (Germany). Rhodamine B-labeled liposome (DPPC: Rh-DPPE = 99.9: 0.1, molar ratio) was prepared by the extrusion method[1] with 100 nm membrane.

Fabrication of DNA-kanamycin microcapsules: The capsule can be prepared into a variety of shapes either by changing the injection pattern or using the pushing and dragging method. Using the spherical capsule as an example, the DNA solution at c(DNA) = 1.0×10^{-2} g/mL to c(DNA) = 5.0×10^{-2} g/mL was added into kanamycin solution (c (kanamycin) = 1.0×10^{-1} g/mL) drop by drop. The size of the droplet can be tuned by changing the diameter

of the outlet. The droplet of DNA solution was transparent. However, a white and thin shell was quickly formed around the entire droplet, resulting in a microcapsule. The shell matured in about 1-10 min, depending on the concentration of DNA and kanamycin. The smallest diameter of the capsule was in the order of few hundred micron. The shell of the capsule was flexible in solution. It can be stretched with ease. However, the capsule would shrink, become brittle, and dry after being pulled out from water.

Microstructure characterization: The interaction of kanamycin and DNA at dilute solution was investigated by laser light scattering (LLS) and X-ray diffraction (XRD) via the osmotic stress method. A commercialized spectrometer BI-200SM Goniometer was used to perform both static light scattering (SLS) and dynamic light scattering (DLS), over a scattering angular range of 20-120°. Detailed LLS procedures were described in our previous papers.[2] Samples for LLS were passed through 0.45 μm syringe filter to remove dust. XRD experiments were performed with an in-house XRD setup (3×10^{7} photons/second, beam size of 0.8×0.8 mm) where radiation damage is negligible. To investigate the interface of the microcapsule, freeze-dried SEM samples (microcapsules formed by adding DNA (c(DNA) = 1.0×10^{-2} g/mL) to kanamycin (c (kanamycin) = 1.0×10^{-1} g/mL)) were stained by Au and examined using Hitachi-S4800 operated at 3 kV.

Encapsulation of molecules and nanoparticles: The mixture of DNA (c(DNA) = 1.0×10^{-2} g/mL) co-dissolved with small molecules Rhodamine B or Rhodamine B-labeled liposome solutions were added into kanamycin solution with a pipette. The small molecules or nanoparticles were encapsulated into the formed capsule. The fluorescent spectra were recorded at room temperature using Hitachi-F7000. DNA co-dissolved with Rhodamine B or Rhodamine B-labeled liposome added to TE buffer was taken as references. The total Rhodamine B intensity was recorded after dissolving the capsule with 2 M NaCl.

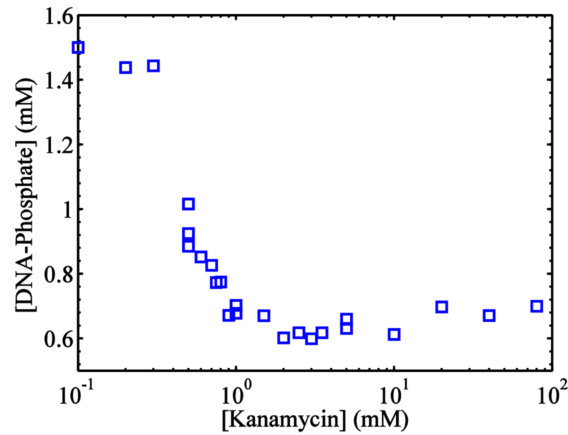

Figure S1. Differential sedimentation assay of kanamycin-induced DNA condensation. DNA and kanamycin stock solutions are mixed at appropriate volumes to give a sample series with constant DNA concentration (1.5 mM DNA-Phosphate) and varied kanamycin concentration. Each sample is vortexed and then centrifuged at 14000×rpm for 15 minutes. The concentration of DNA-Phosphate in the supernatant is shown as a function of kanamycin concentration . 1×TE buffer (10 mM Tris, 1 mM EDTA, pH 7.5) is used in all samples.

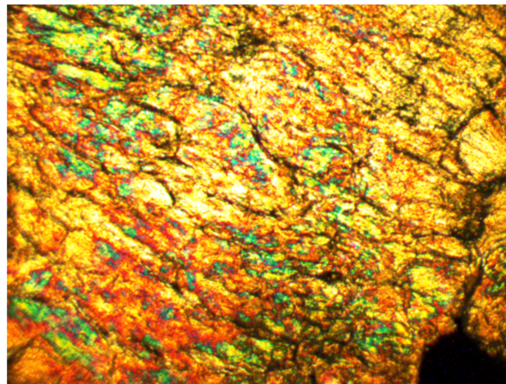

Figure S2. Polarized optical microscopy (POM) of the DNA-kanamycin complex. Strong optical birefringence is observed indicative of liquid crystalline ordering.

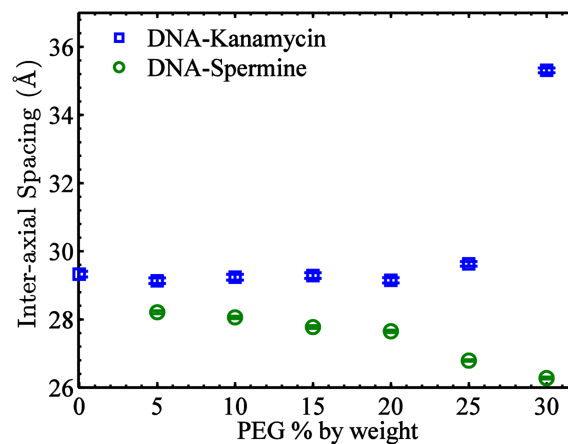

Figure S3. DNA-DNA spacings of the kanamycin- and spermine-DNA complexes as a function of the PEG concentration (weight/weight). Qualitatively different trends are observed.

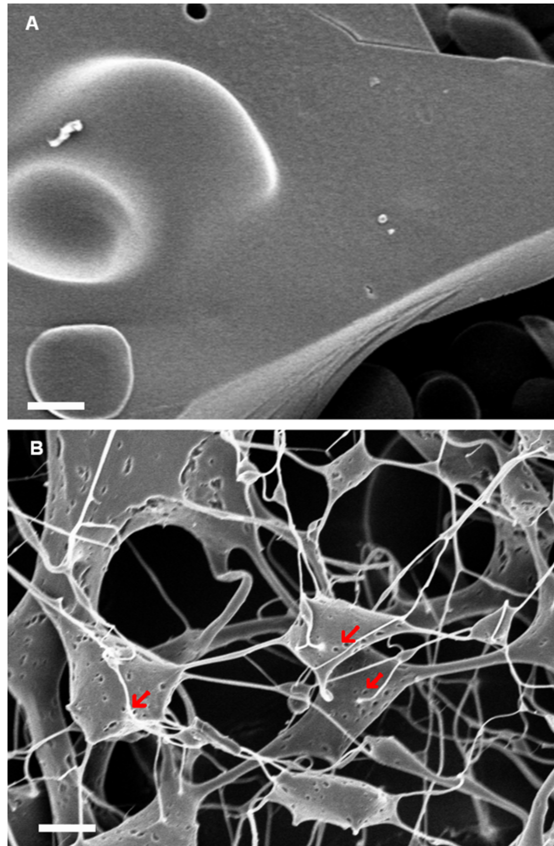

Figure S4. SEM images of kanamycin (A) and liposome-embedded capsule (B). Scale bars are 1μm. The red arrows in (B) indicate the location of liposomes.

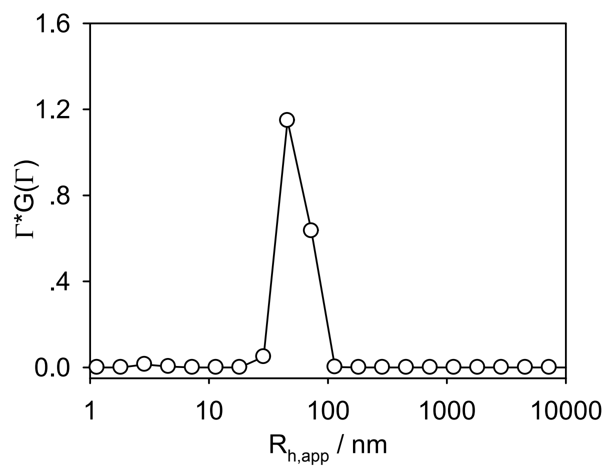

Figure S5. The size distribution of Rhodamine B-labeled liposome at 30°. c(liposome) = 5.0 nM.