Supplementary Material (ESI) for Nanoscale

Supporting information for

Real-time monitoring of lipid transfer between vesicles and hybrid bilayers on Au nanoshells using surface enhanced Raman scattering (SERS)

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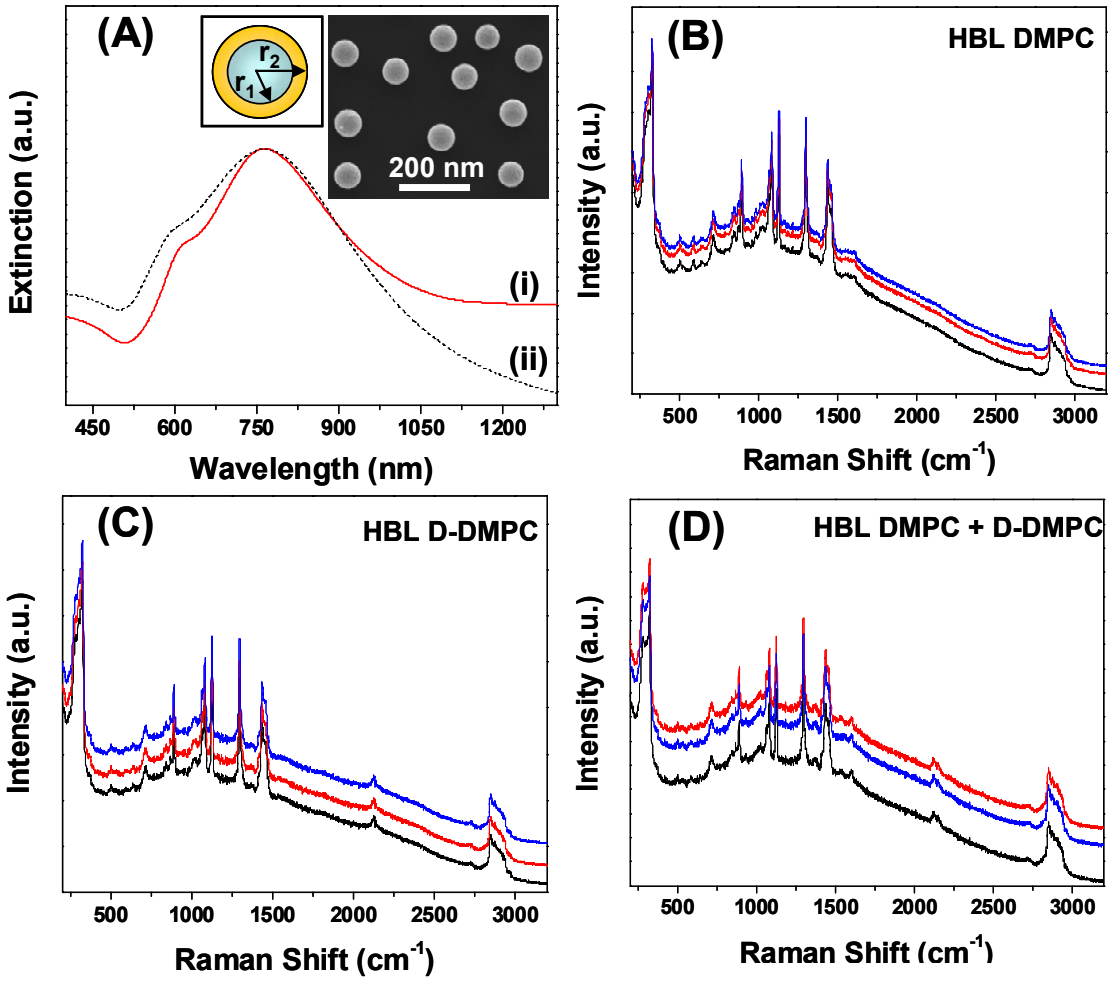

Figure S1. (A) Extinction spectra of silica core-Au nanoshells in water (i) experimental and (ii) Mie theory calculated (parameters $[r_1,r_2]$=[63,84] nm, aqueous medium). The insets show a schematic drawing of nanoshell with inner and outer radii $[r_1,r_2]$ and SEM image of fabricated nanoshells. SERS spectral reproducibility for the systems (B) HBL DMPC, (C) HBL D-DMPC, and (D) HBL DMPC + D-DMPC.

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Experimental procedures:

Fabrication of Au nanoshells: The reported protocol (*1*) was followed for fabrication of Au nanoshells.

Fabrication of hybrid bilayer on Au nanoshells: The reported protocol (*2*) was followed for fabrication of hybrid bilayer on Au nanoshells. Hybrid bilayer fabrication requires the formation of SAM of alkanethiol on nanoshells. The formation of a SAM on Au nanoshells requires the nanoshells to be dispersed in an ethanolic solution of dodecanethiol. The aqueous solutions of nanoshells were centrifuged at 350 RCF for 30 min. The particles were then resuspended in absolute ethanol. Alkanethiol monolayers were first prepared on the nanoshells by separately making a solution of 10 mM 1-dodecanethiol in absolute ethanol. This was diluted to 30 μM solutions with the Au nanoshells in ethanol and allowed to incubate overnight in the dark for covalent attachment. Thirty micromolar solutions were chosen based on the nanoshell surface area and concentration and based on the size of the dodecanethiol molecule (*3*) to provide monolayer coverage in ten times excess. After incubation, the nanoshells had settled and the supernatant was removed, so that the nanoshells were redispersed in fresh ethanol and any unreacted thiol was removed from solution. The dodecanethiol functionalized nanoshells were then allowed to dry completely. Lipid solutions of either 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) or 1,2-dimyristoyl-D54-sn-glycerol-3-phosphocholine (D-DMPC) were prepared by solubilizing the lipids in

isopropyl alcohol(50 μL per 2 μmol of lipid). The DMPC, D-DMPC lipids were added to alkanethiol functionalized nanoshells to give a final concentration of 100 μM DMPC lipids. The solutions were placed in anultrasonicator bath (VWR Model 150D) for 30 min at 30 °C, above the main phase transition temperature of the DMPC lipid (Tm) 24 °C) and DMPC-D54 lipid (Tm) 18.7 °C) where the lipid is in the liquid crystalline phase and the hydrocarbon chains are more compressible and fluid. All measurements were then performed at room temperature around 23 °C. The hybrid bilayer phase behavior was characterized using the fluorescent probe Laurdan, following the excitation generalized polarization technique of Bagatolli et al (*4*). For these measurements, an appropriate amount of hybrid bilayers formed with either DMPC or D-DMPC were mixed with amethanolic solution of Laurdan to achieve a lipid/probe ratio of 300:1. The emission spectra between 400 and 600 nm were obtained at a fixed excitation chosen between 320 and 390 nm. SERS substrates consisted of fused quartz coated with poly(4-vinylpyridine) (PVP). Cut quartz substrates were first treated with a piranha solution (a concentrated solution of sulfuric acid and hydrogen peroxide) for two hours followed by rinsing with ethanol and drying with nitrogen. Films of poly(4-vinylpyridine) were deposited by immersing in dilute (0.1%) solutions in absolute ethanol for two hours followed by rinsing with ethanol, drying with nitrogen, and then were allowed to cure overnight. The hybrid bilayer ibuprofen solutions were drop dried on the functionalized fused quartz substrates and then examined with either an inVia Raman microscope (Renishaw) with a 63× water immersion objective after rehydrating the sample. Water purified by a Milli-Q water system was used throughout the experiments. Excitation generalized polarization spectra were obtained using a JOBIN YVON UV-vis Fluorolog.

Fabrication of vesicles: The reported protocol (*5*) was followed for fabrication of vesicles.

References:

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