Supplementary Material (ESI) for *Soft Matter*

Membrane stabilization and transformation in organoclay/vesicle hybrid constructs

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Supporting Information

Aminopropyl-functionalized magnesium phyllosilicate was synthesized at room temperature as described previously (A. J. Patil, E. Muthusamy and S. Mann, *Angewandte Chemie-International Edition*, 2004, **43**, 4928). In brief, 3-aminopropyltriethoxysilane (3-APTES) (1.3 mL, 5.85 mmol) was added dropwise to an ethanolic solution of magnesium chloride (0.84 g, 3.62 mmol) in ethanol (20 g) to give a white slurry that was stirred overnight, and then isolated by centrifugation, washed with ethanol (50 mL) and dried at 40 °C. A suspension of polycationic organoclay oligomers was produced by dispersing 100 mg of the dried as-synthesized organoclay in distilled water (10 mL) followed by ultrasonication for 5 minutes. The resulting cloudy dispersion was passed through a Sephadex G-50 column (Aldrich) to produce a clear eluate of soluble organoclay oligomers with a concentration of 5-7 mg mL^{-1} and pH of ~10. In most preparations, the pH of the dispersion was reduced to 7 by titration with hydrochloric acid (0.5 M). The neutral oligomeric organoclay sol was subsequently diluted to achieve specific organoclay/lipid mass ratios in the vesicle coating experiments.

Characterization methods: Zeta potentials (Brookhaven Instruments Zeta Potential Analyzer) were determined for uncoated vesicles ([DMPG] = 1 mg mL^{-1}) and organoclay/vesicle constructs ([DMPG] = 0.125 mg mL^{-1}) at room temperature using unbuffered solutions. Samples for scanning electron microscopy, (SEM, JEOL JSM-6330 FEG) were prepared by placing a 100 μL droplet of the organoclay/vesicle suspension onto a 9 mm diameter aluminium stub for 20 minutes. The droplet was then carefully wicked away and the sample air dried before washing the stub twice with water. Transmission electron microscopy (TEM, JEOL JEM 1200 EX) samples of uncoated vesicles were prepared by placing a 5 μL drop of freshly prepared DMPG unilamellar vesicles (0.1 mg mL^{-1}) onto a carbon-coated 3 mm diameter copper grid for 2 minutes, before wicking away with filter paper. The sample was then immediately stained with a 5 μL droplet of uranyl acetate solution (2% w/w) for 20 seconds, and then washed twice with water. Organoclay/vesicle constructs were prepared for TEM in a similar manner but without the staining step.

Ibuprofen release experiments Ibuprofen-loaded DMPG vesicles were prepared by suspending DMPG lipids (10 mg) in an ibuprofen solution (1 M, 100 μL, pH 7) at 50 ºC for 1 hour to produce a turbid, viscous suspension of multilamellar vesicles. The suspension was ultrasonicated at 50 ºC for 30 minutes, and the resulting clear suspension of unilamellar vesicles then diluted with phosphate buffer (10 mM, pH 7) to a concentration of 2 mg mL^{-1}. For control experiments, 1.25 mL of the vesicle suspension was further diluted with 7.5 mL phosphate buffer (10 mM, pH 7) and 1.25 mL of water. Organoclay/vesicle composite samples were similarly prepared by diluting 1.25 mL of the vesicle suspension with 7.5 mL phosphate buffer (10 mM, pH 7) prior to the addition of 1.25 mL of the organoclay oligomers (1.2 mg mL^{-1}). The final ibuprofen concentration was 2.5 mM.

Figure S1

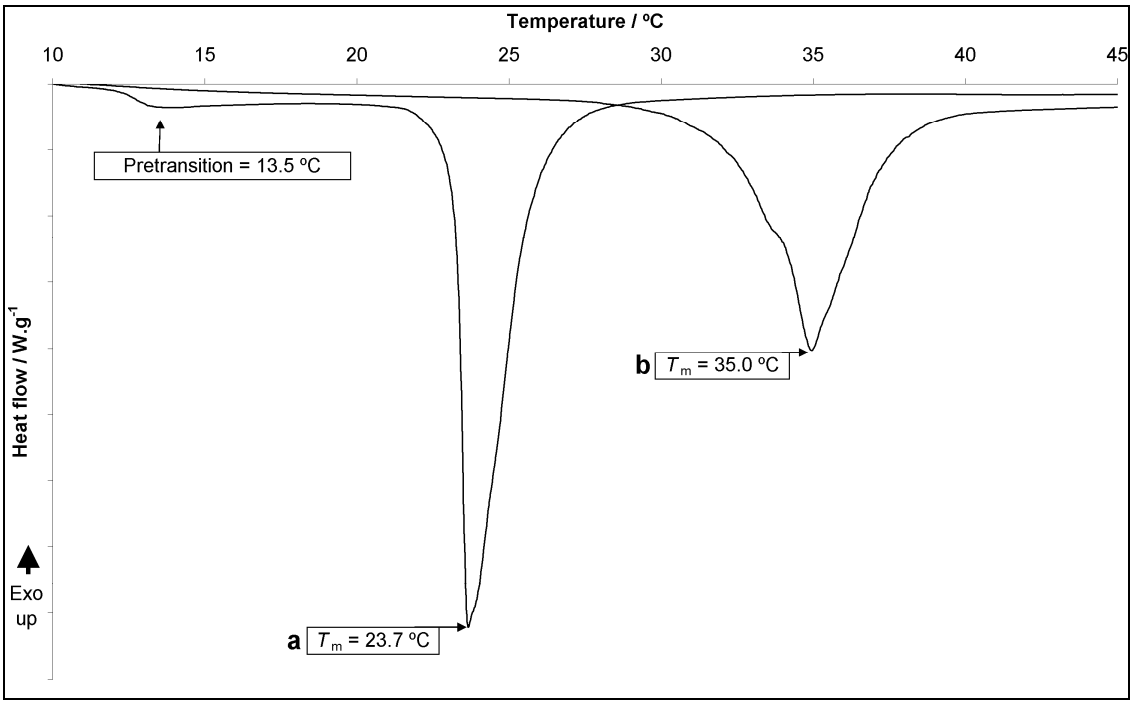

Figure S1 DSC thermograms of (a) DMPG vesicles showing the tilted gel ($L_{\beta'}$) to ripple ($P_{\beta'}$) phase change at 13.5 ºC and the $P_{\beta'}$ to fluid (L_α) state at 23.7 ºC and (b) organoclay/vesicle constructs prepared at R = 0.3 and 50 ºC, showing a single transition at 35.0 ºC.

Figure S2

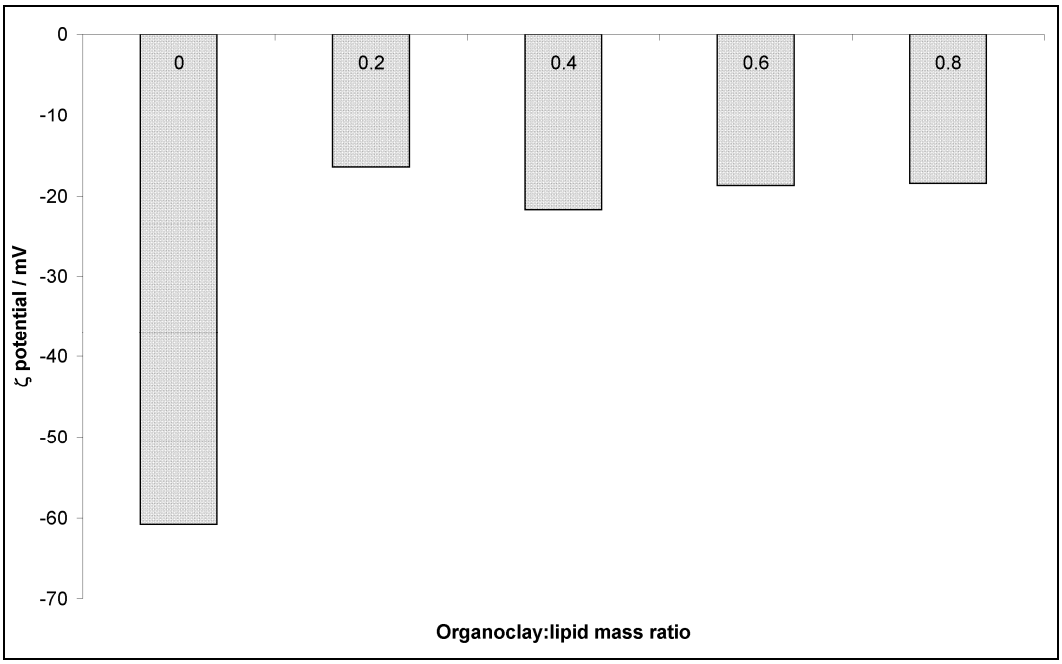

Figure S2 Zeta potential measurements for organoclay/vesicle constructs prepared at 50 ºC over a range of organoclay/lipid mass ratios (R).