Supporting Information Reaction Mediated Artificial Cell Termination: Control of Vesicle Viability using Rh(I)-Catalyzed Hydrogenation

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Experimental

1. General

Starting materials and reagents were purchased from Tokyo Kasei Kogyo (TCI: Tokyo, Japan), Wako (Tokyo, Japan), or Aldrich (Milwaukee, WI). GR grade or dry grade solvents were purchased from Wako, and used without further purification. ¹H spectra were recorded from solutions of the materials in CD₃OD using JEOL JNM-AL300 (300 MHz) FT NMR System. Coupling constants are given in Hertz. Reactions were carried out in oven-dried glassware under an argon atmosphere with magnetic stirring. Optical microscopy (OM) images were measured using a Nikon ECLIPSE ME600 microscope. Dynamic Light Scattering (DLS) profiles of the vesicles were measured using a Beckman Coulter DelsaTM Nano C Particle analyser using a 1 cm plastic cell.

2. Synthesis of catalyst

The hydrogenation catalyst Rh(amphos) was synthesized according to Ref. S1 and S2.

Norbornadienyl rhodium (I) dimer (2.5 mg) and Amphos tetrafluorobotate (3.90 mg, 2 eq.) were dissolved in MeOH (0.5 mL), stirred for 10 min then dried in vacuo. The catalyst was used after dissolution in water.

3. Reaction screening of oleate

Sodium oleate (20 mg) was dissolved in water, catalyst (5 mol%) was added and hydrogen donor (i.e., H_2 (gas), hydrazine (2 eq.), Hantsch's ester (2 eq.), cyclohexadiene (2 eq.) or hydrazine tosylate (2 eq.) was introduced. Progress of the reaction was monitored using NMR spectroscopy.

4. Oleate vesicle reduction

Oleate vesicles were synthesized according to Ref. S3. Sodium oleate (28.2 mg) was dissolved in 5 mL of buffer (pH 8.5, 0.22 M bicine). Catalyst (Rh(amphos)) was added followed by purging with H_2 (1 atm). Progress of the reaction was monitored using OM, NMR and DLS.

5. EggPC vesicle reduction

EggPC was dissolved in *t*-butanol, heated to 50 °C and sonicated. The solution was freeze-dried overnight. The resulting material was dissolved in PBS (50 mM, pH 7.0) and heated to 50 °C then sonicated. The liposome suspension was purified by high pressure extrusion through a track etched membrane (6 times, pore diameter 100 nm, pressure 2-6 MPa) to obtain a narrow-size distribution of liposomes (~ 100 nm). Catalyst (5 mol%) was added to the EggPC liposome suspension and it was purged with H₂ (1 atm). Progress of the reaction was monitored using NMR and DLS.



Figure S1. Optical micrograph of oleate vesicles.



Figure S2(a)(i). ¹H-NMR spectra. Upper: sodium oleate prior to reduction; lower: sodium oleate following reduction in its vesicular form. Yield of the oleate reduction reaction performed on vesicles (H₂, 8h, Rh(I) catalyzed) is based on lower intensity of the alkene resonance (5.35 ppm) relative to the intensity of the terminal methyl group (0.85 ppm).



Figure S2(a)(ii). Expansion of the ¹H-NMR spectrum in Fig. S2(a)(i). Reduced double bond of oleate vesicle.(H₂, 8h, Rh(I) catalyzed).



Figure S2 (b). ¹H-NMR spectra of Egg PC (assigned according to Ref. S4) prior to and following reduction (H₂, 2h, Rh(I) catalyzed). Yield of the Egg PC reduction reaction performed on liposomes (H₂, 2h, Rh(I) catalyzed) is based on the lower intensities of the alkene proton resonance (~5.30 ppm) and the resonance of the adjacent methylene protons (2.04 ppm) relative to the intensity of the terminal methyl group (0.85 ppm).

References

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