Electronic Supporting Information

Artificial Metalloenzymes via Encapsulation of Hydrophobic Transition-Metal Catalysts in Surface Cross-Linked Micelles

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General Method

All reagents and solvents were of ACS-certified grade or higher, and were used as received from commercial suppliers. Millipore water was used to prepare all aqueous solutions. ^{1}H NMR spectra were recorded on a BRUKER DRX-400 or a VARIAN VXR-400 spectrometer. Dynamic light scattering (DLS) was performed on a PD2000DLS^{PLUS} dynamic light scattering detector. UV-vis spectra were recorded at ambient temperature on a Cary 100 Bio UV-visible spectrophotometer. GC and GC-MS analysis were performed on an Agilent 6890 series GC system. The inductively coupled plasma (ICP) measurements were performed on a Thermo-Finnigan Element I Sector Field ICP-MS.

Caution: *Small organic azides are potentially explosive* and must be handled with care and avoid high temperatures, particularly in concentrated forms and/or in large quantities.

Synthesis

Synthesis of compounds **1** and **2** and the general preparation and characterization of the SCMs were previously reported.[1] The SCMs were characterized by NMR spectroscopy, DLS, and TEM. The crosslinking was confirmed by the cleavage of the 1,2-diol groups on the SCMs by periodic acid, followed by ESI-MS of the digested products.[1]

Typical Preparation of the SCM-encapsulated rhodium catalyst. (1,5-Cyclooctadiene)bis(triphenylphosphine)rhodium(I) hexafluorophosphate dichloromethane complex (1:1) (4.0 mg, 0.004 mmol) was added to a micellar solution of surfactant **1** (97 mg, 0.2 mmol) in millipore water (4.0 mL). The solution was gently rocked until the catalyst dissolved. 1,4-Diazidobutane-2,3-diol (52 mg, 0.03 mmol), $CuCl_2$ (10 μL of 67 mg/mL aqueous solution, 5 μmol), and sodium ascorbate (100 μL of 99 mg/mL aqueous solution, 50 μmol) were added to the above mixture. The reaction mixture was stirred slowly at room temperature for 12 h before 2-azidoethanol (17 mg, 0.2 mmol) was added. After another 6 h, the mixture was dialyzed against deionized water using a 6000-8000 Da molecular weight cut-off tubing.

Typical Preparation of SCM-encapsulated rhodium catalyst with the additive. To a micellar solution of surfactant **1** (97 mg, 0.2 mmol) and 1-dodecanol (9 mg, 0.05 mmol) in millipore water (4.0 mL), (1,5-cyclooctadiene)bis(triphenylphosphine)rhodium(I) hexafluorophosphate dichloromethane complex (1:1) (4.0 mg, 0.004 mmol) was added. The solution was gently rocked until the catalyst dissolved. 1,4-Diazidobutane-2,3-diol (52 mg, 0.03 mmol), $CuCl_2$ (10 μL of 67 mg/mL aqueous solution, 5 μmol), and sodium ascorbate (100 μL of 99 mg/mL aqueous solution, 50 μmol) were added to the above mixture. The reaction mixture was stirred slowly at room temperature for 12 h before 2-azidoethanol (17 mg, 0.2 mmol) was added. After another 6 h, the mixture was

[1] Zhang, S.; Zhao, Y. *Macromolecules* **2010**, *43*, 4020-4022.

dialyzed against deionized water using a 6000-8000 Da molecular weight cut-off tubing and diluted by Millipore water to give the Rh(I)-$[PPh_3]_2$@SCM stock solution (6.0 mL).

Determination of the concentration of rhodium in the Rh(I)-$[PPh_3]_2$@SCM stock solution. A portion (0.5 mL) of the above stock solution was diluted to 100.0 mL using Millipore water. The concentration of Rh was determined by ICP-MS to be 315.02 ± 10.93 ppb. The concentration of the Rh(I)-$[PPh_3]_2$@SCM stock solution was calculated to be 63 ± 2 mg/L or 0.612 ± 0.02 mM. Assuming that surfactant **1** reacted completely in the cross-linking and one SCM consisted of 50 cross-linked surfactants, the concentration of SCM in the stock solution was 0.667 mM. The number of rhodium atom in the SCM, therefore, was 0.612 ± 0.02/0.667 or 0.92 ± 0.03.

General procedure for the hydrogenation of alkenes. The biphasic hydrogenation was carried out in a 300 mL stainless reactor. The appropriate amounts of the Rh(I)-$[PPh_3]_2$@SCM catalyst, alkene, water, and a magnetic stirring bar were added into a 20 mL glass vial, which was placed inside the reactor. The reactor was sealed, flushed 3 times with 500 psi of H_2, and charged to the desired pressure. The reaction was continued at room temperature for 24 h with vigorous stirring. After careful depressurization, the reaction mixture was extracted by CH_2Cl_2 (3 × 3 mL). The organic layers were combined and concentrated in vacuo. The yields of the reactions were determined by ^1H NMR spectroscopy and, if necessary, by gas chromatography.

Recycling Experiment. The hydrogenation of 1-octene was performed as above. After each cycle of reaction, the aqueous phase (2 mL), where the catalyst was, was extracted with methylene chloride (3 × 3 mL) and left standing at 50 °C for ~2 min to evaporate the residual methylene chloride. Another batch of 1-octene was added and the next cycle of biphasic hydrogenation was performed. Extraction and solvent evaporation were performed in air without special protection.

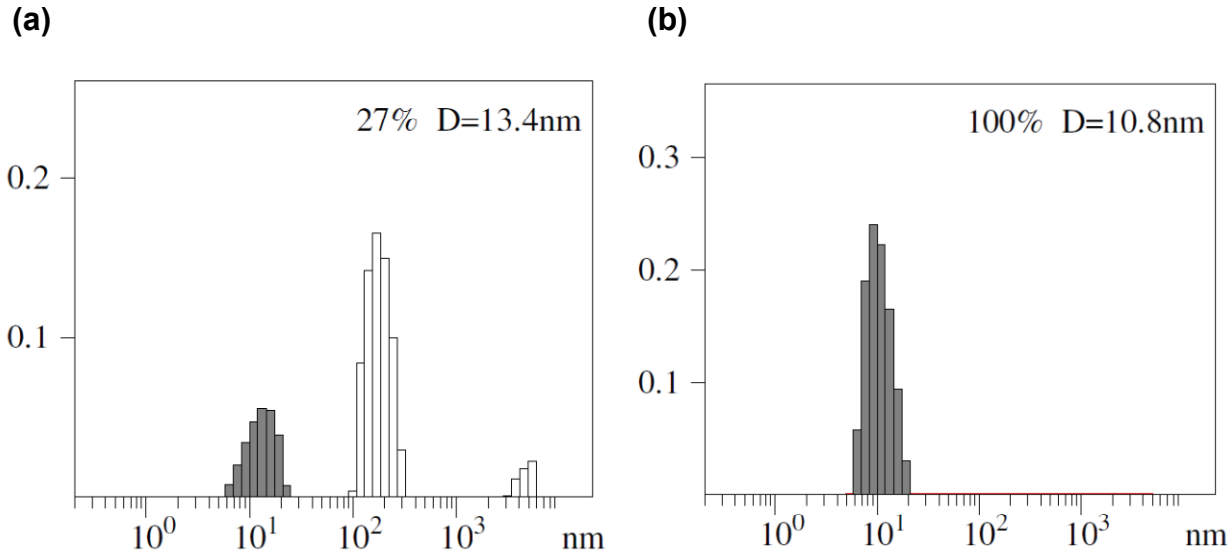

Figure 1S. Distribution of the hydrodynamic diameters of Rh(I)-$[PPh_3]_2$@SCM determined by DLS (a) without and (b) with molecular weight normalization. MW normalization provides a concentration normalized distribution of particles, as large particles scatter much more than small particles even when they are present in very small concentration. The MW-normalized size distribution was calculated by the PRECISION DECONVOLVE program assuming the intensity of scattering is proportional to the mass of the particle squared.

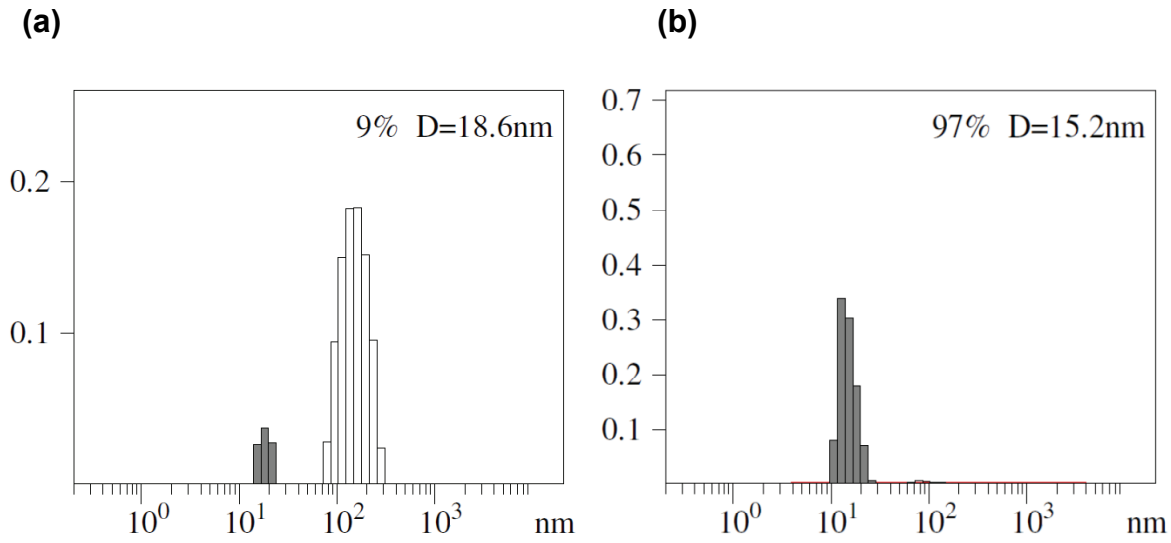

Figure 2S. Distribution of the hydrodynamic diameters of Rh(I)-$[PPh_3]_2$@SCM with 1-dodecanol as the additive determined by DLS (a) without and (b) with molecular weight normalization. MW normalization provides a concentration normalized distribution of particles, as large particles scatter much more than small particles even when they are present in very small concentration. The MW-normalized size distribution was calculated by the PRECISION DECONVOLVE program assuming the intensity of scattering is proportional to the mass of the particle squared.

GC and GC-MS analysis of the hydrogenation of 1, 2, 3, and 4-octenes catalyzed by Rh(I)-$[PPh_3]_2$@SCM in water.

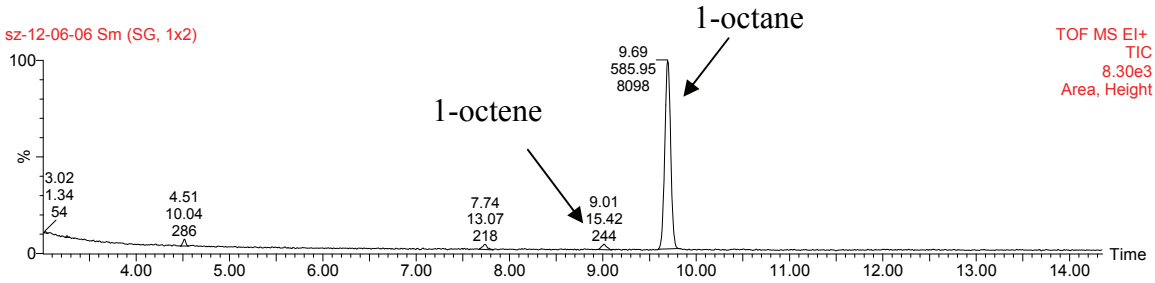

Figure 3S. GC data for the hydrogenation of 1-octene, with the product yield of 98%. The yields were determined from corrected TIC peak areas adjusted by response factors calculated from standards.

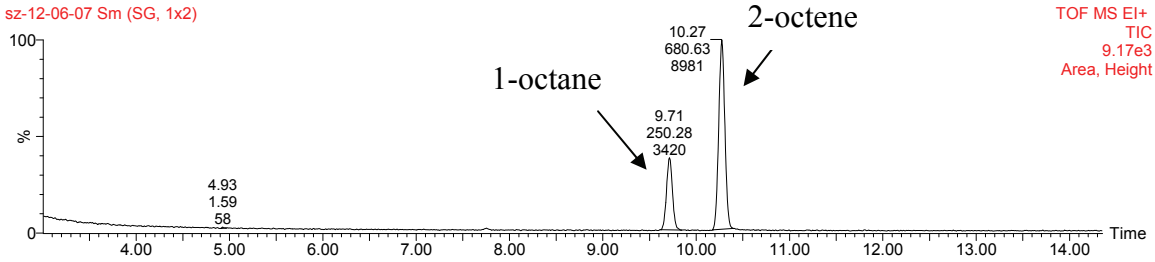

Figure 4S. GC data for the hydrogenation of 2-octene, with the product yield of 22%. The yields were determined from corrected TIC peak areas adjusted by response factors calculated from standards.

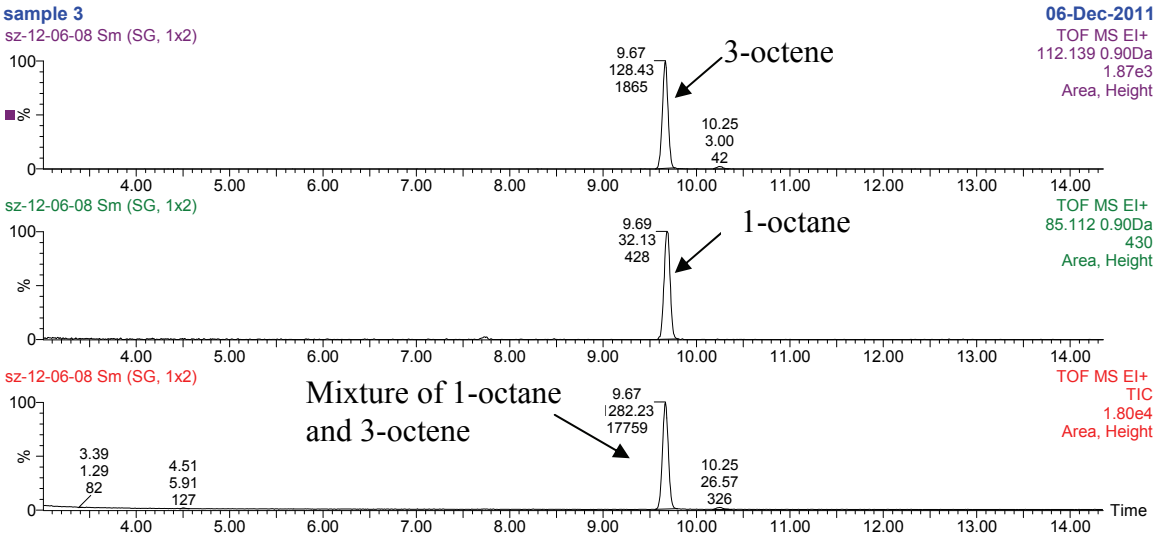

Figure 5S. GC data for the hydrogenation of 3-octene, with the product yield of 10%. Because the starting material and the product overlap in the GC trace, quantitation ions were used to obtain corrected TIC areas. This required calculating quantitation factors by running standards. The yields were determined from corrected TIC peak areas adjusted by response factors calculated from standards.

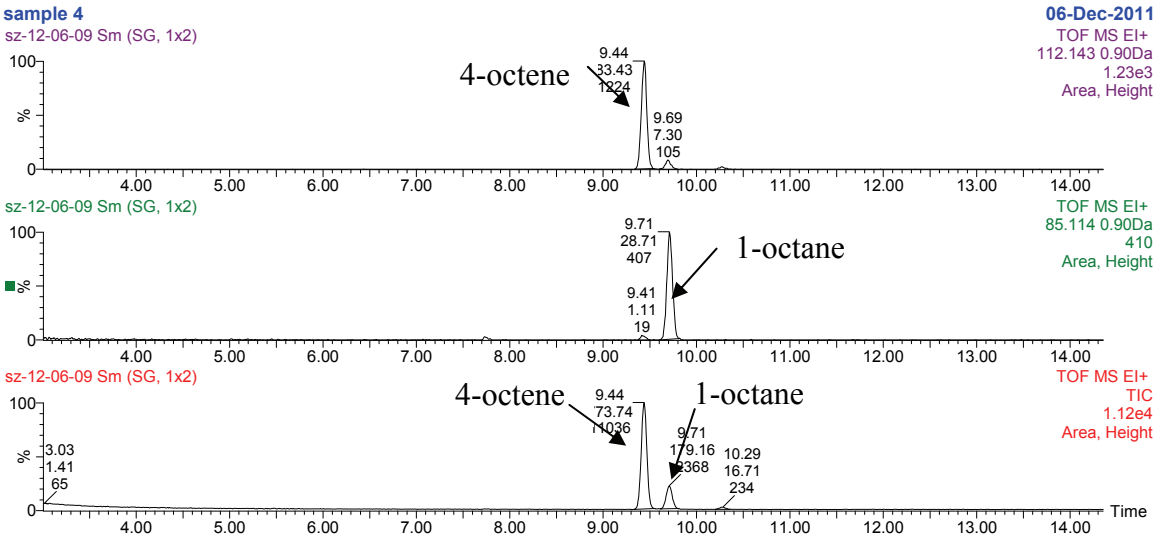

Figure 6S. GC data for the hydrogenation of 4-octene, with the product yield of 18%. The yields were determined from corrected TIC peak areas adjusted by response factors calculated from standards.

Table 1S. Hydrogenation of 1-octene using Rh(I)-$[PPh_3]_2$@SCM [a]

Reaction cycle	Yield (%)	TOF (h^{-1})
1	94	19.6
2	97	20.2
3	88	18.3
4	95	19.8
5	86	17.9
6	93	19.4
7	90	18.8
8	77	16.0

[a] Catalytic hydrogenation was carried out with 0.2 mol % Rh catalyst and 1200 psi H_2 for 24 h. Yields were determined by ^{1}H NMR spectroscopy after the reaction mixture was extracted with dichloromethane.

Table 2S. Hydrogenation of 1-octene using Rh(I)-$[PPh_3]_2$@SCM [a]

Reaction cycle	Yield (%)	TOF (h^{-1})
1	38.9	32.4
2	45.1	37.6
3	42.7	35.6
4	34.7	28.9
5	42.9	35.7
6	24.4	20.3
7	39.3	32.7
8	42.7	35.6
9	38.6	32.2
10	40	33.3
11	36.1	30.1
12	33.9	28.2
13	29.6	24.6
14	23.7	19.8

[a] Catalytic hydrogenation was carried out with 0.2 mol % Rh catalyst and 1200 psi H_2 for 6 h. Yields were determined by ^{1}H NMR spectroscopy after the reaction mixture was extracted with dichloromethane.