Supplementary Information

Rh-Coordinated Histidyl Bolaamphiphile Assembly: A Catalyst for the Isomerization of *cis*-Stilbene and *cis*-Alkene

Junsang Lee, Minji Kim, Hyesung Lee, and Sang-Yup Lee*

Department of Chemical and Biomolecular Engineering, Yonsei University

50 Yonsei-ro, Seodaemun-gu, Seoul 03722 Republic of Korea

1. Comparison of the reaction conditions and catalytic activity

Table S1. Yield of the trans-stilbene by catalytic isomerization

Catalyst	Type	Temp (ºC)	Solvent	Reaction time (h)	Yield (%)	Ref.
Elemental Se	Homogeneous	210	Not specified	1	~65	1
$Ru_3(CO)_9(PPh_2H)_3$	Homogeneous	120	n-octane	1	51	2
Diaryl disulfide	Homogeneous	66	THF	4	99	3
ZnI_2 + pyridyl triazine	Heterogeneous (photocatal.)	R.T.	cyclohexane	6 23	~47 ~77	4
HisC7[Rh]	Heterogeneous	50	H_2O+ACN	12	69.4	This work

[1] J. D. Fitzpatrick, M. Orchin, *J. Org. Chem.* **1957,** 22, 1177-1179.

[2] M. Castiglioni, R. Giordano, E. Sappa, *J. Organomet. Chem.* **1989,** 369, 419-431.

[3] M. A. Ali, Y. Tsuda, *Chem. Pharm. Bull.* **1992,** 40, 2842-2844.

[4] K. Ohara, Y. Inokuma, M. Fujita, *Angew. Chem. Int. Ed.* **2010,** 49, 5507-5509.

2. Synthesis of His-C7

The histidine-terminated amphiphilic molecule of HisC7 was synthesized by conjugating L-histidine with azelaic acid via carbodiimide chemistry. L-histidine monohydrochloride monohydrate (≥ 99.0%, Sigma-Aldrich) was modified to produce L-histidine benzyl ester which is advantageous to increase the conjugation efficiency. Carbodiimide conjugation was conducted using the carbodiimide conjugation reagents of *N*-hydroxy-succinimide (NHS), N-N, diisopropylethylamine (DIEA), and *N,N,N',N'*-tetramethyl-o-uranium hexafluorophosphate (HBTU). Synthesis procedures are as follows; first, dissolve 0.3 g and 1.04 g of azelaic acid (98%, Sigma-Aldrich) and HBTU (≥ 98.0%, Sigma-Aldrich) in 20 mL DMF, respectively. HBTU activates the carboxyl groups of azelaic acid for conjugation. Then, add 0.3 g of NHS (98.0%, Sigma-Aldrich) and 1 mL of DIEA (99.5%, Sigma-Aldrich), which assist the carbodiimide conjugation, to the azelaic acid DMF solution. The peptide conjugation is conducted by adding the histidine benzyl ester to the reactant mixture in DMF. The reactant mixture was stirred at room temperature overnight under magnetic stirring to conduct the conjugation reaction. The intermediate product was filtered and then washed with ethyl ether and DMF to remove the remaining chemicals from the product. The intermediate product was hydrolyzed by washing with 140mL NaOH (0.1M) and 20 mL HCl (1.0 M) in sequence. The product of HisC7 was obtained by removing solvent using a rotary evaporator. The obtained powder was washed with cold water and cold acetone thrice. The obtained HisC7 product was dried in the drying oven at 60ºC to obtain HisC7 powder. The dried HisC7 powder was dispersed again in water and dialyzed twice against deionized water for 2.5 h each to remove the salt. The dialyzed HisC7 was obtained in powder by rotary evaporation.

3. Cryo-TEM image of HisC7[Rh] and Az[Rh] assemblies

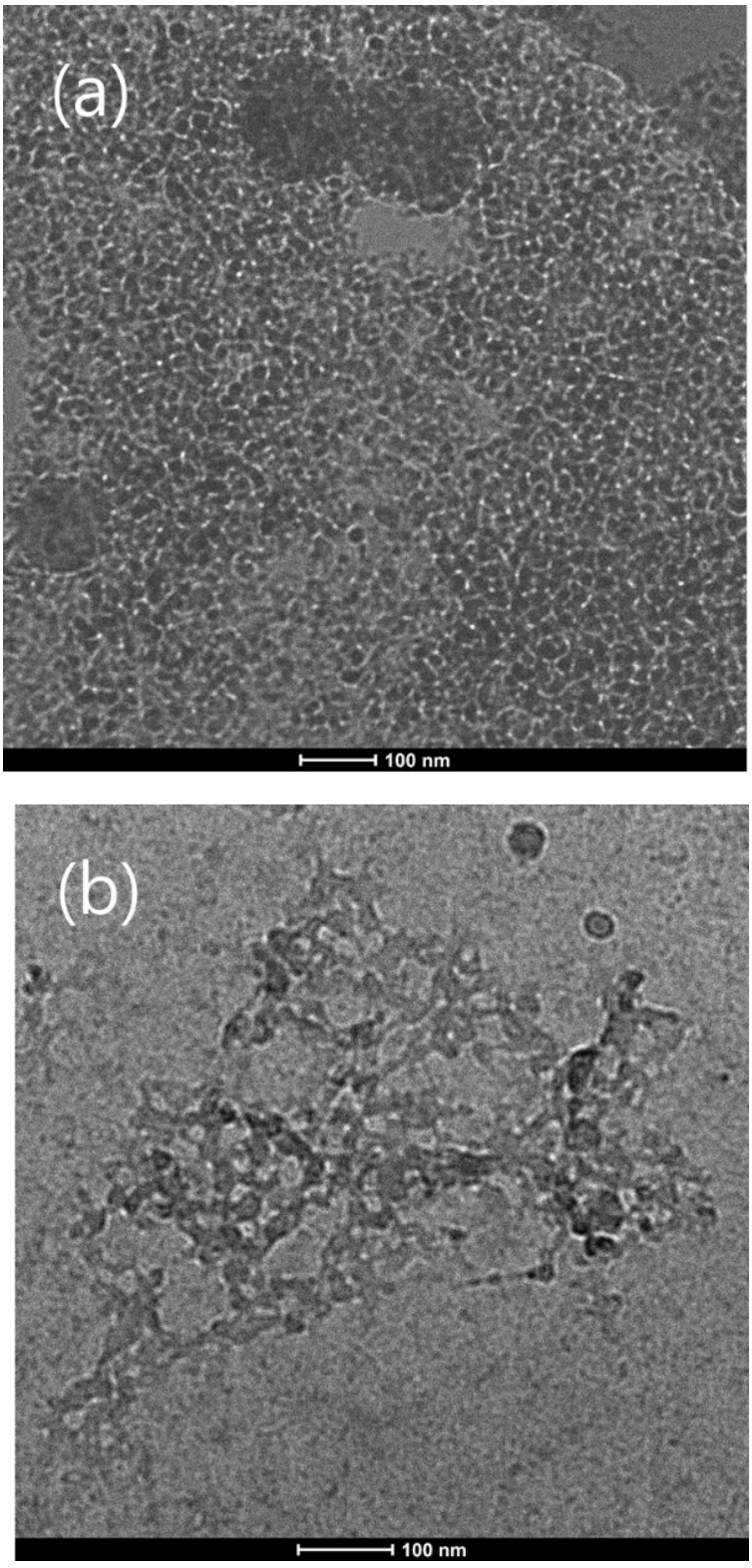
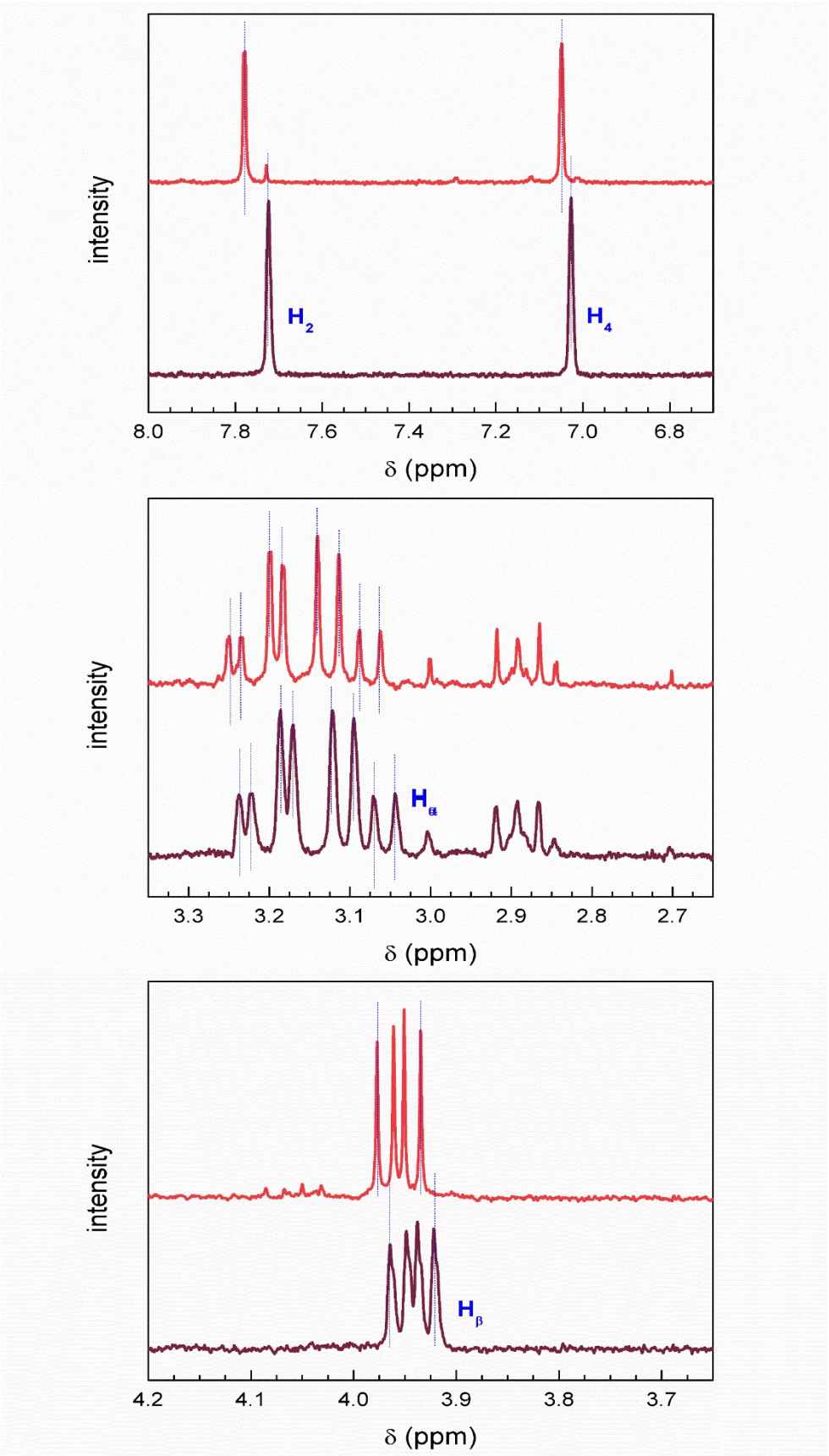


Figure S1. Cryo-TEM images of (a) HisC7[Rh] and (b) Az[Rh] assemblies (scale bar: 200 nm)

4. ^{1}H-NMR spectroscopy before/after the Rh coordination to HisC7 assembly



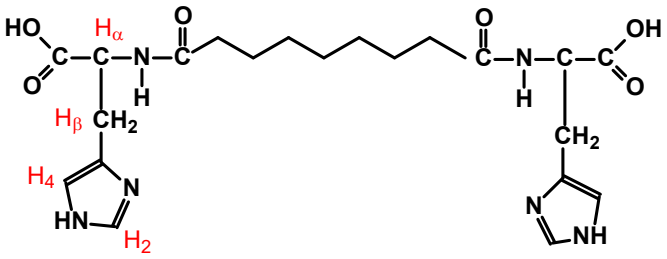


Figure S2. ^{1}H NMR spectra of HisC7 before (black lines) and after (red lines) the Rh coordination. The positions of each proton are illustrated in the molecular structure of HisC7. NMR samples were prepared at a concentration of 2 mg/mL using D_2O as a solvent and sodium trimethylsilylpropanesulfonate (DSS) as a standard.

Table S2. Characteristic peak positions of HisC7 and peak shift after the Rh coordination

Proton	HisC7 (ppm)	HisC7[Rh] (ppm)	Δδ (ppm)
H_2	7.72	7.78	- 0.06
H_4	7.02	7.04	- 0.02
H_α	3.04	3.06	- 0.02
H_β	3.92	3.93	- 0.01

5. Post-reaction assessment of HisC7[Rh]: FT-IR spectra

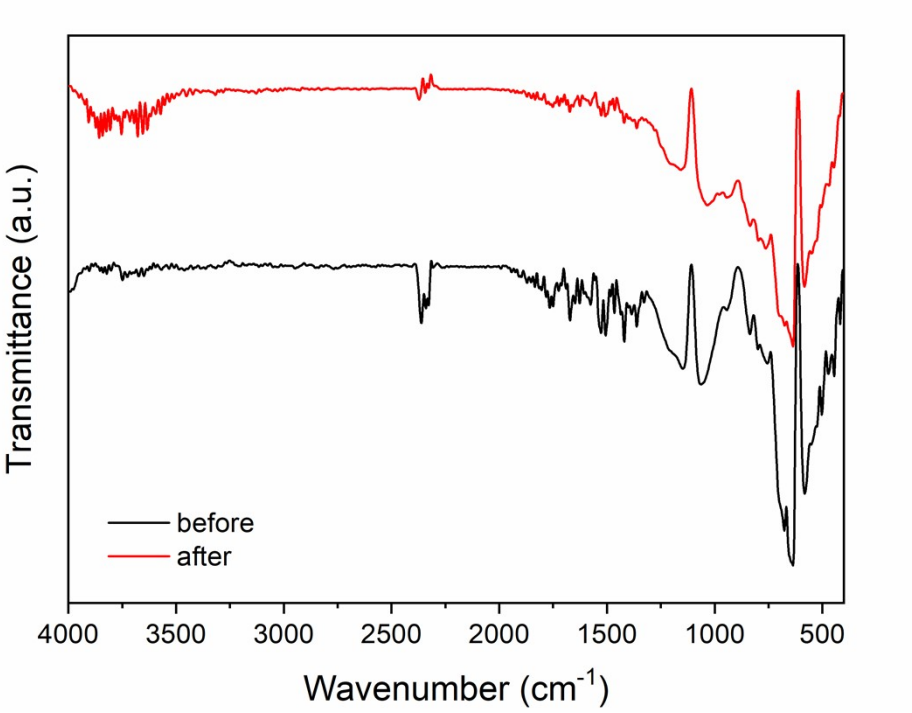


Figure S3. FT-IR spectra of HisC7[Rh] before and after the cis-stilbene isomerization reaction

6. Changes in the catalytic activity with concentrations of L-histidine

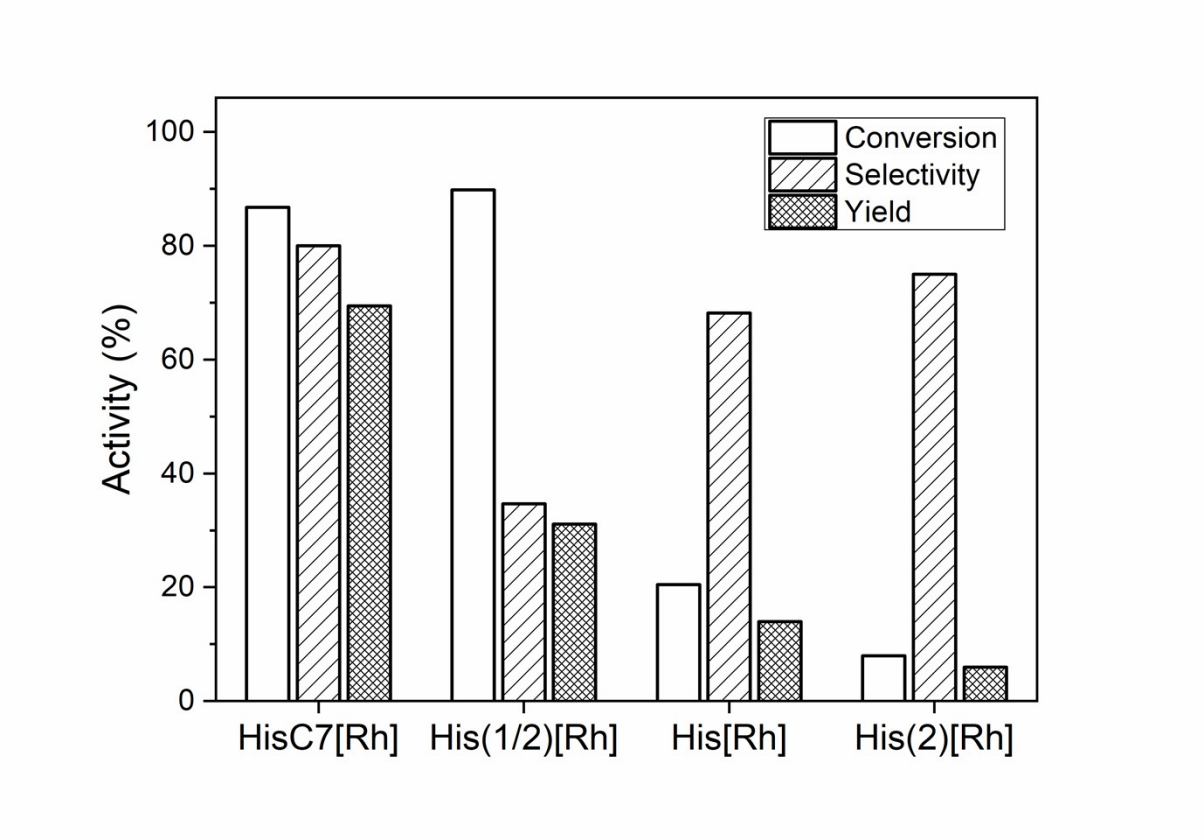
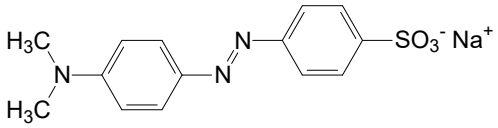
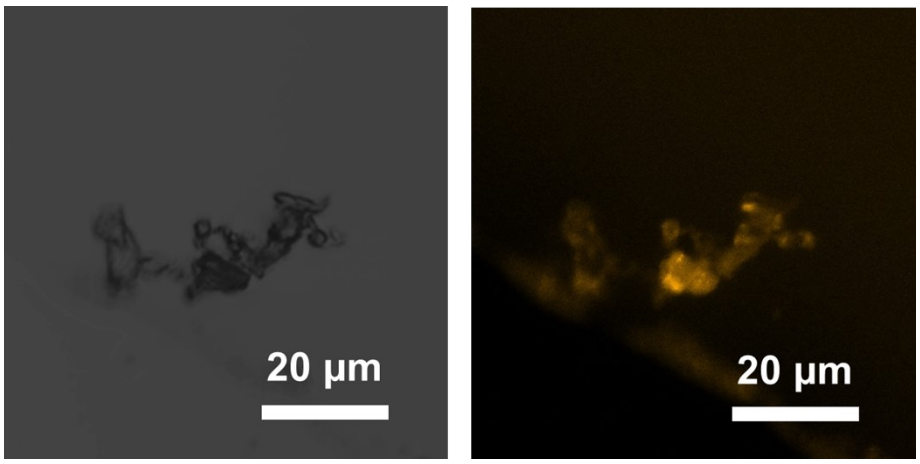


Figure S4. Comparison of the catalytic activity with variation of L-histidine. His[Rh] was prepared at the same concentrations of HisC7 and Rh(cod)2: 216.56 μM and 172.38 μM, respectively. His(1/2)[Rh] and His(2)[Rh] was prepared by adding L-histidine at half and double concentrations (108. 28 μM and 433.12 μM), respectively. (Reaction conditions are as follows; temperature: 50 ºC; solvent: a mixture of MES buffer (pH 6.0) and ACN at v/v = 2:1; H_2 pressure: 7 atm; reaction time: 12 h).

7. Visualization of substrate binding on HisC7[Rh]*



(a)



(b)

Figure S5. Fluorescence micrographs showing adsorption of methyl orange on HisC7[Rh] aggregates. (a) Molecular structure of methyl orange used as a substituent of cis-stilbene for visualization, (b) Optical (left) and corresponding fluorescence (right) images of MO-bound HisC7[Rh].

*The binding of methyl orange (MO), instead of *cis*-stilbene, on HisC7[Rh] was investigated because photoluminescence emission from *cis*-stilbene was hardly observed, For the fluorescence microscopy, 2.5 mL HisC7[Rh] suspension (conc. 0.1 mg/mL) was mixed with 100 μM MO. After 1 h mixing, 50 μL of the mixture was dropped on a glass slide and observed using a confocal microscope (LSM 980, Carl Zeiss, λ_{ex} = 548 nm).

8. Changes in the catalytic activity by the removal of remaining chemicals via dialysis

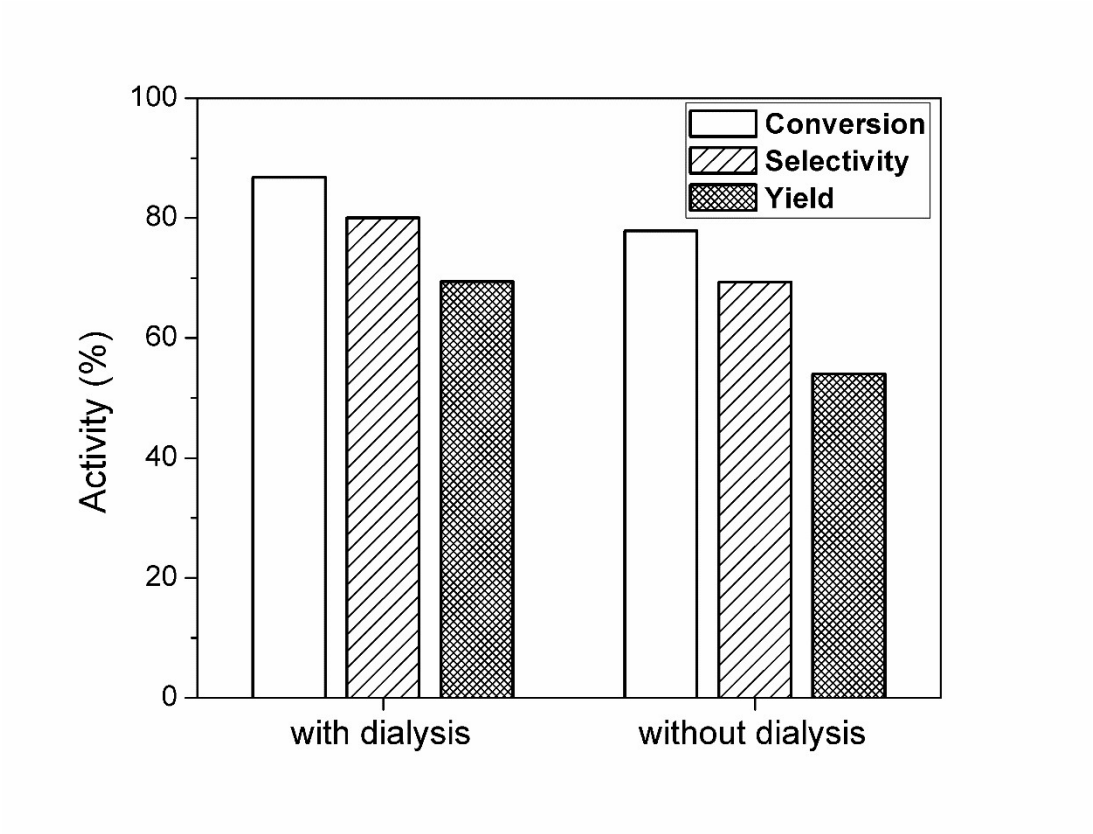


Figure S6. Comparison of the catalytic activity with/without the dialysis of HisC7[Rh] to remove remaining chemicals including unbound $Rh(cod)_2BF_4$ and cod ligands (Temperature: 50 ºC; Solvent: a mixture of MES buffer (pH 6.0) and ACN at v/v = 2:1; H_2 pressure: 7 atm; reaction time: 12 h).

9. Catalytic activity under N_2 environment

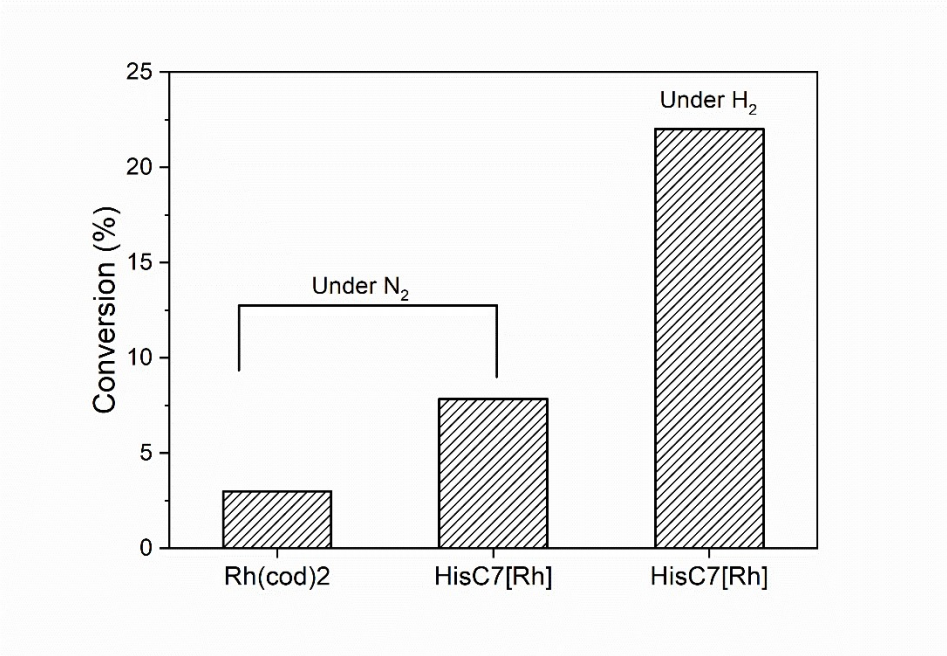


Figure S7. Conversion of *cis*-stilbene under N_2 environment. The reactor was filled with N_2 (1 atm) instead of H_2 for the control experiment. Conversion efficiency markedly decreased regardless of the catalysts (HisC7[Rh] and $Rh(cod)_2$) under N_2. Reaction conditions are as follows; temperature: 50 ºC, solvent: mixture of MES buffer (pH 6.0) and ACN at v/v =1:1; N_2 or H_2 pressure: 1 atm; reaction time: 12 h).

10. Denaturation of HisC7[Rh] at high temperature

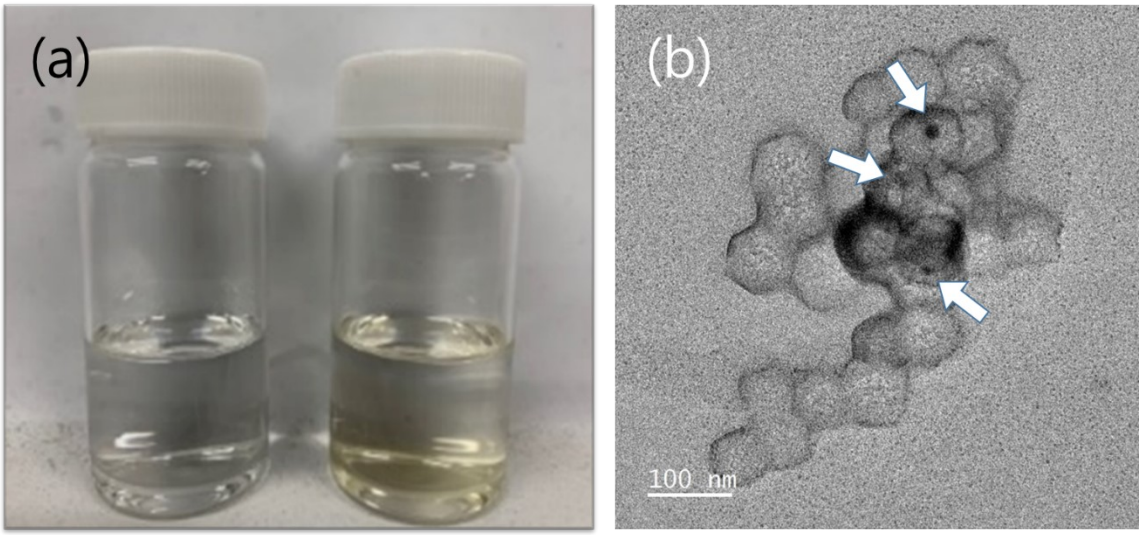


Figure S8. Deterioration of HisC7[Rh] after the reaction at 70ºC. (a) Photo image of the HisC7[Rh] after reaction at 40 ºC (left) and 70ºC (right), (b) TEM image of HisC7[Rh] showing Rh_2O_3 nanoparticle formation after the 70 ºC reaction. Arrows indicate nanoparticles (scale bar: 100 nm).

11. Variation of the hydrodynamic diameter of HisC7[Rh] with temperature

Table S3. Hydrodynamic diameters of HisC7[Rh] with the temperature variation

Temp. (ºC)	30	40	50	60	70
Diameter (nm) Mean ± S.D.	120.6 ± 14.6	62.0 ± 7.8	62.9 ± 5.0	51.5 ± 1.9	41.3 ± 1.5

12. Dynamic light scattering of HisC7[Rh] in the water-acetonitrile mixture

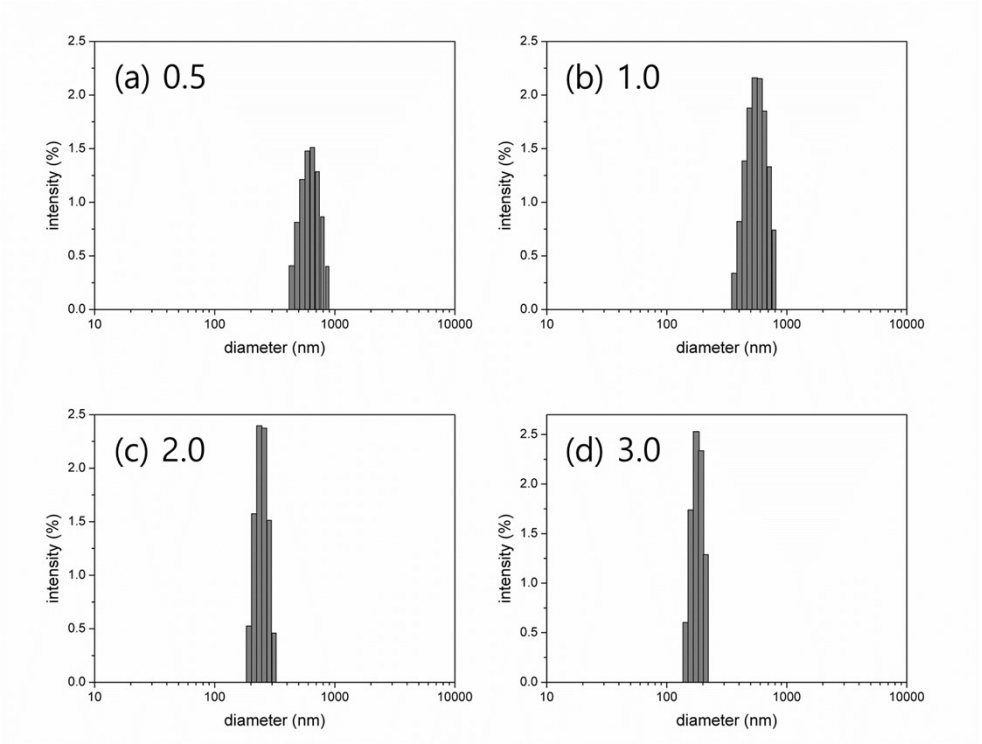


Figure S9. Size distribution of HisC7[Rh] in water-acetonitrile mixtures at volumetric ratio of (a) 0.5, (b) 1.0, (c)2.0, and (d) 3.0. Apparent hydrodynamic diameter and standard deviation is summarized in table.

Solvent volume ratio (water:CAN)	0.5:1	1:1	2:1	3:1
Diameter (nm)	631.4 ± 110.0	569.5 ± 105.1	247.9 ± 29.4	181.1 ± 19.1
*Viscosity (cp)	0.53	0.62	0.72	0.77

*Solvent viscosity is estimated by $\mu_{mix} = \phi_1\mu_1 + \phi_2\mu_2$, where μ_{mix}, $\mu_{1,}$ and μ_2 are the viscosities of the mixture, water, and ACN, respectively. ϕ_1 and ϕ_2 are volume fractions of water and ACN. $\mu_1 = 0.91$ cp and $\mu_2 = 0.36$ cp at 25ºC [1]. These estimated viscosities are applied to determine apparent hydrodynamic diameter of HisC7[Rh] based on Stokes-Einstein equation.

[1] Viscosity of acetonitrile, Anton Paar. https://wiki.anton-paar.com/en/acetonitrile/ (accessed Apr. 10, 2023)