Electronic Supplementary Information

Phase-reversible Pd Containing Sphere-to-bridge-shaped Peptide Nanostructure for Cross-coupling Reactions

Seongsoo Kim,[a1] Hong-Jun Cho,[b1] Namhun Lee,[a] Yoon-Sik Lee,[b*] Dong-Sik Shin[c*],

Sang-Myung Lee[a*]

[a] Department of Chemical Engineering, Kangwon National University, Gangwon-do 24341, Republic of Korea

[b] School of Chemical and Biological Engineering, Seoul National University, Sseoul 08826, Republic of Korea

[c] Department of Chemical and Biological Engineering, Sookmyung Women's University, Seoul 04310, Republic of Korea

[*]Corresponding authors

Prof. Sang-Myung Lee

Department of Chemical Engineering, Kangwon National University, Gangwon-do 24341, Republic of Korea. Fax: (+82)-33-251-3658; phone: (+82)-33-250-6335; e-mail: sangmyung@kangwon.ac.kr

Prof. Yoon-Sik Lee

Department of Chemical and Biological Engineering, Seoul National University, Seoul 08826, Republic of Korea.Fax: (+82)-2-880-1604; phone: (+82)-2-880-7073; e-mail: yslee@snu.ac.kr

Prof. Dong-Sik Shin

Department of Chemical and Biological Engineering, Sookmyung Women's University, Seoul 04310, Republic of Korea.Fax: (+82)-2-2077-7450; phone: (+82)-2-2077-7236; e-mail: dshin@sm.ac.kr

Contents

Experimental Section

Materials and Method

YC_7 peptide (H-YYACAYY-OH) was purchased from GL Biochem. All other chemicals were purchased from Sigma-Aldrich and Daejung Chemicals and were used directly without any further purification. IR spectra were recorded on a Nicolet Fourier transform infrared spectrometer (FT-IR-6700) equipped with a Smart iTX monolithic diamond ATR crystal ATR system. The spectra were recorded over the range 660 -4000cm^{-1} with the average of 64 scans. XRD spectra were acquired by using PAN analytical X'Pert-pro MPD X-ray diffractometer with Cu Kα radiation. The rotation time was 16 s and the scan range from 30° to 90° in 0.0525° steps. Images of $YC_7@Pd^{2+}$ particles were obtained using a transmission electron microscope (TEM, JEOL JEM-2100F) and a scanning electron microscope (SEM, Hitachi S-4800). Thermogravimetric analysis (TGA) were recorded on a SDT Q600 V20.9 Build 20 at a heating rate of 20 °C/min. Pd 3*d* binding energy of $YC_7@Pd^{2+}$ was obtained using XPS (Thermo Scientific K Alpha+).

Preparation of Peptide Assembly

To synthesize $YC_7@Pd^{2+}$, YC_7 (1.5 mg) was added to 1.5 mL of deionized water (1 mg/mL). The peptide solution was heated to 90 °C and held at this temperature for 1 h, followed by cooling to 60 °C at 3 °C/min for 10 min. $PdCl_2$ aqueous solution (20 mM, 0.15 mL) was added to the peptide solution and stirred for 20 min at 60°C. After cooling to room temperature for 10 min, $YC_7@Pd^{2+}$ was isolated by centrifugation (5500 rpm, 10 min). Finally, the $YC_7@Pd^{2+}$ was re-dispersed in water (1 mg/mL) for TEM analysis and freeze-dried for SEM, XPS and XRD.

Suzuki Coupling Reaction in Aqueous Phase

For the Suzuki coupling reaction, $YC_7@Pd^{2+}$ (0.1 mol% Pd, 178 μL; 1 mg/mL, Pd 0.087 mmol) solution was dispersed in 1 mL of water. Then, 4-iodoanisole (36.27 mg, 0.155 mmol) or aryl halides (0.155 mmol), phenylboronic acid (22.68 mg, 0.186 mmol), and K_2CO_3 (37.87 mg, 0.274 mmol) were added to the catalyst solution. For base screening, Na_3PO_4, K_2CO_3, Cs_2CO_3, CH_3COONa, K_3PO_4, tributylamine and Na_2CO_3 were used under the same conditions. As a phase-transfer catalyst, cetyl trimethyl ammonium bromide (CTAB, 28.43 mg, 0.078 mmol) was added to the reaction mixture, which was allowed to react at 80 °C for 1–6 h. The corresponding biphenyl products were obtained by extraction using diethyl ether (2 mL × 3) and were analyzed using gas chromatography (GC).

Sonogashira Coupling Reaction in Aqueous Phase for Base Screening

For the Sonogashira coupling reaction, $YC_7@Pd^{2+}$ (0.1 mol% Pd, 178 μL; 1 mg/mL YC_7 (0.087 mmol)) solution was dispersed in 1 mL of water. Then, 4-iodoanisole (36.27 mg, 0.155 mmol) or aryl halides (0.155 mmol), phenylacetylene (23.69 μL, 0.232 mmol), CuI (0.19 mg, 0.001 mmol) and pyrrolidine (22.50 μL, 0.274 mmol) were added to the catalyst solution. For base screening, Na_3PO_4, K_2CO_3, KOH, Cs_2CO_3, CH_3COONa, K_3PO_4, pyridine, tributylamine, pyrrolidine, piperidine and triethylamine were used under the same conditions. As a phase-transfer catalyst, CTAB (28.43 mg, 0.078 mmol) was added to the reaction mixture, and reacted at 50 °C for 1–6 h. The corresponding diphenylacetylene products were obtained by extraction using diethyl ether (2 mL × 3) and were analyzed by GC.

Heck Coupling Reaction in Aqueous phase for Base Screening

For the Heck coupling reactions, $YC_7@Pd^{2+}$ (0.1 mol% Pd, 178 μL; 1 mg/mL, Pd 0.087 mmol) solution was dispersed in 1 mL of water. Then, 4-iodoanisole (36.27 mg, 0.155 mmol) or aryl halides (0.155 mmol), styrene (19.37 μL, 0. 186 mmol) and various bases (Na_3PO_4, K_2CO_3, KOH, Cs_2CO_3, CH_3COONa, K_3PO_4, 0.274 mmol) were added to the catalyst solution. Finally, as a phase transfer catalyst, CTAB (28.43 mg, 0.078 mmol) was added to the reaction mixture. The mixture was reacted at 80 °C for 6 h. The corresponding stilbene products were obtained by extraction using diethyl ether (2 mL × 3) and were analyzed by GC.

Reusability test of the $YC_7@Pd^{2+}$ in Suzuki coupling reaction

A mixture of 4-iodoacetophenone (0.155 mmol, 38.14 mg) or 4-iodophenol (0.155 mmol, 34.10 mg), phenylboronic acid (0.186 mmol, 22.68 mg), $YC_7@Pd^{2+}$ (0.1 mol% Pd, 178 μL; 1 mg/mL, Pd 0.087 mmol) and K_2CO_3 (37.87 mg, 0.274 mmol) was added into a sealed tube and stirred at 80 °C for the desired time (see times in Table 1, entries 1 and 2). After the reaction, the YC_7@PdNP nanostructure was isolated by centrifugation (5500 rpm, 10min) and washed with distilled water (2 mL × 3) and diethyl ether (2 mL × 3). Finally the isolated YC_7@PdNP (1 mL) was subjected to the second Suzuki-Miyaura coupling reaction by charging with the same substrates (aryl halide 1 or 2, phenylboronic acid and K_2CO_3).

Supplementary Figures and Tables

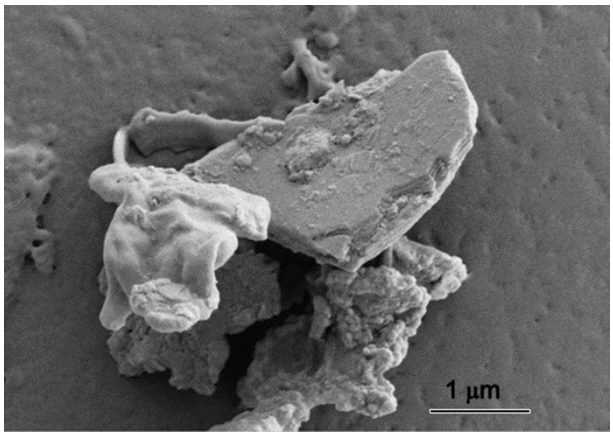


Figure S1. SEM image of YC_7 peptide.

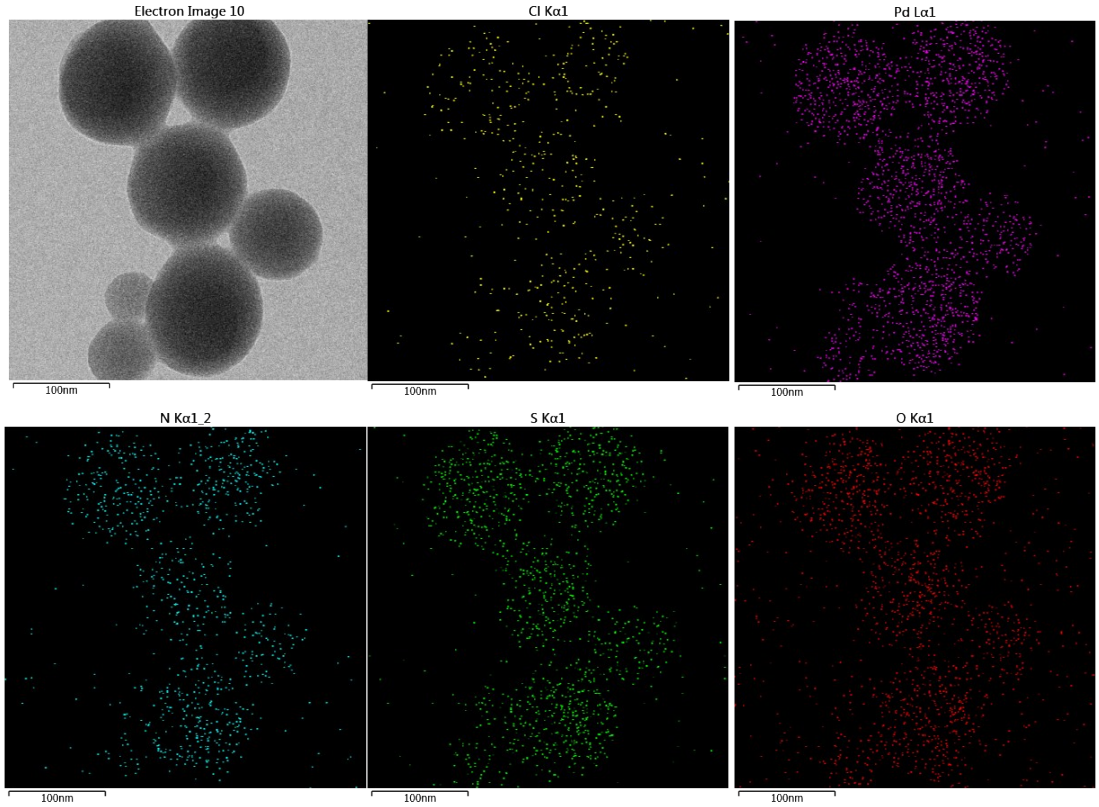


Figure S2. TEM-energy-dispersive X-ray microanalysis images of $YC_7@Pd^{2+}$ nanostructure.

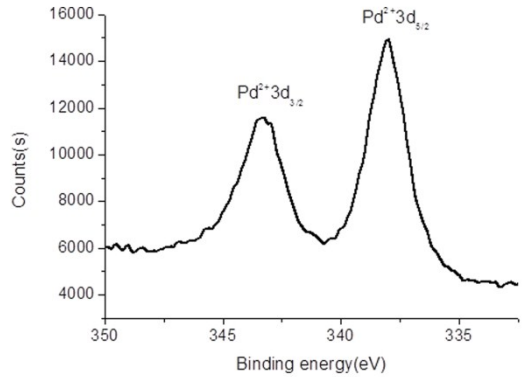


Figure S3. XPS spectrum of YC_7@Pd^{2+} nanostructure.

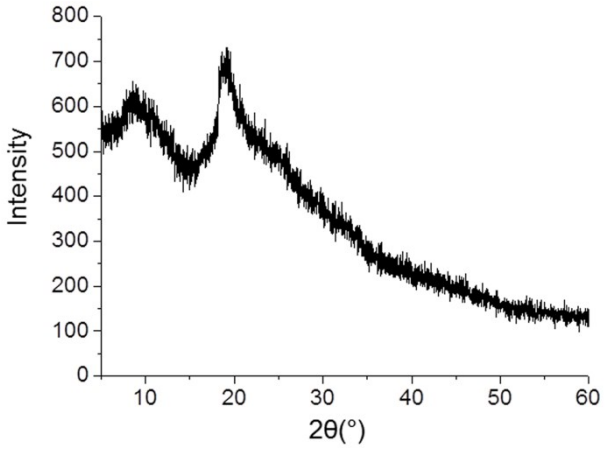


Figure S4. XRD pattern of YC_7 peptide.

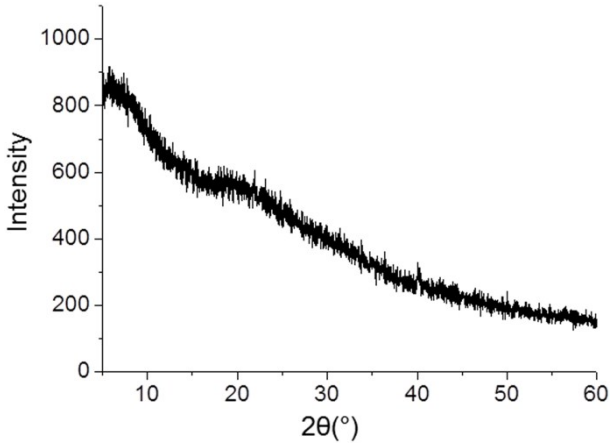


Figure S5. XRD pattern of $YC_7@Pd^{2+}$ nanostructure.

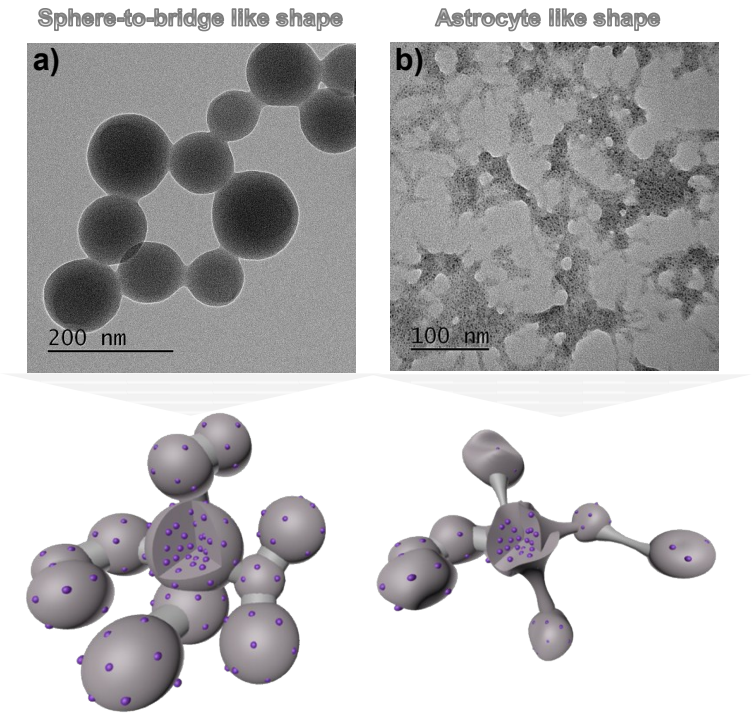


Figure S6. Schematics of morphological re-assembly and TEM images of (a) $YC_7@Pd^{2+}$ nanostructure and (b) re-assembled YC_7@PdNP nanostructure after first Suzuki cross-coupling.

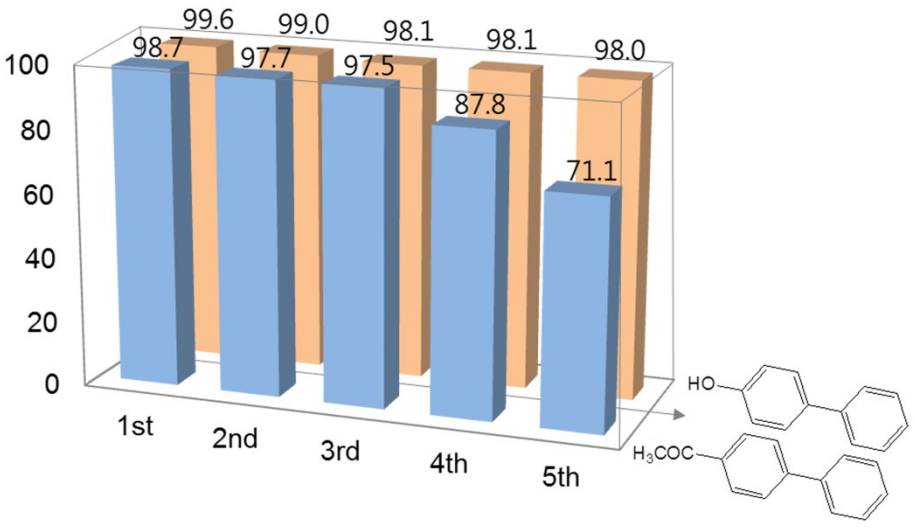
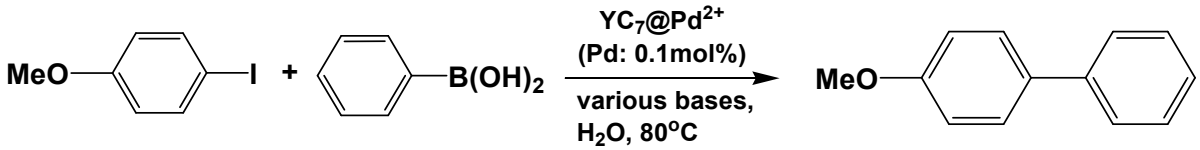


Figure S7. Recycling efficiency of $YC_7@Pd^{2+}$ nanostructure in the Suzuki coupling reactions.

Table S1. Base screening in Suzuki coupling reaction of 4-iodoanisole with phenylboronic acid in the presence of $YC_7@Pd^{2+}$.[a]

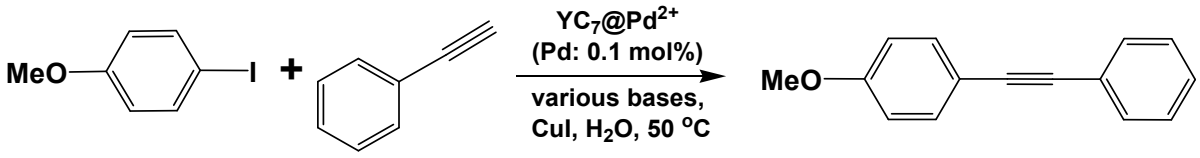


Entry	Base	Yield (%)[b]
1	Na_3PO_4	87.2
2	K_2CO_3	92.9
3	Cs_2CO_3	89.0
4	CH_3COONa	38.5
5	K_3PO_4	91.1
6	tributylamine	66.6
7	Na_2CO_3	67.2

[a] 4-Iodoanisole and phenylboronic acid (0.155 mmol), phenylboronic acid (0.186 mmol), $YC_7@Pd^{2+}$ (0.1 mol%), bases (0.274 mmol), in water (1 mL) at 80 °C for 6 h.

[b] GC yields.

Table S2. Base screening in Sonogashira coupling reaction of 4-iodoanisole with phenylacetylene in the presence of $YC_7@Pd^{2+}$.[a]

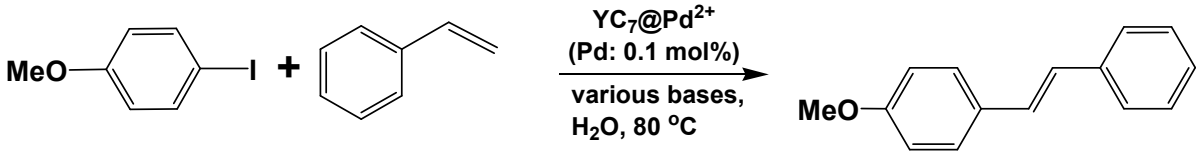


Entry	Base	Yield (%)[b]
1	Na_3PO_4	2.3/4.6
2	KOH	2.5/5.1
3	Cs_2CO_3	3.4/3.4
4	K_3PO_4	2.6/5.2
5	K_2CO_3	2.2/6.8
6	CH_3COONa	2.3/4.6
7	pyridine	18/6.5
8	tributylamine	35.7/17.4
9	pyrrolidine	45.2/17.8
10	piperidine	31.7/11.1
11	triethylamine	1.1/1.1

[a] Conditions : 4-Iodoanisole (0.155 mmol), phenylacetylene (0.232 mmol), $YC_7@Pd^{2+}$ (0.1 mol%), Cu(I)I (0.001 mmol), bases (0.274 mmol) in water(1 mL) at 50 °C for 6 h.

[b] GC yields : product/byproduct (1,4-diphenylbuta-1,3-diyne).

Table S3. Base screening in Heck coupling reaction of 4-iodoanisole with styrene in the presence of $YC_7@Pd^{2+}$.[a]



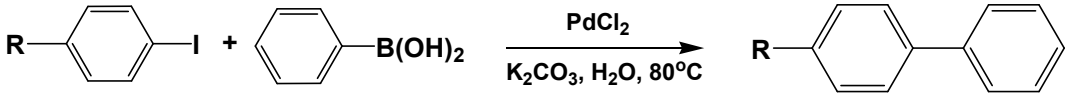
Entry	Base	Yield (%)[c]
1	Na_3PO_4	1.2/1.0[b]
2	K_2CO_3	0.3/0.5[b]
3	Cs_2CO_3	1.0/0.8[b]
4	CH_3COONa	1.3/1.0[b]
5	K_3PO_4	0.4/0.2[b]
6	KOH	0.1/0.1[b]

[a] Conditions : aryl iodine (0.155 mmol), styrene (0.186 mmol), $YC_7@Pd^{2+}$ (0.1 mol%), bases (0.274 mmol), CTAB (0.077 mmol) in water (1 mL) at 80 °C for 6 h.

[b] 0.5 equivalent of CTAB was used.

[c] GC yields.

Table S4. Suzuki-Miyaura coupling reactions for various aryl iodides in the presence of $PdCl_2$.[a]

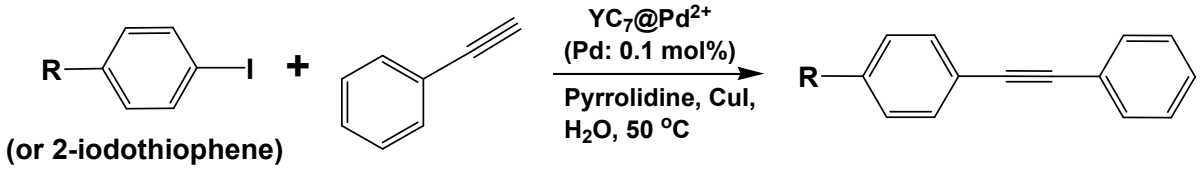


Entry	R	Time (h)	Yield (%)[b]
1	$COCH_3$	1	94.8
2	OH	3	95.6
3	OCH_3	3	64.0
4	CH_3	3	54.1

[a] Conditions: aryl iodine and heterocyclic halides (0.155 mmol), phenylboronic acid (0.186 mmol), $PdCl_2$ (0.1 mol%), K_2CO_3 (0.274 mmol) in water (1 mL) at 80 °C.

[b] GC yields.

Table S5. Sonogashira coupling reaction of aryl iodides with phenylacetylene in the presence of $YC_7@Pd^{2+}$ catalyst.[a]



Entry	R	Time (h)	Yield (%)[c]
1	$COCH_3$	1	86.1/6.6[b]
2	2-iodothiophene	3	66.9/0.5[b]
3	OCH_3	3	44.3/1.8[b]
4	H	3	60.8/2.5[b]
5	CH_3	3	43.1/0.2[b]
6	OH	3	14.8/0.4[b]

[a] Conditions : aryl iodine and heterocyclic halaides (0.155 mmol), phenylacetylene (0.232 mmol), $YC_7@Pd^{2+}$ (0.1 mol%), Cu(I)I (0.001 mmol), pyrrolidine (0.274 mmol) in water (1 mL) at 50 °C.

[b] GC yields when 0.5 eq of CTAB was used.

[c] GC yields.