Electronic Supplementary Information

Synthesis of surfactant-free palladium nanoclusters for their use in catalytic cross-coupling reactions

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Chemicals

PdCl₂ was obtained from Wako Chemical Co. All solvents and other regents were obtained from Wako Chemical Co, TCI, and ALDRICH and were used without further purification.

Experimental details (Synthesis of Pd NCs)

Preparation of Pd NCs. A solution of 150 μ L of 0.1 M aqueous PdCl₂ was added to 15 mL of DMF that had been preheated to 140 °C, and the DMF solution was refluxed in a 140 °C oil bath with stirring for 6 h. The surfactant-free palladium nanoclusters were obtained as the 1 mM Pd NCs in DMF. After vacuum evaporation of excess solvent, the residue was redissolved in selected solvents such as methanol, tetrahydrofuran (THF), and *N*-methylpyrrolidone (NMP) for the TEM measurement and the cross-coupling reactions.

Photophysical properties of Pd NCs. UV-visible absorption spectra were measured using a JASCO V-670 spectrometer. Fluorescence emission spectra were obtained on a JASCO FP-6200 fluorospectrophotometer at a UV excitation of 350 nm (Figure S1)



Fig. S1. (a) UV-visible absorption spectra of DMF-protected Pd NCs (red), and PdCl₂ before reduction (blue). (b) Photoluminescene emission spectrum in methanol of DMF-protected Pd NCs.

High-resolution transmission electron microscope image of the Pd NCs (**HRTEM**). A drop of Pd NCs dispersed in methanol was placed on a carbon-coated Cu grid, and TEM images were recorded with a JEOL JEM-2010F at an acceleration voltage of 200 kV (Figure S2).



Fig. S2. HRTEM image and the TEM-EDX spectrum recorded at point 1 in a red circle of the image of DMF-protected Pd NCs. Si and Cu peaks originated from the carbon-coated Cu grid.

Experimental procedure

General

GLC analysis was performed with a flame ionization detector using a 0.22 mm \times 25 m capillary column (BP-5). ¹H and ¹³C NMR were measured at 400 and 100 MHz, respectively, in CDCl₃ with Me₄Si as an internal standard. The products were characterized by ¹H NMR, ¹³C NMR, and GC-MS. The yields of products were estimated from the peak areas based on the internal standard technique using GC.

All starting materials were commercially available and used without any purification.

Compounds $3a^1$, $3b^1$, $3c^1$, $3d^2$, $3e^3$, $3f^1$, $3g^4$, $3h^3$, $3i^5$, $5a^6$, $5b^6$, $5c^6$, $5d^7$, $5e^8$, $5f^9$, $5g^{10}$ and $5h^{11, 12}$ were reported previously.

Preparation of Pd NCs catalysts

The surfactant-free palladium nanoclusters were obtained as the 1 mM Pd NCs in DMF.

Preparation of 10 µM Pd NCs in DMF (10⁻³ mol %)

The DMF solution of 100 μ L of the obtained 1 mM Pd NCs was added to 10 mL of DMF, and the solution of 10 μ M Pd NCs in DMF was prepared.

Preparation of 1 µM Pd NCs in DMF (10⁻⁴ mol %)

The DMF solution of 1 mL of the prepared 10 μ M Pd NCs was added to 10 mL of DMF, and the solution of 1 μ M Pd NCs in DMF was prepared.

Preparation of 100 nM Pd NCs in DMF (10⁻⁵ mol %)

The DMF solution of 100 μ L of the prepared 10 μ M Pd NCs was added to 10 mL of DMF, and the solution of 100 nM Pd NCs in DMF was prepared.

Preparation of 1 nM Pd NCs in DMF (10⁻⁷ mol %)

The DMF solution of 100 μ L of the prepared 100 nM Pd NCs was added to 10 mL of DMF, and the solution of 1 nM Pd NCs in DMF was prepared.

Preparation of 10 µM Pd NCs in NMP (10⁻³ mol %)

The solvent was evaporated under vacuum from the 1mM Pd NCs synthesized in DMF, and the residue was redissolved in 15 mL of *N*-methylpyrrolidone (NMP) to prepare 1 mM Pd NCs in NMP. Then, the NMP solution of 100 μ L of the prepared 1 mM Pd NCs

was added to 10 mL of NMP, and the solution of 10 μ M Pd NCs in NMP was prepared.

Preparation of 1 µM Pd NCs in NMP (10⁻⁴ mol %)

The NMP solution of 1 mL of the prepared 10 μ M Pd NCs was added to 10 mL of NMP, and the solution of 1 μ M Pd NCs in NMP was prepared.

Preparation of 100 nM Pd NCs in NMP (10⁻⁵ mol %)

The NMP solution of 100 μ L of the prepared 10 μ M Pd NCs was added to 10 mL of NMP, and the solution of 100 nM Pd NCs in NMP was prepared.

Preparation of 10 µM Pd NCs in THF (10⁻³ mol %)

The solvent was evaporated under vacuum from the 1mM Pd NCs synthesized in DMF, and the residue was redissolved in 15 mL of tetrahydrofuran (THF) to prepare 1 mM Pd NCs in THF. Then, the THF solution of 100 μ L of the prepared 1 mM Pd NCs was added to 10 mL of THF, and the solution of 10 μ M Pd NCs in THF was prepared.

Preparation of 100 nM Pd NCs in THF (10⁻⁵ mol %)

The THF solution of 100 μ L of the prepared 10 μ M Pd NCs was added to 10 mL of THF, and the solution of 100 nM Pd NCs in THF was prepared.

Preparation of 10 µM Pd NCs in MeOH (10⁻³ mol %)

The solvent was evaporated under vacuum from the 1mM Pd NCs synthesized in DMF, and the residue was redissolved in 15 mL of methanol (MeOH) to prepare 1 mM Pd NCs in MeOH. Then, the MeOH solution of 100 μ L of the prepared 1 mM Pd NCs was added to 10 mL of MeOH, and the solution of 10 μ M Pd NCs in MeOH was prepared.

A typical reaction procedure for Pd NCs catalyzed Suzuki–Miyaura Cross–coupling reaction of 1a with 2a (Table 1, entry 3)

A mixture of iodotoluene **1a** (109 mg, 0.5 mmol), phenylboronic acid **2a** (91 mg, 0.75 mmol), K_2CO_3 (69 mg, 0.5 mmol) and 10 μ M Pd NCs in *N*-methylpyrrolidone (NMP) (1 mL) as a catalyst in H₂O (1 mL) was stirred at 100 °C for 5 h under Ar. The conversions and yields of products were estimated from peak areas based on an internal standard (tridecane) using GC and the product **3a** was obtained in 99% yield. The product **3a** was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane) in 95% yield (80 mg).



Fig. S3. Time course for Suzuki-Miyaura cross-coupling reaction using NMP (blue) and DMF (red) as solvents.

A typical procedure for the catalyst-recycling sequence in the Pd NCs-catalyzed Suzuki-Miyaura cross-coupling reaction (Figure S4)

After the reaction was performed under the conditions of Table 1, entry 4, hexane (8 mL) and internal standard (tridecane, 0.3 mmol) were added to the mixture. Then, the reaction mixture was extracted with hexane (8 mL) for four times, and 4-iodotoluene (1a), 4-methylbiphenyl (3a) and internal standard (tridecane) were extracted in organic layer. Resulting aqueous layer containing Pd NCs dispersed in water/methanol, were used for next catalytic sequence under the same reaction conditions as entry 4, Table 1, by adding 4-iodotoluene 1a (109 mg, 0.5 mmol), phenylboronic acid 2a (91 mg, 0.75 mmol) and K₂CO₃ (69 mg, 0.5 mmol).

Fig. S4. Depiction of the catalyst-recycling sequence in the Pd NCs-catalyzed Suzuki-Miyaura cross-coupling reaction



A typical reaction procedure for Pd NCs catalyzed Mizoroki-Heck reaction of 1g with 4a (Table 3, entry 3)

A mixture of iodobenzene 1g (204 mg, 1 mmol), ethyl acrylate 4a (120 mg, 1.2 mmol), triethylamine (101 mg, 1 mmol) and 100 nM Pd NCs in DMF (1 mL) as a catalyst in DMF (1 mL) was stirred at 140 °C for 15 h under Ar. The conversions and yields of products were estimated from peak areas based on an internal standard using GC and the product 5a was obtained in 99% yield. The product 5a was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane / ethyl acetate = 20 / 1) in 85% yield (149 mg).

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