

Supporting Information for

Facile preparation of linear polystyrene-stabilized palladium nanoparticles in water

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General comments

¹H NMR spectra in DMSO-*d*₆ or CDCl₃ were recorded with a 300 MHz NMR spectrometer (UNITY 300, Varian, Palo Alto, CA) using tetramethylsilane ($\delta = 0$) as an internal standard. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed using ICPS-8100 (Shimadzu Co., Kyoto, Japan). Pd nanoparticles were investigated by transmission electron microscopy (TEM) on a JEM 2100F transmission electron microscope (JEOL Ltd., Tokyo, Japan). The samples were prepared by placing a drop of the solution on carbon coated copper grids and allowed to dry in air. Polystyrene of narrow molecular weight distribution standards was purchased from Tosoh Co., Ltd. (Tokyo, Japan). Pd(OAc)₂ was obtained from Sigma-Aldrich Co. (Missouri, USA). Pd/Al₂O₃ (5 wt% Pd) was obtained from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan).

Preparation of 1a

To a screw-capped vial with a stirring bar were added 9.0 mg of polystyrene (85 μ mol of styrene unit), Pd(OAc)₂ 5.5 mg (25 μ mol), and 1.5 M aqueous K₂CO₃ solution (3 mL). After stirring at 90 °C for 1 h, the reaction mixture was filtered with hot water. Subsequently, the polystyrene stabilized Pd nanoparticles were washed with hot water (5 \times 1.0 mL) and acetone (5 \times 1.0 mL).

Reduction by benzyl alcohol (**1a'**)

To a screw-capped vial with a stirring bar were added 1.8 mg of polystyrene (17 μmol of styrene unit), $\text{Pd}(\text{OAc})_2$ 1.0 mg (5 μmol), benzyl alcohol 5.2 μL (50 μmol), and water (1 mL). After stirring at 90 °C for 1 h, the aqueous solution was decanted. Subsequently, the polystyrene stabilized Pd nanoparticles were washed with water (5×1.0 mL) and acetone (5×1.0 mL).

Determination of loading of the palladium

1a (2.9 mg) was placed in a screw-capped vial and then added 13 M nitric acid (5 mL). The mixture was heated at 80 °C to dissolve completely. After cooled to room temperature, the solution was adjusted to 50 mL by water and then measured the amount of Pd metal by ICP-AES analysis (15.3 ppm). The amount of Pd in **1b-1f** was as follows; **1b**: 11.1 ppm, **1c**: 9.38 ppm, **1d**: 6.12 ppm, **1e**: 2.53 ppm, **1f**: 1.56 ppm.

Typical procedures for Suzuki coupling reaction

To a screw-capped vial with a stirring bar were added 0.5 mmol of bromobenzene, 0.75 mmol of *p*-methylphenylboronic acid, **1a** (2.9 mg, 1.5 mol% of Pd), and 1.5 M aqueous KOH solution (1 mL). After stirring at 80 °C for 1 h, the reaction mixture was filtered with hot water. Subsequently, the catalyst was washed with hot water (5×1.0 mL). The filtrate was cooled to room temperature to afford crystals of 4-methylbiphenyl. The recovered **1a** was dried in vacuo and reused. Furthermore, the amount of Pd metal in the recovered **1a** determined by ICP-AES analysis was 15.3 ppm.

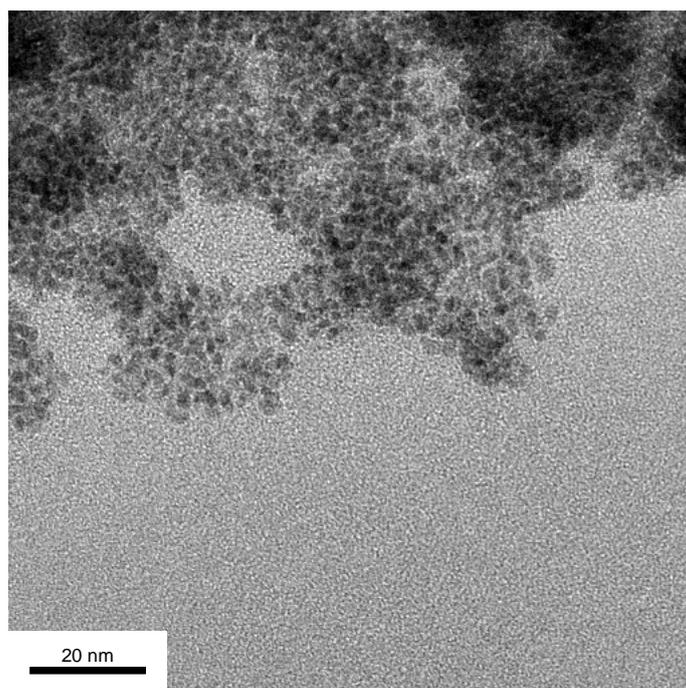


Figure S1. TEM image of **1b**

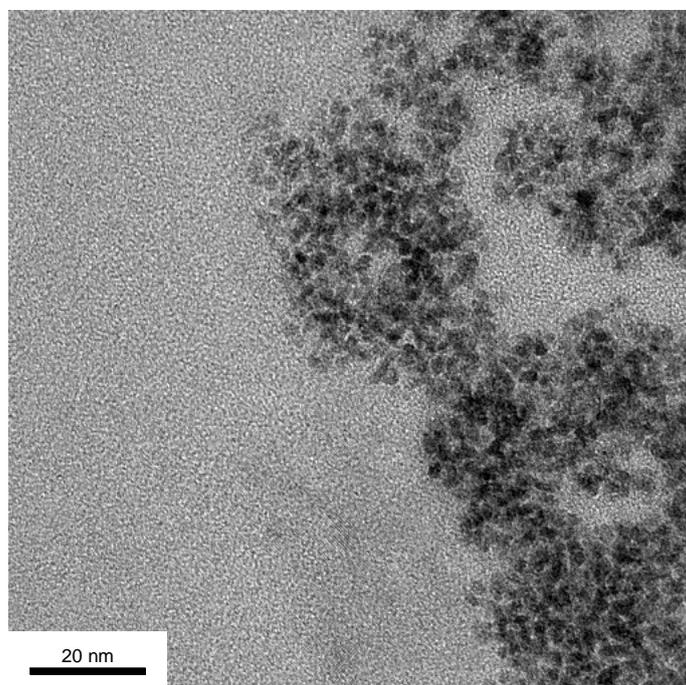


Figure S2. TEM image of **1c**

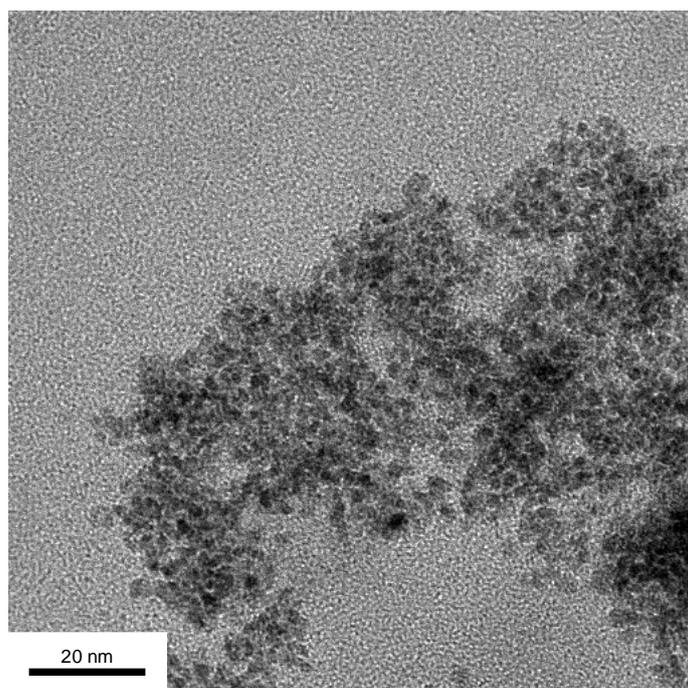


Figure S3. TEM image of **1d**

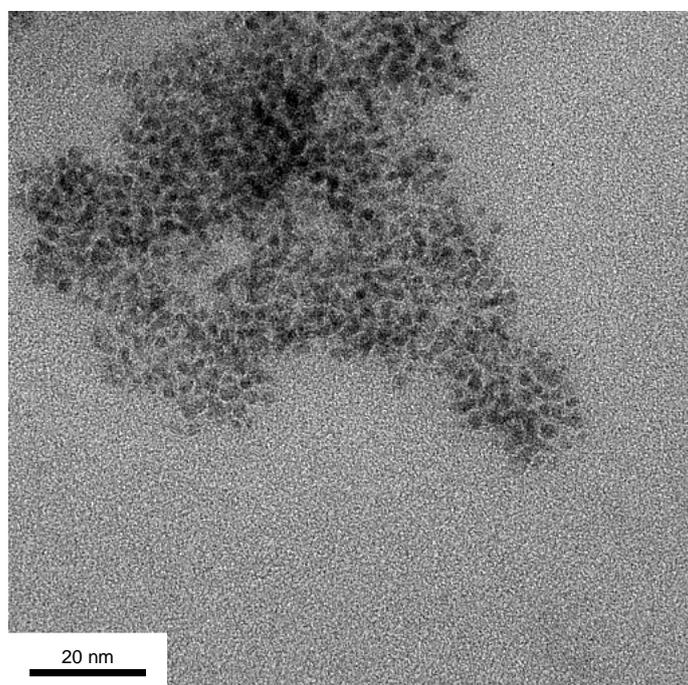


Figure S4. TEM image of **1e**

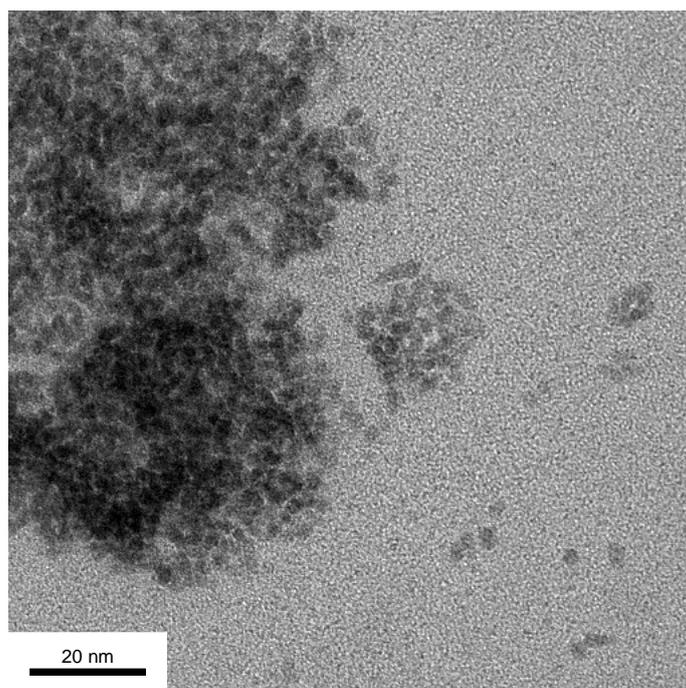


Figure S5. TEM image of **1f**

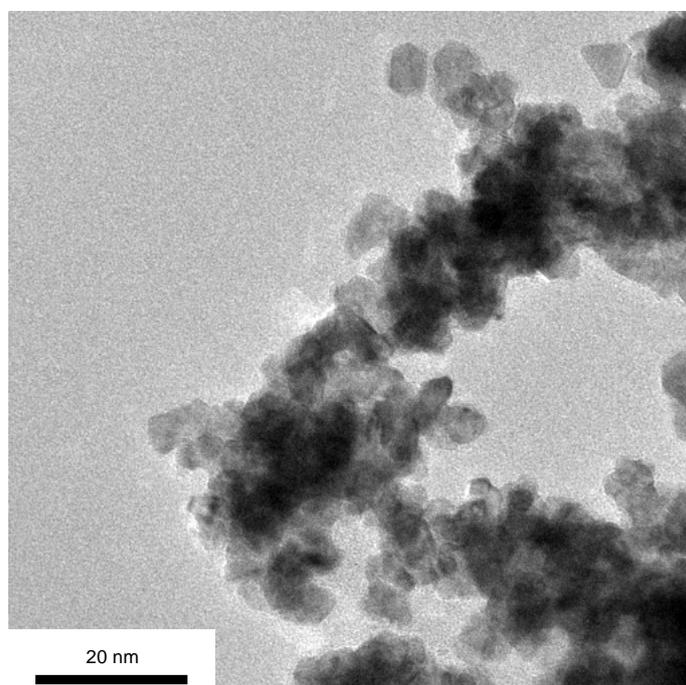


Figure S6. TEM image of **1a'**