In-situ Coupled Oxidation Cycle Catalyzed by Highly Active and Reusable Pt-catalysts: Dehydrogenative Oxidation Reactions in the presence of a Catalytic Amount of *o*-Chloranil Using Molecular Oxygen as the Terminal Oxidant

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Electronic Supplementary Information

Contents

1. General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, or JNM-LA600 spectrometer. Tetramethylsilane ($\delta = 0$) was used as an internal standard for ^{1}H NMR and $CDCl_3$ ($\delta = 77.0$) for ^{13}C NMR. The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature. GC analysis was performed on

Shimadzu GC-2010 apparatus (column = J & W SCIENTIFIC DB-1; Gas pressure: 157.5 kPa, Total flow: 41.3 mL/min, column folw: 0.93 mL/min, linear velocity: 21.1 cm/s, sprit ratio: 40.1, injection temperature: 300 °C, detector temperature: 300 °C). ICP analysis was performed on Shimadzu ICPS-7510 equipment. High-resolution electrospray ionization mass spectra (HR-MS) were measured with JEOL JMS-T100TD AccuTOF TLC. Water was treated by MILLIPORE Elix-UV before use. Column chromatography was performed on silica gel 60 (Merck), and preparative TLC was carried out by using Wakogel B-5F (Wako Pure Chemical Industry). The structures of the known compounds were confirmed by comparison with commercially available compounds or literature data. TEM and STEM images were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All TEM specimens were prepared by placing a drop of the solution on carbon-coated Cu grids and allowed to dry in air (without staining).

2. Test of oxidation resistance of benzyloxy moieties in polymer for polymer incarcerated Pt catalyst

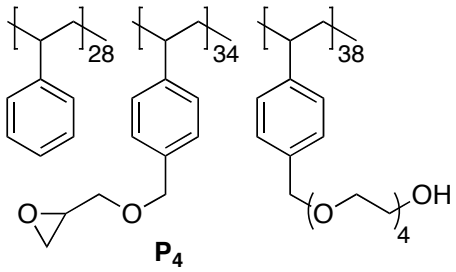
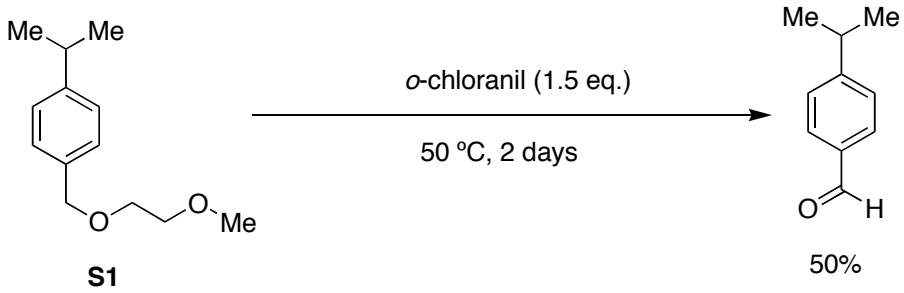


Figure S- 1. Polymer for polymer incarcerated Pt catalyst (PI Pt)

Scheme S- 1. Oxidation resistance test of benzyloxy moieties



1-((2-Methoxyethoxy)methyl)-4-isopropylbenzene S1: To sodium hydride (60% in mineral oil, 0.54 g, 13.5 mmol) suspended in DMF (10 mL), (4-isopropylphenyl)methanol (2.30 mL, 15.0 mmol) was added at 0 °C. After the reaction mixture was stirred for 1 h at room temperature,

1-chloro-2-methoxyethane (0.90 mL, 9.85 mmol) was added and the mixture was further stirred for 12 h. The mixture was cooled to 0 °C and diluted with diethyl ether, saturated aqueous ammonium chloride was added to quench the reaction and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chromatography (Hexane : Ethylacetate = 20 : 1) to afford 1-((2-Methoxyethoxy)methyl)-4-isopropylbenzene **S1**(1.00 g, 49%). ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 6H, J = 8.27), 2.93 (septet, 1H, J = 6.89), 3.42 (s, 3H), 3.5-3.7 (m, 4H), 4.57 (s, 2H), 7.22-7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 23.99, 33.85, 59.06, 69.15, 71.99, 73.20, 126.42, 127.95, 127.96, 135.48, 148.34.

Oxidation of 1-((2-Methoxyethoxy)methyl)-4-isopropylbenzene (Scheme S-1): 1-((2-Methoxyethoxy)methyl)-4-isopropylbenzene (49.8 mg, 0.24 mmol) and *o*-chloranil (91.2 mg, 0.37 mmol) were combined in mixture of $CHCl_3$ (2.5ml) and H_2O (0.15 mL). Reaction mixture was stirred for 48 h at 50 °C. Solvent was removed *in vacuo*, residue was analyzed by ^{1}H NMR and the ratio of 1-((2-Methoxyethoxy)methyl)-4-isopropylbenzene and 4-ispropylbenzaldehyde was determined as 1 : 1.

3. Preparation of organic-inorganic hybrid platinum nanocluster catalyst (HB Pt)

Preparation of polymer 1[1]: Styrene (7.50 g, 72.0 mmol), *p*-styryltrimethoxysilane (4.04 g, 18.0 mmol), and AIBN (148 mg, 0.90 mmol) were mixed in chloroform (12.0 mL). The mixture was stirred for 24 h at 80 °C and then cooled to room temperature. The resulting polymer solution was poured slowly into hexane. After the crude copolymer was precipitated and the liquid removed, the obtained solid was dissolved in dichloromethane. The solution was poured slowly into hexane, and the same procedure repeated twice. The purified copolymer was filtered, washed with hexane several times, and dried (12 h at room temperature *in vacuo*) to afford the desired copolymer **1** (9.97 g, 86% yield). The molar ration of the component was determined by ^{1}H NMR spectroscopic analysis (x/y 80:20). M_w, M_n and M_w M_n ratio were measured by gel-pemeation chromatography (GPC) based on standard polystyrene calibration (M_w = 14500, M_n = 7460, M_w M_n = 1.95).

Preparation of HB Pt (Scheme 2)[1]: Copolymer **1** (250.2 mg) and $NaBH_4$ (10.6 mg) were dissolved in diglyme (5 mL) at room temperature, to this solution was slowly added sodium hexachloro platinate (VI) hexahydrate (10.8 mg) with 1 mL of diglyme then the solution turned dark brown.

The mixture was stirred for 3 h at room temperature and 1 to 1 mixture of 1N NaOH aq. and *i*PrOH (2.5 mL) was added quickly to the mixture at room temperature. Black catalyst capsules were precipitated and the resultant suspension was heated at 90 ˚C. Solvent was removed by decantation and catalyst capsules were washed by *i*PrOH for several times. The catalyst capsules were crushed using pestle and mortar. The resultant powder was heated at 120 ˚C for 5 h and washed with water, *i*PrOH and CH_2Cl_2. Powder was dried *in vacuo* for 5 h to give organic-inorganic hybrid platinum cluster catalyst (HB Pt, 226.9 mg). The platinum metal loading was determined by ICP analysis (0.085 mmol/g).

4. Preparation of oxidation resistant polymer incarcerated platinum catalyst (RPI Pt)

Preparation of 1-(3-Bromopropyl)-4-vinylbenzene : Magnesium (4.92 g, 200 mmol) and 4-bromostyrene (25.4 g, 130 mmol) were mixed in THF (160 mL) at 0 °C under argon atmosphere overnigtht and the Grinard regent was obtained. Dried CuBr (0.740 g, 0.5 mmol) and LiBr (0.965 g, 1.1 mmol) were mixed in THF (15 mL) for 1 h at room temperature under argon atmosphere and the metal reagent was obtained. The metal reagent was added to 1,3-dibromopropane (50.7 g, 250 mmol) in THF (80 mL) at room temperature under argon atmosphere and cooled to 0 °C. At 0 °C, the Grinard reagent was slowly added, and the mixture was stirred at room temperature overnight. Then, the mixture was cooled to 0 °C, washed with saturated aqueous ammonium chloride, and extracted by diethyl ether. After washing with water and concentration with reduced pressure, the residue was purified by column chromatography (silica gel, Hexane : Ethylacetate = 10 : 1) to give 1-(3-Bromopropyl)-4-vinylbenzene (20.2 g, 65.3% yield). ^{1}H NMR ($CDCl_3$) δ 7.34 (d, 2H, *J* = 8.60 Hz), 7.16 (d, 2H, *J* = 8.60 Hz), 6.69 (q, 1H, *J* = 9.55 Hz), 5.71 (q, 1H, *J* = 7.01 Hz), 5.21 (q, 1H, *J* = 4.00 Hz), 3.39 (t, 2H, *J* = 6.30 Hz), 2.77 (t, 2H, *J* = 6.30 Hz), 2.16 (m, 2H) ^{13}C NMR δ 32.76, 33.42, 33.84, 112.93, 126.10, 128.47, 135.34, 136.33, 139.96

2-((3-(4-Vinylphenyl)propoxy)methyl)oxirane : To sodium hydride (60% in mineral oil, 7.21 g, 180 mmol) suspended in DMF (170 mL), gricidol (20 mL, 300 mmol) was slowly added at 0 °C under argon atmosphere. Then, 1-(3-Bromopropyl)-4-vinylbenzene (13.4 g, 60 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. The mixture was cooled to 0 °C and saturated aqueous ammonium chloride was added to quench the reaction. The aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the

solvent was removed *in vacuo*. The residue was purified by flash chlomatography (silica gel, Hexane : Ethylacetate = 6 : 1) to afford 2-((3-(4-Vinylphenyl)propoxy)methyl)oxirane (4.89 g, 64.4% yield). ^{1}H NMR ($CDCl_3$) δ 7.33 (d, 2H, *J* = 8.05 Hz), 7.15 (d, 2H, *J* = 8.00 Hz), 6.69 (q, 1H, *J* = 9.53 Hz), 5.70 (d, 1H, *J* = 17.8 Hz), 5.19 (d, 1H, *J* = 10.9 Hz), 3.71 (q, 1H, *J* = 4.95Hz), 3.50 (m, 2H), 3.38 (q, 1H, *J* = 5.92 Hz), 3.15 (m, 1H), 2.80 (t, 1H, *J* = 4.58 Hz), 2.69 (t, 2H, *J* = 7.73 Hz), 2.62 (m, 1H), 1.91 (m, 2H) ^{13}C NMR δ 31.14, 31.91, 44.24, 50.80, 70.54, 71.48, 112.91, 126.17, 128.58, 135.24, 136.62, 141.56. HR-MS (m/z) calcd. for $C_{14}H_{19}O_2(MH^+)$: 219.13850, found: 219.13764.

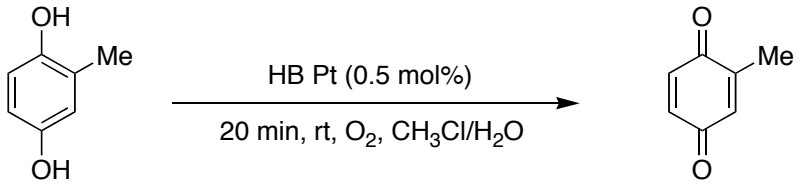
15-(4-Vinylphenyl)-3,6,9,12-tetraoxapentadecan-1-ol : To sodium hydride (60% in mineral oil, 3.06 g, 80 mmol) suspended in DMF (130 mL), tetraetylenglycol (40 mL, 240 mmol) was slowly added at 0 °C under argon atmosphere. Then, 1-(3-Bromopropyl)-4-vinylbenzene (8.66 g, 40 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. The mixture was cooled to 0 °C and saturated aqueous ammonium chloride was added to quench the reaction. After adding brine, the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chlomatography (silica gel, Hexane : Ethylacetate = 3 : 1) to afford 15-(4-Vinylphenyl)-3,6,9,12-tetraoxapentadecan-1-ol (4.80 g, 63.5% yield). ^{1}H NMR ($CDCl_3$) δ 7.32 (d, 2H, *J* = 8.05 Hz), 7.14 (d, 2H, *J* = 8.00 Hz), 6.69 (q, 1H, *J* = 9.55 Hz), 5.70 (d, 1H, *J* = 17.8 Hz), 5.19 (d, 1H, *J* = 10.9 Hz), 3.71 (s, 2H), 3.65 (m, 11H), 3.59 (m, 4H), 3.46 (t, 2H, *J* = 6.58 Hz), 2.67 (t, 2H, *J* = 7.73 Hz), 1.89 (m, 2H) ^{13}C NMR δ 30.60, 31.45, 61.03, 69.62, 69.78, 69.82, 70.05, 70.10, 72.19, 112.39, 125.70, 128.16, 134.70, 136.22, 141.22. HR-MS (m/z) calcd. for $C_{19}H_{31}O_5(MH^+)$: 339.21715, found: 339.21790.

Preparation of polymer : Styrene (0.777 g, 0.7 mmol), 2-((3-(4-Vinylphenyl)propoxy)methyl)oxirane (1.49 g, 0.7 mmol), 15-(4-Vinylphenyl)-3,6,9,12-tetraoxapentadecan-1-ol (2.81 g, 0.7 mmol), and v-70 (74.3 mg, 0.024 mmol) were mixed in chloroform (4.7 mL). The mixture was stirred for 2 nights at room temperature under argon atmosphere. The resulting polymer solution was poured into diethyl ether. After the crude polymer was precipitated and the liquid removed, the obtained product was dissolved in THF. The solution was poured into diethyl ether, and the same procedure repeated twice. The purified polymer was dried to afford the desired polymer (2.12 g, 47.7%). The molar ration of the component was determined by ^{1}H NMR spectroscopic analysis (33 : 34 : 33).

Preparation of RPI Pt : Polymer (0.8 g) and $NaBH_4$ (32.5 mg) were dissolved in diglyme (18 mL) at room temperature. To this solution, sodium hexachloro pratinate (IV) hexahydrate (29.0 mg) with 5 mL of diglyme was slowly added, then the solution turned black. The mixture was stirred at room temperature overnight and diethyl ether was added to the mixture. The resultant black solid was washed with diethyl ether, and the solvent was removed by decantation. Then the catalyst was heated at 150 °C for 5 h and washed with water, *i*PrOH, and CH_2Cl_2. Powder was dried at 170 °C for 5 h to give polymer incarcerated platinum catalyst (PI Pt, 0.43 g). The platinum loading was determined by ICP analysis (0.088 mmol/g).

5. *In-situ* coupled oxidation reactions catalyzed by HB Pt and RPI Pt

Scheme S- 2. Aerobic oxidation of hydroquinone catalyzed by HB Pt



>99% yield

A typical procedure for oxidation reaction of hydroquinones with HB Pt (Scheme S-2): Methylhydroquinone (30.7 mg) and HB Pt (16.3 mg, 0.085 mmol Pt/g) were combined in chloroform (2.5 ml) and water (0.15 ml). The mixture was stirred at room temperature for 20 min under oxygen atmosphere. After filtration, the organic phase and aqueous phase were separated. To the organic phase was added the known amount of anisole in approximately 1:1 weight ratio to the initial substrate. The organic phase was dried over sodium sulfate and yield of toluquinone was determined by GC analysis (>99%).

A typical procedure for preparation of Hantzsch dihydropyridines: Benzaldehyde (21.06 g, 0.2 mol), methyl acetoacetate (46.31 g, 0.4 mol), 25% NH_3 aqueous solution (20 mL) and MeOH (40 mL) were combined and heated at reflux for 1 h. The mixture was cooled to room temperature and water was added. Yellow precipitate was filtered and washed with water. Resultant yellow solid was recrystallized from EtOH to give 1,4-dihydro-2,6,- dimethyl-4-phenyl-3,5-pyridinedicarboxylic acid dimethyl ester **3c** (31.67 g, 53% yield).

1,4-Dihydro-2,6,-dimethyl-4-phenyl-3,5-pyridinedicarboxylic acid dimethyl ester (3c)[2]:

^{1}H NMR ($CDCl_3$) δ 2.34 (s, 6H), 3.64 (s, 6H), 5.01 (s, 1H), 5.64 (br, 1H), 7.11-7.14 (m, 1H), 7.19-7.27 (m, 4H). ^{13}C NMR δ 19.61, 39.29, 50.96, 103.97, 126.19, 127.62, 128.02, 144.10, 147.37, 167.99

1,4-Dihydro-2,6,-dimethyl-4-ethyl-3,5-pyridinedicarboxylic acid dimethyl ester (3b)[7]:

Recrystallized from EtOH (32% yield). ^{1}H NMR ($CDCl_3$) δ 0.74 (t, 3H, *J* = 7.38 Hz), 1.37 (dq, 2H, *J* = 5.64, 7.45 Hz), 2.29 (s, 6H), 3.71 (s, 6H), 3.90 (t, 1H, *J* = 5.64 Hz), 5.52 (br, 1H). ^{13}C NMR δ 8.98, 19.33, 29.21, 33.99, 50.87, 102.40, 145.15, 168.57

1,4-Dihydro-2,6,-dimethyl-3,5-pyridinedicarboxylic acid dimethyl ester (3a)[2]: Recrystallized from hexane/EtOH (>40% yield). ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 6H), 3.27 (s, 2H), 3.71 (2, 6H), 5.18 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 19.14, 24.75, 51.03, 99.28, 145.09, 150.41, 168.35.

1,4-Dihydro-2,6,-dimethyl-4-(4-chlorophenyl)-3,5-pyridinedicarboxylic acid dimethyl ester (3d)[5]:

Recrystallized from EtOH (72% yield). ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 6H), 3.64 (s, 6H), 4.97 (s, 1H), 5.62 (br, 1H), 7.16-7.26 (m, 4H). ^{13}C NMR δ 19.62, 51.00, 103.73, 128.13, 129.08, 131.83, 144.18, 145.95, 167.78

1,4-Dihydro-2,6,-dimethyl-4-styryl-3,5-pyridinedicarboxylic acid dimethyl ester (3g)[5]:

Recrystallized from EtOAc/Hexane (41% yield). ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 6H), 3.73 (s, 6H), 4.61 (d, 1H, *J* = 5.10 Hz), 5.64 (br, 1H), 6.13-6.22 (m, 2H), 7.14-7.17 (m, 1H), 7.23-7.33 (m, 5H). ^{13}C NMR δ 19.49, 36.14, 51.13, 101.37, 126.27, 126.89, 128.00, 128.34, 131.73, 137.70, 145.15, 167.93

1,4-Dihydro-2,6,-dimethyl-4-(4-methoxyphenyl)-3,5-pyridinedicarboxylic acid dimethyl ester (3e)[5]:

Recrystallized from EtOH (>50% yield). ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 6H), 3.64 (s, 6H), 3.74 (s, 3H), 4.94 (s, 1H), 5.68 (br, 1H), 6.74-6.76 (m, 2H), 7.16-7.23 (m, 2H). ^{13}C NMR δ 19.51, 38.38, 38.40, 50.93, 50.95, 55.11, 104.06, 113.38, 128.56, 139.92, 143.93, 157.93, 168.08

1,4-Dihydro-2,6,-dimethyl-4-(4-trifluoromethylphenyl)-3,5-pyridinedicarboxylic acid dimethyl

ester (3f)[2]:

Recrystallized from EtOH (>50% yield). ^{1}H NMR ($CDCl_3$) **δ** 2.34 (s, 6H), 3.65 (s, 6H), 5.06 (s, 1H), 5.71 (br, 1H), 7.36-7.38 (m, 2H), 7.45-7.48 (m, 2H). ^{13}C NMR δ 19.61, 39.51, 51.05, 51.07, 53.15, 69.47, 103.45, 124.99, 125.02, 127.98, 144.51, 151.25, 167.67

A typical procedure for preparation of non-symmetric dihydropyridiines: 3,5 Dimethylisoxazole (257.5 mg, 2.65 mmol), $Rh_2(OAc)_2$ (7.0 mg, 0.016 mmol and toluene (14 mL) were combined into two-necked round bottom flask under Ar atmosphere and heated at 60 ˚C for 0.5 h. Into this reaction mixture was dropwise added (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (783.3 mg, 3.88 mmol) dissolved in toluene (7 mL) by syringe pump over 30 min. Then the solution was heated at reflux for 4 h and solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, 1 : 2 diethyl ether : hexane) to give methyl 5-acetyl-6-phenyl-1,4-dihydropyridine-2-carboxyrate **4a** (248.4 mg, 35% yield).

Methyl 5-acetyl-6-phenyl-1,4-dihydropyridine-2-carboxyrate (4a)[3]:

^{1}H NMR ($CDCl_3$) **δ** 2.01 (s, 3H), 2.41 (s, 3H), 3.37 (s, 3H), 4.70 (d, 1H, *J* = 5.64 Hz), 6.08 (dd, 1H, *J* = 5.97, 2.27 Hz), 6.28 (br, 1H) 7.19-7.34 (m, 5H) ^{13}C NMR δ 22.90, 30.07, 31.73, 123.51, 128.55, 179.08

Methyl 5-acetyl-6-(4-methoxyphenyl)-1,4-dihydropyridine-2-carboxyrate (4b)[3]:

(60% yield) ^{1}H NMR ($CDCl_3$) **δ** 2.02 (s, 3H), 2.41 (s, 3H), 3.76 (s, 3H), 3.85 (s, 3H), 4.63 (d, 1H, *J* = 5.63 Hz), 6.07 (dd, 1H, *J* = 6.19, 2.00 Hz), 6.40 (br, 1H) 6.82-6.86 (m, 2H), 7.12-7.17 (m, 2H).

Methyl 5-acetyl-6-(4-trifluoromethylphenyl)-1,4-dihydropyridine-2-carboxyrate (4c)[3]:

(60% yield) ^{1}H NMR ($CDCl_3$) **δ** 2.06 (s, 3H), 2.42 (s, 3H), 3.79 (s, 3H), 4.81 (d, 1H, *J* = 5.64 Hz), 6.05 (dd, 1H, *J* = 6.31, 1.73 Hz), 6.40 (br, 1H) 7.34-7.36 (m, 2H), 7.55-7.58 (m, 2H).

A typical procedure for oxidation of dihydropyridine catalyzed by HB Pt (Table 3): 1,4-Dihydro-2,6,-dimethyl-3,5-pyridinedicarboxylic acid dimethyl ester **3a** (1.1102 g), *o*-chloranil (32.7 mg) and HB Pt (90.6 mg, 0.143 mmol/g) were combined in mixture of CH_2Cl_2 (10 mL) and water (0.5 mL). The mixture was stirred at room temperature for 6 h under oxygen atmosphere. After filtration of the catalyst, the organic phase and aqueous phase were separated. Aqueous phase

was extracted by CH_2Cl_2 and solvent was removed *in vacuo* from combined organic layer. Residue was purified by column chromatography to give 2,6,-dimethyl-3,5-pyridinedicarboxylic acid dimethyl ester **5a** (1.079 g, 99% yield).

2,6,-Dimethyl-3,5-pyridinedicarboxylic acid dimethyl ester (5a)[2]:

^{1}H NMR ($CDCl_3$) **δ** 2.85 (s, 6H), 3.93 (s, 6H), 8.71 (s, 1H). ^{13}C NMR δ 24.82, 52.17, 122.49, 140.91, 162.50, 166.08

2,6,-Dimethyl-4-phenyl-3,5-pyridinedicarboxylic acid dimethyl ester (5c)[2]:

^{1}H NMR ($CDCl_3$) **δ** 2.60 (s, 6H), 3.53 (s, 6H), 7.22-7.26 (m, 2H), 7.36-7.40 (m, 3H). ^{13}C NMR δ 22.77, 51.94, 126.59, 127.62, 128.01, 128.33, 136.31, 146.02, 155.38, 168.18.

2,6,-Dimethyl-4-ethyl-3,5-pyridinedicarboxylic acid dimethyl ester (5b)[8]:

^{1}H NMR ($CDCl_3$) **δ** 1.17 (t, 3H, *J* = 7.60 Hz), 2.50 (s, 6H), 2.59 (q, 2H, *J* = 3.90 Hz), 3.94 (s, 6H). ^{13}C NMR δ 40.16, 48.04, 50.00, 77.48, 151.91, 173.98, 180.45, 194.07

2,6,-Dimethyl-4-(4-methoxyphenyl)-3,5-pyridinedicarboxylic acid dimethyl ester (5e)[6]:

^{1}H NMR ($CDCl_3$) **δ** 2.59 (s, 6H), 3.58 (s, 6H), 3.82 (s, 3H), 6.89-6.92 (m, 2H), 7.16-7.19 (m, 2H). ^{13}C NMR δ 22.82, 52.12, 55.09, 113.63, 126.91, 128.45, 129.08, 145.73, 155.25, 159.66, 168.53

2,6,-Dimethyl-4-(4-chlorophenyl)-3,5-pyridinedicarboxylic acid dimethyl ester (5d)[6]:

^{1}H NMR ($CDCl_3$) **δ** 2.59 (s, 6H), 3.57 (s, 6H), 7.17-7.19 (m, 2H), 7.35-7.37 (m, 2H). ^{13}C NMR δ 22.86, 52.15, 126.48, 128.37, 129.18, 134.66, 134.73, 144.81, 155.64, 168.00

2,6,-Dimethyl-4-(4-trifluoromethylphenyl)-3,5-pyridinedicarboxylic acid dimethyl ester (5f)[2]:

^{1}H NMR ($CDCl_3$) **δ** 2.61 (s, 6H), 3.54 (s, 6H), 7.37-7.39 (m, 2H), 7.64-7.66 (m, 2H). ^{13}C NMR δ 22.97, 52.17, 122.91, 124.72, 125.04. 125.06, 126.34, 128.38, 130.52, 130.73, 140.16, 144.73, 155.97, 167.85

2,6,-Dimethyl-4-styryl-3,5-pyridinedicarboxylic acid dimethyl ester (5g)[9]: ^{1}H NMR ($CDCl_3$) **δ** 2.56 (s, 6H), 3.85 (s, 6H), 6.80 (d, 1H, *J* = 17.2 Hz), 7.09 (d, 1H, *J* = 16.4 Hz), 7.10-7.41 (m, 3H), 7.42-7.43 (m, 2H). ^{13}C NMR δ 22.99, 52.50, 122.70, 125.32, 126.87, 128.76, 136.11, 136.61, 142.38, 155.78, 168.74

Methyl 5-acetyl-6-methyl-4-phenylpicolinate (6a)[3]:

^{1}H NMR ($CDCl_3$) δ 2.02 (s, 3H), 2.63 (s, 3H), 4.03 (s, 3H), 7.38-7.40 (m, 2H), 7.46-7.48 (m, 3H), 8.03 (s, 1H). ^{13}C NMR δ 22.87, 31.69, 53.06, 53.08, 123.47, 128.51, 129.10, 129.41, 136.92, 138.72, 147.31, 154.61, 165.31, 205.30

Methyl 5-acetyl-6-methyl-4-(4-methoxyphenyl)picolinate (6b)[3]:

^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H), 2.62 (s, 3H), 3.86 (s, 3H), 4.03 (s, 3H), 6.97-7.01 (m, 2H), 7.32-7.34 (m, 2H), 8.01 (s, 1H). ^{13}C NMR δ 22.89, 31.64, 53.09, 55.39, 114.61, 123.42, 129.95, 147.25, 154.58, 160.68, 165.45, 205.76

Methyl 5-acetyl-6-methyl-4-(4-trifluoromethylphenyl)picolinate (6c)[3]:

^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H), 2.62 (s, 3H), 3.86 (s, 3H), 4.03 (s, 3H), 6.97-7.01 (m, 2H), 7.32-7.34 (m, 2H), 8.01 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.83, 31.92, 122.55, 123.18, 126.04 (q, J = 3.58 Hz), 128.97, 131.50 (q, J = 33.38 Hz), 138.67, 140.40, 147.51, 154.77, 165.02, 204.71.

A typical procedure for oxidation of dihydropyridine catalyzed by HB Pt (leaching test): 1,4-Dihydro-2,6,-dimethyl-3,5-pyridinedicarboxylic acid dimethyl ester **3a** (211.7 mg), *o*-chloranil (6.9 mg) and HB Pt (16.6 mg, 0.143 mmol/g) were combined in mixture of CH_2Cl_2 (10 mL) and water (0.5 mL). The mixture was stirred at room temperature for 6 h under oxygen atmosphere. After filtration of the catalyst, the organic phase and aqueous phase were separated. Aqueous phase was extracted by CH_2Cl_2 and solvent was removed *in vacuo* from combined organic layer. Half of residue was purified by column chromatography to give 2,6,-dimethyl-3,5-pyridinedicarboxylic acid dimethyl ester **5a** (103.7 g, 50% yield). Another half of residue was heated in mixture of sulfuric acid and nitric acid at 200 ˚C for 3 h and the mixture was cooled to room temperature and aqua regia was added. The amount of gold in the resulting solution was measured by ICP analysis to determine the leaching of gold (Not detected).

Recovery and reuse of HB Pt (Table 2): The collected catalyst after the reaction was stirred in a 1 to 1 mixture of 1N NaOH and *i*PrOH at room temperature for 12 h. The catalyst was collected by filtration and washed with water, *i*PrOH and CH_2Cl_2 then dried *in vacuo*. Then the catalyst was used for next reaction.

Oxidation of 2-methyl indoline catalyzed by HB Pt (Scheme 3): 2-Methyl indoline (31.0 mg), *o*-chloranil (7.3 mg) and HB Pt (16.4 mg, 0.085 mmol/g) were combined in mixture of CH_2Cl_2 (1 mL) and water (0.1 mL). The mixture was stirred at room temperature for 6 h under oxygen atmosphere. After filtration of the catalyst, the organic phase and aqueous phase were separated. To the organic phase was added the known amount of anisole in approximately 1:1 weight ratio to the initial substrate. The organic phase was dried over sodium sulfate and yield of 2-methyl indole was determined by GC analysis (93%).

Preparation of 7[4]: *p*-Chloroaniline (62.0 mg, 0.49 mmol), benzaldehyde (80.1 mg, 0.76 mmol), α-methylstyrene (166.2 mg, 1.41 mmol), $Sc(OTf)_3$ (25 mg), CH_2Cl_2 (2 mL) and CH_3CN (1 mL) were combined under Ar atmosphere at 40 ˚C for 18 h. Solvent was removed *in vacuo* and residue was purified by preparative TLC to give **7** (140.6 mg, 86% yield, major/minor = 85:15).

7 (major):

^{1}H NMR ($CDCl_3$) **δ** 1.80 (s, 3H), 1.94 (dd, 1H, *J* = 2.76, 13.74 Hz), 2.24 (dd, 1H, *J* = 12.37, 12.37 Hz), 4.16 (br, 1H), 4.58 (dd, 1H, *J* = 2.70, 11.70 Hz), 6.51-6.54 (m, 1H), 6.62-6.63 (m, 1H), 6.93-6.96 (m, 1H) 7.14-7.43 (m, 10H).

Oxidation of 7 using HB Pt and catalytic amount of *o*-chloranil: 7 (124.8 mg), *o*-chloranil (20.7 mg) and HB Pt (58.7 mg, 0.143 mmol/g) were combined in mixture of CH_2Cl_2 (4 mL) and water (0.2 mL). The mixture was stirred at room temperature for 96 h under oxygen atmosphere. After filtration of the catalyst, the organic phase and aqueous phase were separated. Aqueous phase was extracted by CH_2Cl_2 and solvent was removed *in vacuo* from combined organic layer. Residue was purified by column chromatography to give **8** (113.4 g, 88% yield).

8:

^{1}H NMR ($CDCl_3$) **δ** 1.92 (s, 3H), 7.02 (d, 2H, *J* = 7.32 Hz), 7.21-7.45 (m, 8H), 7.62 (d, 1H, *J* = 7.97 Hz), 7.82 (d, 2H, *J* = 7.38 Hz); ^{13}C NMR ($CDCl_3$) **δ** 21.59, 55.17, 127.02, 127.68, 128.18, 128.32, 128.74, 128.95, 129.14, 131.04, 131.33, 133.81, 134.67, 138.42, 138.58, 140.32, 158.84, 196.67. HR-MS (m/z) calcd. for $C_{22}H_{17}ClNO(MH^+)$: 346.09987, found: 346.09933.

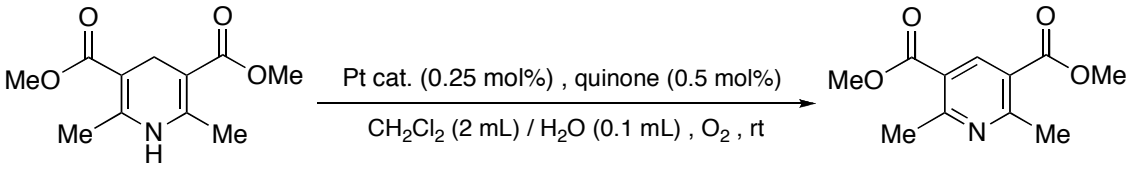
9:

^{1}H NMR ($CDCl_3$) **δ** 1.84 (s, 3H), 7.12 (d, 1H, *J* = 2.28 Hz), 7.18-7.26 (m, 3H), 7.35-7.46 (m, 6H),

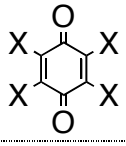
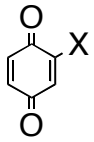
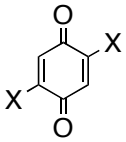
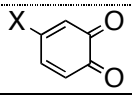
7.58 (dd, 2H, J = 1.68, 11.59 Hz), 7.64 (d, 1H, J = 8.47 Hz); ^{13}C NMR ($CDCl_3$) **δ** 21.36, 50.55, 55.37, 112.13, 112.34, 116.85, 124.87, 125.00, 127.29, 127.83, 128.34, 128.36, 128.39, 128.73, 129.93, 130.70, 130.95, 134.30, 134.78, 135.01, 136.08, 140.68, 143.45, 144.00, 160.70. HR-MS (m/z) calcd. for $C_{28}H_{27}Cl_5NO_2(MH^+)$: 573.97019, found: 573.96954.

Deprotection of *p*-methoxybenzyl group using catalytic amount of PI Pt and o-chloranil : 1-methoxy-4-[(2-phenylethoxy)methyl]-benzene (69.6 mg, 28.7 mmol), *o*-chloranil (7.4 mg, 0.030 mmol), and PI Pt (12.2 mg) were combined in mixture of CH_2ClCH_2Cl (1 mL) and water (0.1 mL). The mixture was stirred at 100 °C for 7 h under oxgen atmosphere. After filtration of the catalyst, the organic phase was added the known amount of anisole in approximately 1:1 weight ratio to the desired alcohol and yield of 2-phenylethylalcohol was determined by GC analysis (78%).

6. Coupled oxidation reaction using other quinones with RPI Pt



0.25 mmol scale

Entry	quinone	X	Time (h)	Yield (%)
1		F	57	75
2		Cl	2	97
3		Br	2	91
4		Cl	6	79
5		Br	6	66
6 [a]		Me	50	44
7 [a]		*t*-Bu	50	34
8		Cl	3	97
9 [a]		*t*-Bu	4.5	97

[a] Catechol was used instead of quinone.

7. TEM images of HB Pt

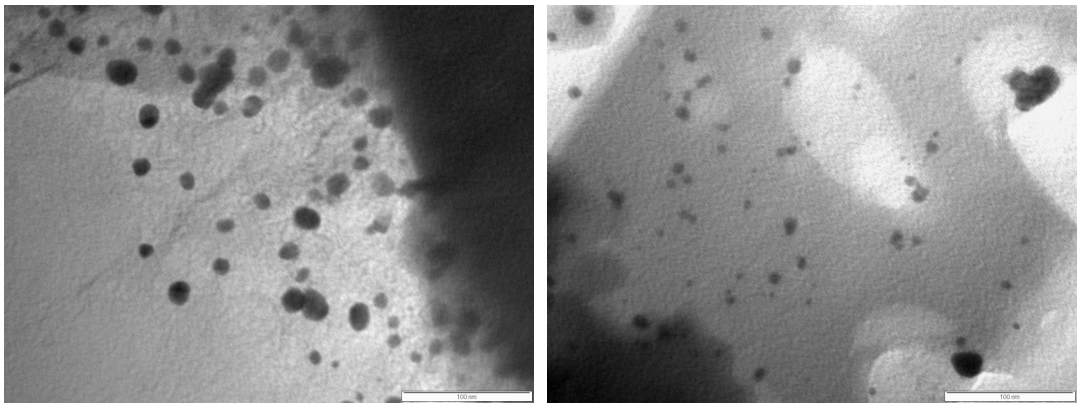


Figure S- 2. Typical TEM images of HB Pt before use

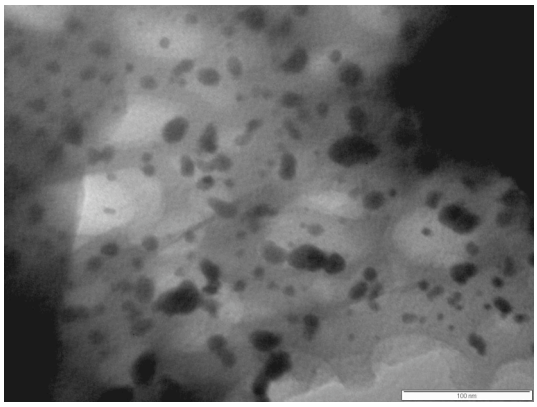
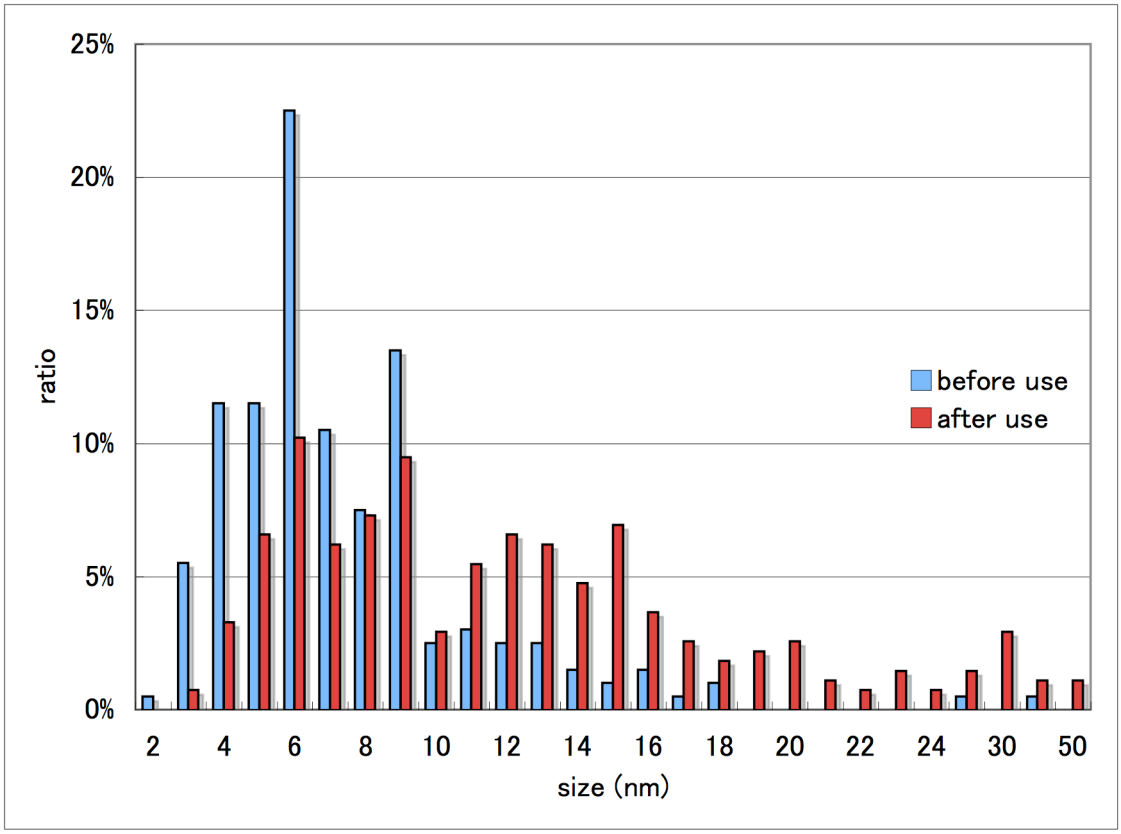


Figure S- 3. Typical TEM image of HB Pt after 9th use in Table 2



N = 200 (before use), average = 8.0 N = 272 (after use), average =13.3

Figure S- 4. Size distribution of Pt nanoclusters of before and after 9th use

8. TEM images of RPI Pt

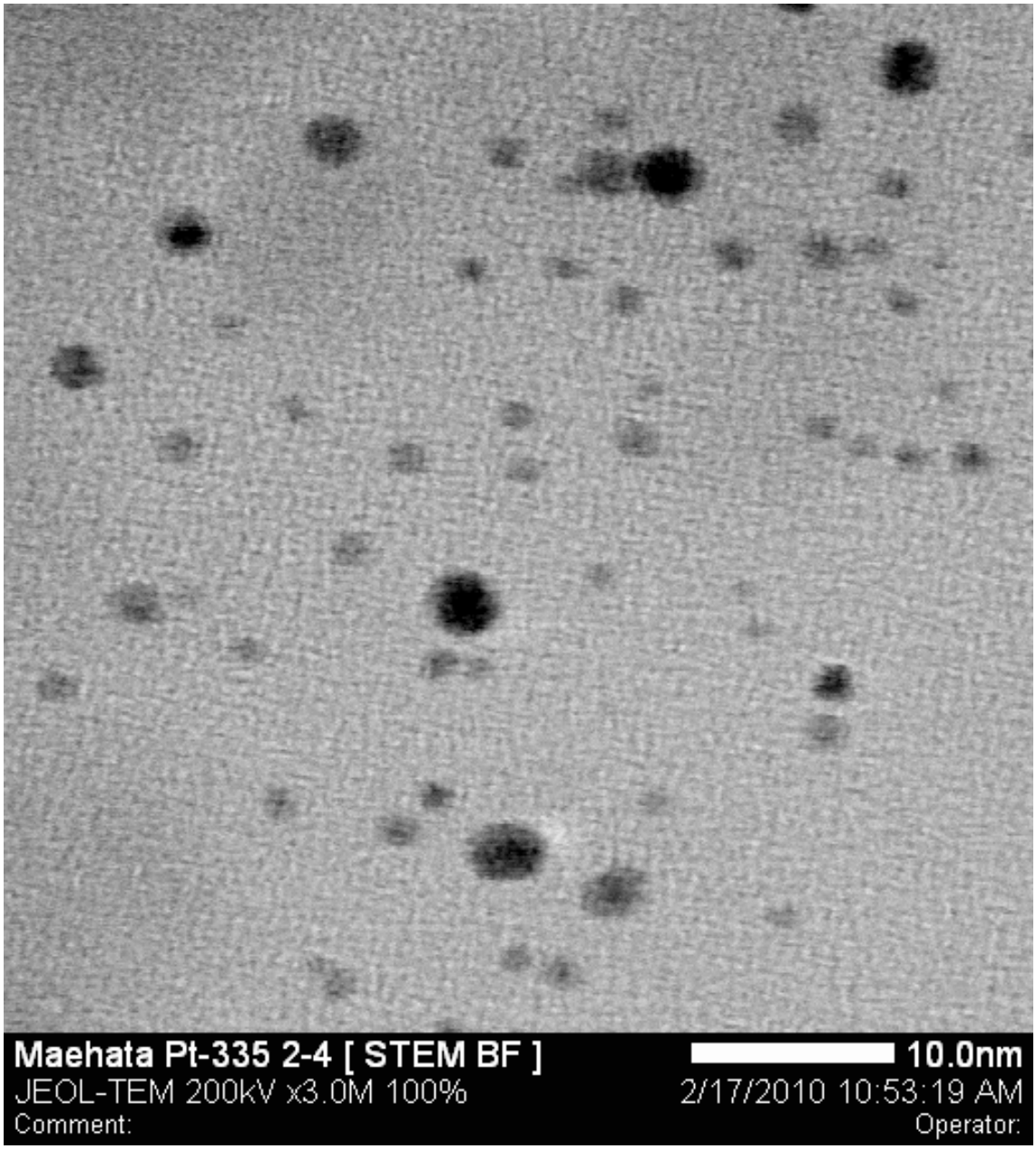


Figure S- 5. Typical STEM images of RPI Pt

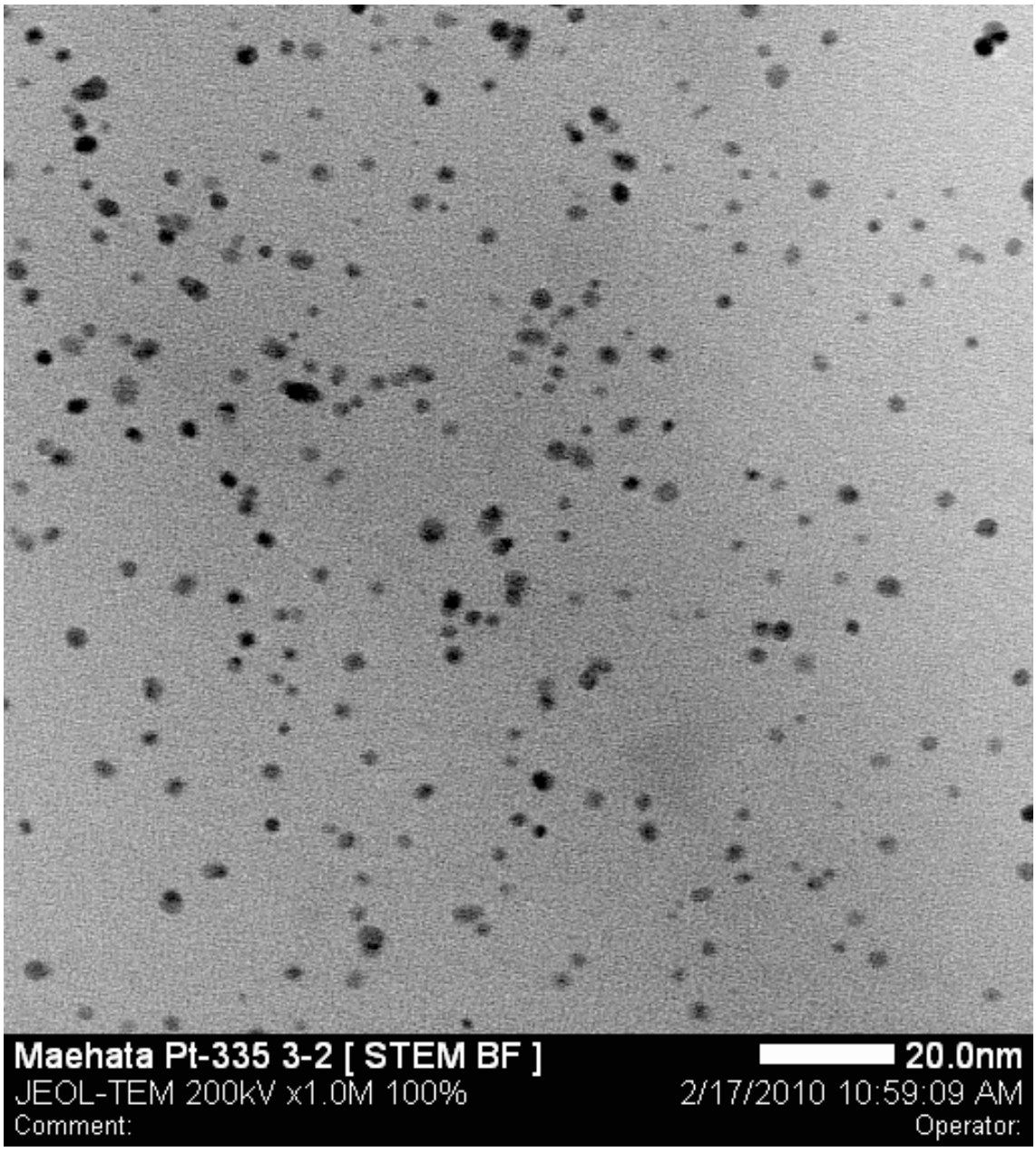
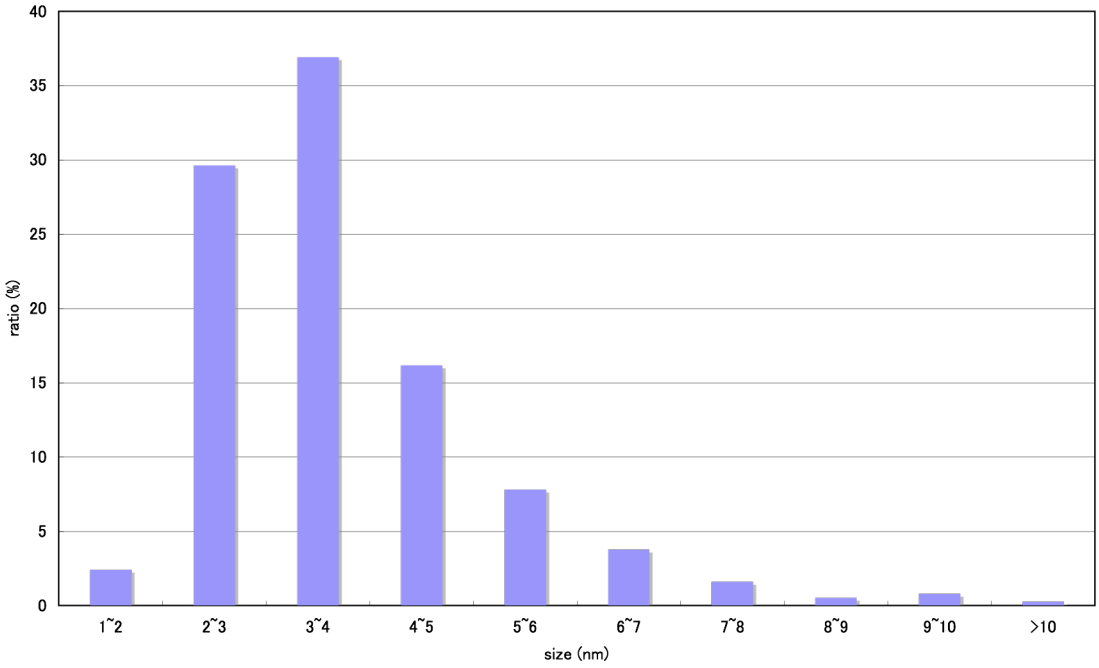


Figure S- 6. Typical STEM images of RPI Pt



N = 371 (before use), average = 3.7

Figure S- 7. Size distribution of RPI-Pt

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