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Supporting Information

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Aerobic Oxidation of Hydroquinones and Their Derivatives Catalyzed by Polymer Incarcerated Platinum Catalyst

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Supporting Information

1. General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400, JNM-LA500 or JNM-LA600 spectrometer in $CDCl_3$. Tetramethylsilane (TMS) served as internal standard (δ =0) for ^{1}H NMR and $CDCl_3$ was used as internal standard (δ =77.0) for ^{13}C NMR. Gas chromatography analysis was performed on SHIMADZU GC-2010 equipped with DB-1 (60m, Agilent technologies) column (career gas pressure 157.5 kPa, total flow 45.0 ml/min, column flow 1.02 ml/min, linear velocity 21.8 cm/s, spread ratio 40.1, injection temperature 250 ^{o}C, detection temperature 250 ^{o}C). The structures of the known compounds were confirmed by comparison with commercially available compounds or reported data in literature. Inductively Coupled Plasma analysis (ICP) was measured with SHIMADZU ICPS-7510. TEM images were obtained using a JEOL JEM-1010 instrument operated at 80 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. Preparation of PI Pt

2-1. Preparation of co-polymer

Co-polymer was prepared along the method shown in Ref. 19 in the text.

2-2. Preparation of PI Pt

Preparation of PI Pt (0.05-0.07 mmol Pt/g):

Co-polymer (836 mg) and $NaBH_4$ (21.2 mg) were dissolved in diglyme (12 ml) at room temperature, to this solution was slowly added sodium hexachloroplatinate (IV) hexahydrate (31.3 mg) in diglyme (3 ml). The mixture was stirred for 3 h at room temperature, and diethyl ether (100 ml) was slowly added to the mixture at room temperature. Brown coaservates enveloped the metal and were dispersed in the medium. The catalyst capsules were then washed with diethyl ether several times and dried at room temperature. The

catalyst capsules were then heated at 150 °C for 5 h without solvent to prepare brown solid, which was washed with dichloromethane and water then grinded by pestle and mortar. The resulting powder was heated at 170 °C for 5 h without solvent to afford PI Pt (733 mg). 10-20 mg of PI Pt was heated in a mixture of sulfuric acid and nitric acid at 200 °C for 3 h, the mixture was cooled to room temperature and aqua regia was added. The amount platinum in the resulting solution was measured by ICP analysis to determine the loading of platinum (0.059 mmol Pt/g).

Preparation of PI Pt (0.1-0.13 mmol Pt/g):

Co-polymer (805.5 mg) and $NaBH_4$ (21.4 mg) were dissolved in diglyme (15 ml) at room temperature, to this solution was slowly added sodium hexachloroplatinate (IV) hexahydrate (31.4 mg) in diglyme (1 ml). The mixture was stirred for 1 h at room temperature and $NaBH_4$ (21.4 mg) were dissolved in this mixture. Additional sodium hexachloroplatinate (IV) hexahydrate (31.4 mg) in diglyme (1 ml) was added and the mixture was stirred for another 1 h. Diethyl ether (100 ml) was slowly added to the mixture at room temperature. Brown coaservates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethyl ether several times and dried at room temperature. The catalyst capsules were then heated at 150 °C for 5 h without solvent to prepare brown solid, which was washed with dichloromethane and water then grinded by pestle and mortar. The resulting powder was heated at 170 °C for 5 h without solvent to afford PI Pt (818.3 mg). 10-20 mg of PI Pt was heated in a mixture of sulfuric acid and nitric acid at 200 °C for 3 h, the mixture was cooled to room temperature and aqua regia was added. The amount platinum in the resulting solution was measured by ICP analysis to determine the loading of platinum (0.125 mmol Pt/g).

TEM image of PI Pt:

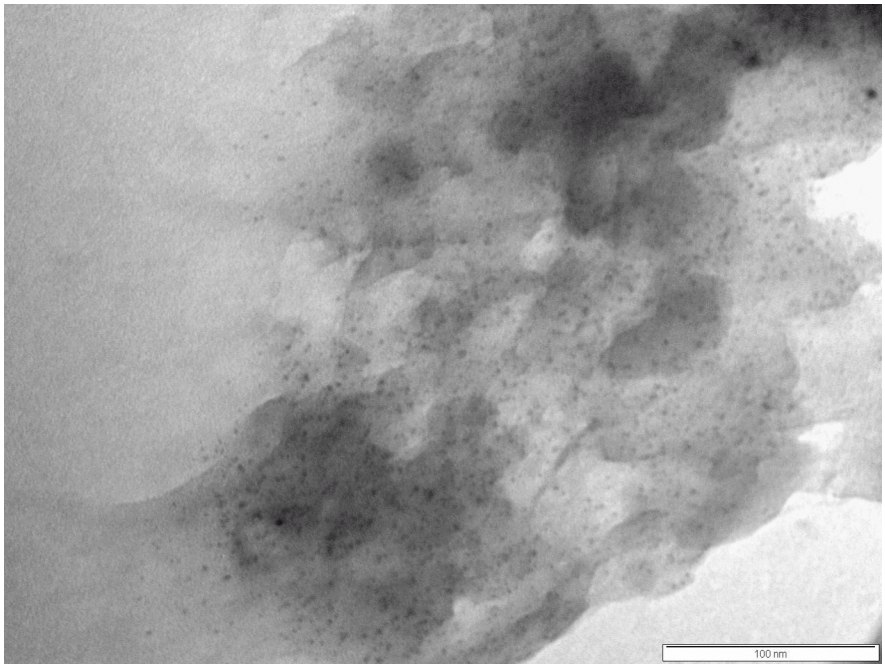

Figure I. A typical TEM image of PI Pt (0.059 mmol Pt/g, average particle diameter 1.8 nm, standard deviation 0.8 nm)

3. Oxidation of hydroquinones catalyzed by PI Pt

3-1. A typical procedure for oxidation reaction of hydroquinones with PI metal

Methylhydroquinone (31.5 mg) and PI Au (22.0 mg, 0.112 mmol Au/g) were combined in chloroform (1.9 ml) and water (0.1 ml). The mixture was stirred at room temperature for 1 h under oxygen atmosphere, during which PI metal catalyst was completely insoluble in either phase and was dispersed uniformly in the whole reaction by vigorous stirring.

3-2. A typical procedure of GC analysis

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 analyzed by GC, using anisole as an internal standard.

In in-situ analysis, the known amount of anisole in approximately 1:1 weight ratio to the initial substrate was combined with the reaction mixture. After each indicated time, a small fraction of organic phase was taken and transferred through a short Pasteur column which contains cotton and sodium sulfate. The column was washed with chloroform and the washing was combined with the sample. The organic solution thus obtained was analyzed by GC, using anisole as an internal standard.

3-3. A typical procedure of in-situ ^{1}H NMR analysis

The oxidation was conducted in $CDCl_3$. A known amount of acetophenone in approximately 1:1 molar ratio to the initial substrate was combined with the reaction mixture. After each indicated time, a small fraction of organic phase was taken and transferred through a short Pasteur column, which contains cotton and sodium sulfate. The column was washed with $CDCl_3$ and the washing was combined with the sample. The $CDCl_3$ solution thus obtained was analyzed by ^1H NMR. Yield was determined from the average integral value of protons of quinone structure (typically within the range of 6.5-7.2 ppm). The average integral value of 7.45-7.48 ppm (2H), 7.55-7.58 ppm (1H) and 7.96 ppm (2H) of acetophenone was used as a standard.

3-4. A typical procedure of metal leaching detection

The reaction mixture was separated to organic phase and aqueous phase. Sulfuric acid and aqua regia were added to the aqueous phase and the amount of metal was analyzed by ICP. The organic phase was dried over sodium sulfate and concentrated. The resultant solid product was heated in a mixture of sulfuric acid and nitric acid at 200 ^oC for 3 h to induce complete decomposition to afford a clear solution. The solution was cooled to room temperature and aqua regia was added. The amount of metal was analyzed by ICP.

3-5. Synthesis of 2-(1-hydroxyethyl)-1,4-benzenediol (1h)

2,5-Dihydroxyacetophenone (1.83 g) was dissolved in THF (60 ml). To this was added NaBH3CN (2.28 g) and a drop of an aqueous solution of methyl orange. The mixture was stirred for 8 h while maintaining the red color of the indicator by dropwise addition of 1N HCl at a sufficient rate. Rate of reaction was estimated by acid consumed and by TLC of the mixture. After dilution with H_2O (150 ml), the product was extracted with diethyl ether. After dried over sodium sulfate, the organic layer was concentrated under reduced pressure to afford a crude product as brownish oil. Purification by column chromatography on silica gel (hexane/ethyl acetate=2/1) afforded **1p** (0.52 g, 23 %) as colorless oil. ^1H NMR (400 MHz, CD_3CN) δ 1.40 (d, 3H, J=6.4 Hz), 3.66 (m, 2H), 4.95 (q, 1H, J=6.4 Hz), 6.54 (dd, 1H, J=2.8, 8.8 Hz). ^{13}C NMR (100 MHz, CD_3CN) δ 23.8, 68.5, 113.1, 115.1, 117.3, 132.3, 148.3, 150.4.

4. NMR spectrometry data of quinone products

All compouns are literature known (Ref. 5-18 in the text).

2-Methyl-1,4-benzoquinone (3a):

^1H NMR (500 MHz, $CDCl_3$) δ 2.07 (s, 3H), 6.63 (d, 1H, J = 1.8 Hz), 6.72 (dd, 1H, J = 2.3, 9.7 Hz), 6.78 (d, 1H, J = 10.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.76, 133.27, 136.42, 136.52, 145.79, 187.50, 187.67.

1,4-Benzoquinone (3b):

^1H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.53, 187.28.

2,3-Dimethyl-1,4-benzoquinone (3c):

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.04 (s, 6H), 6.73 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.10, 136.15, 140.89, 187.28.

Tetramethyl-1,4-benzoquinone (3d):

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.23, 140.26, 187.28.

2-tert-Butyl-1,4-benzoquinone (3e):

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.29 (s, 9H), 6.60 (s, 1H), 6.68 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.11, 35.28, 131.54, 134.63, 138.68, 156.05, 187.49, 188.45.

2-Phenyl-1,4-benzoquinone (3f):

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (dd, 1H, J = 2.10, 10.3 Hz), 6.87-6.89 (m, 2H), 7.44-7.50 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.55, 129.24, 130.14, 132.68, 136.25, 137.05, 145.89, 186.56, 187.52.

2-Methoxy-1,4-benzoquinone (3g):

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.96 (s, 1H), 6.73 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.19, 107.65, 134.40, 137.18, 158.56, 181.66, 187.42.

2-(2-hydroxyethyl)-1,4-benzoquinone (3h):

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (d, 3H, J = 6.3 Hz), 4.79 (apparent d, 1H, J = 6.3 Hz), 6.69 (apparent s, 2H), 6.73 (d, 1H, J = 1.15 Hz). ^{13}C NMR (150 MHz; $CDCl_3$) δ 22.5, 64.7, 130.5, 136.4, 136.8, 150.6, 187.7, 187.8.

1, 4-Napthtoquinone (3i):

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 7.74-7.76 (m, 2H), 8.05-8.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 126.38, 131.88, 133.92, 138.65, 184.98.

2-(Methoxycarbonyl)-1,4-benzoquinone (3o): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 3H), 6.81-6.86 (m, 2H), 7.12 (d, 1H, J = 1.70 Hz). ^{13}C NMR (125 MHz; $CDCl_3$) δ 53.2, 136.2, 136.6, 137.0, 163.2, 183.1, 186.9.

2-Acetyl-1,4-benzoquinone (3p): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.57 (s, 3H), 6.80 (d, 1H, J = 10.3 Hz), 6.85 (dd, 1H, J = 2.3, 10.3 Hz), 7.01 (d, 1H, J = 2.3 Hz). ^{13}C NMR (150 MHz; $CDCl_3$) δ 30.9, 135.3, 136.4, 136.7, 142.5, 185.5, 187.3, 196.8.

4-*tert*-Butyl-1,2-benzoquinone (4a):

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (s, 9H), 6.28 (d, 1H, J = 2.3 Hz), 6.39 (d, 1H, J = 10.9 Hz), 7.19 (dd, 1H, J = 2.3, 10.9 Hz).

3,5-di-*tert*-Butyl-1,2-benzoquinone (4b):

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.27 (s, 9H), 6.22 (d, 1H, J = 2.3 Hz), 6.93 (d, 1H, J = 2.3 Hz). ^{13}C NMR (125 MHz; $CDCl_3$) δ 27.90, 29.23, 35.50, 36.04, 122.13, 133.45, 149.98, 163.26, 180.08, 181.17.