

Electronic Supplementary Information for

***In situ* electrogeneration of *o*-benzoquinone and high yield reaction with benzenethiols in a microflow system**

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Instrumentation

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1. Instrumentation

Nuclear magnetic resonance (^1H NMR, ^{13}C NMR) spectra were measured on JEOL JNM EX-270 spectrometer operating at 270 MHz (^1H NMR), 67.8 MHz (^{13}C NMR) in CDCl_3 . All ^1H NMR chemical shifts were reported in ppm relative to internal references of TMS at δ 0.00. ^{13}C NMR chemical shifts were reported in ppm relative to carbon resonance in chloroform- d_1 at δ 77.00. EI mass spectra were measured with a Shimadzu GCMS-QP5050A mass spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. Cyclic voltammetry was performed by using a computer-controlled electrochemical analyzer (ALS/CH Instruments 630C). Preparative electrolyses were carried out with a HOKUTO DENKO HA-501 Potentiostat/Galvanostat.

2. Materials

Acetonitrile and 4-isopropylbenzenethiol were purchased from Wako PureChemical Industries and used as received. Catechol, 4-methoxybenzenethiol, 4-nitrobenzenethiol and 2,6-lutidine were purchased from Tokyo Chemical Industry and used as received. Sodium perchlorate was purchased from Kanto Chemical and used as purchased.

3. Microflow Reactor

Figure S1 shows schematic illustration of the electrochemical microflow reactor. The reactor was constructed from platinum (Pt) plate (3 cm width, 3 cm length) and graphite (G) plate (3 cm width, 3 cm length). A spacer (NITOFLO[®] 80 μm thickness adhesive tape, Nitto Denko) was used to leave a rectangular channel exposed, and the two electrodes were simply sandwiched together (area of the two electrodes: $1 \times 3 \text{ cm}^2$). After connecting Teflon tubing to inlets and outlet, the cell was sealed with epoxy resin. As shown in Figure S1, the inlets 1 and 2 were provided for introducing the catechol and benzenethiol solutions, respectively.

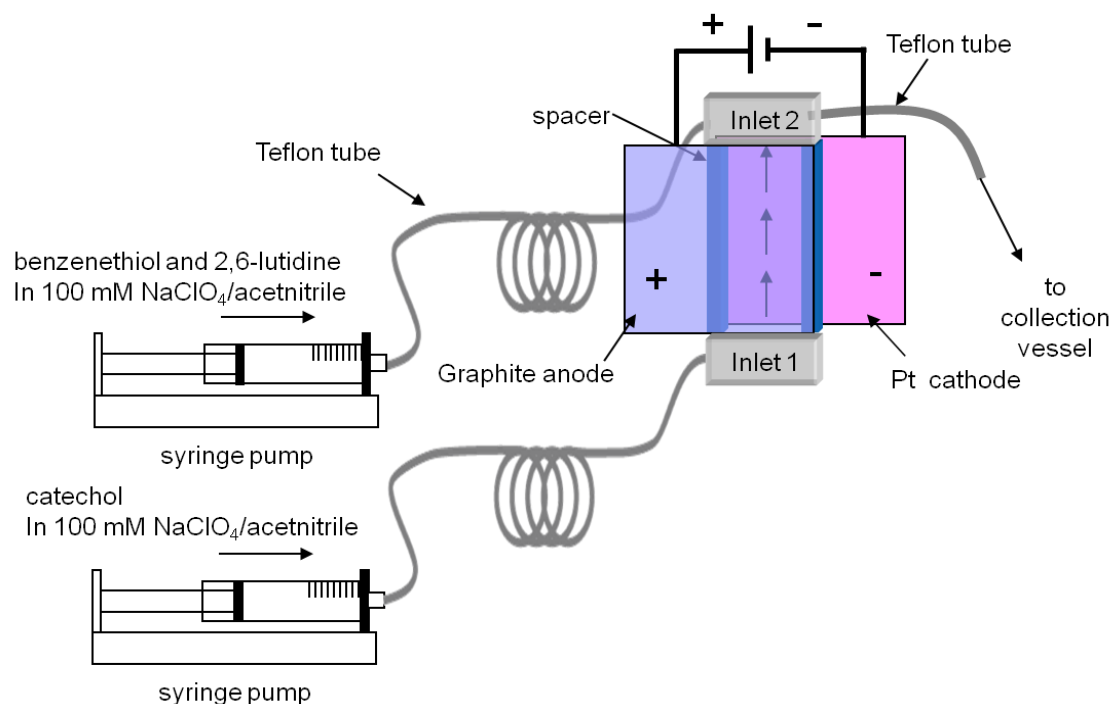


Figure S1. Schematic illustration of the microflow system.

4. *I-E* Curve Measurement

I-E curve measurements for the oxidation of catechol and 4-isopropylbenzenethiol were performed by using a computer-controlled electrochemical analyzer (ALS/CH Instruments 630C). *I-E* Curves were recorded at a temperature of 25 ± 2 C° using an undivided cell equipped with a working electrode (graphite disk electrode, 4 mm ϕ), an auxiliary electrode (Pt plate, 2×2 cm²), and a saturated calomel reference electrode (SCE).

5. General Procedure for Preparative Electrolysis Using Microflow Reactor

Bulk electrolysis of catechol (10 mM) in acetonitrile was conducted with a constant current (1.5 mA cm^{-2}) and solution flowing through the electrolysis cell. The solution containing 4-isopropylbenzenethiol (10 mM) and 2,6-lutidine (10 mM) was introduced at the inlet 2 in Figure 5. The flow rates of two solutions were fixed at 0.1 mL min^{-1} . The flow rates were controlled by using syringe pump (KdScientific model 100). Reaction mixture was collected and then analyzed by HPLC to determine the product yield. HPLC analysis was performed by an external standard method with a Shimadzu 880-PU equipped with UV detector (875-UV, Shimadzu) and an ODS column (Inertsil ODS-4, GL Science).

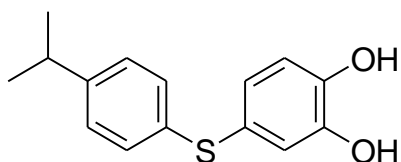
6. General Procedure for Preparative Electrolysis Using Bath Type Reactor

As for In-cell method, bulk electrolysis was carried out using an undivided cell equipped with a working electrode (graphite plate, $1 \times 3 \text{ cm}^2$) and an auxiliary electrode (Pt plate, $1 \times 3 \text{ cm}^2$) in 100 mM NaClO_4 /acetonitrile solution (10 mL) containing catechol (10 mM), 4-isopropylbenzenethiol (10 mM), and 2,6-lutidine (10 mM). Constant current (1.5 mA cm^{-2}) was applied for the electrolysis. After the charge was passed (2.8 F mol^{-1}), reaction mixture was analyzed by HPLC to determine the product yield. As for Ex-cell method, bulk electrolysis was carried out using an undivided cell equipped with a working electrode (graphite plate, $1 \times 3 \text{ cm}^2$) and an auxiliary electrode (Pt plate, $1 \times 3 \text{ cm}^2$) in 100 mM NaClO_4 /acetonitrile solution (10 mL) containing catechol (10 mM). Constant current (1.5 mA cm^{-2}) was applied for the electrolysis. After the charge was passed (2.8 F mol^{-1}), 4-isopropylbenzenethiol (10 mM) and 2,6-lutidine (10 mM) in acetonitrile solution (10 mL) were added followed by stirring for 10 min. Reaction mixture was analyzed by HPLC to determine the product yield.

7. Synthesis and characterization of authentic samples for HPLC analysis

4-(4-Isopropyl-phenylsulfanyl)-benzene-1,2-diol

A solution of catechol (0.2 g, 1.8 mmol) and Ag_2O (0.85g, 3.7 mmol) in acetonitrile (10 mL) were stirred for 10 min. Ag_2O was removed from solution by gravity filtration. The resulting filtrate was added to the solution of 4-isopropyl benzenethiol (0.27 g, 1.8 mmol) and 2,6-lutidine (1.9 g, 17.7mmol) in acetonitrile (10 mL) and stirred for 1 h at room temperature. Resulting mixture was then acidified with 1 M HCl and extracted with diethyl ether. The organic layer was dried with sodium sulfate and diethyl ether was removed by rotary evaporation. Crude product was purified by silica gel column chromatography (Hex / EtOAc) to give viscous yellow oil (16% yield).



$^1\text{H-NMR}$ (270 kHz; CDCl_3): δ 7.12-6.98 (m, 6H), 6.84 (t, 1H), 2.84 (m, $J = 7.02 \text{ Hz}$, 1H), 1.21 (d, $J = 7.02 \text{ Hz}$, 6H)

$^{13}\text{C-NMR}$ (270 kHz; CDCl_3): δ 23.84, 33.60, 117.17, 121.24, 127.46, 144.304, 147.372

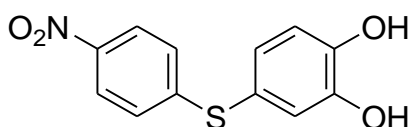
IR (neat NaCl v/cm^{-1}) 3415, 2960, 2930, 2875, 1715, 1595, 1495, 1475, 1455, 1250, 1225,

1155, 1145, 1110

HRMS (ESI) m/z calculated for $C_{12}H_9NO_4S$ 260.0871, found 260.0873

4-(4-nitro-phenylsulfanyl)-benzene-1,2-diol

A solution of catechol (0.5 g, 4.5 mmol) and Ag_2O (2.13 g, 9.3 mmol) in acetonitrile (25 mL) were stirred for 10 min. Ag_2O was removed from solution by gravity filtration. The resulting filtrate was added to the solution of 4-nitro benzenethiol (0.75 g, 4.8 mmol) and 2,6-lutidine (1.9 g, 17.7mmol) in acetonitrile (25 mL) and stirred for 1 h at room temperature. Resulting mixture was then acidified with 1 M HCl and extracted with diethyl ether. The organic layer was dried with sodium sulfate and diethyl ether was removed by rotary evaporation. Crude product was purified by silica gel column chromatography (chloroform) and then recrystallized from chloroform-acetone-hexane solution to give yellow crystal (20% yield).



1H -NMR (270 kHz; $CDCl_3$): δ 7.00 (d, 3H), 7.22 (d, 2H), 8.10 (d, 2H)

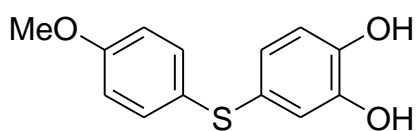
^{13}C -NMR (270 kHz; $CDCl_3$): δ 207.21, 150.94, 148.07, 146.97, 128.66, 126.18, 124.50, 122.84, 119.36, 117.48

IR (neat KBr v/cm^{-1}) 3543, 3455, 2365, 1859, 1578, 1500, 1441, 1338, 1330, 1317, 1186, 1109

HRMS (ESI) m/z calculated for $C_{12}H_9NO_4S$ 263.052, found 286.0147 ($M+Na$) $^+$

4-(4-methoxy-phenylsulfanyl)-benzene-1,2-diol

A solution of catechol (0.5 g, 4.5 mmol) and Ag_2O (2.13 g, 9.3 mmol) in acetonitrile (25 mL) were stirred for 10 min. Ag_2O was removed from solution by gravity filtration. The resulting filtrate was added to the solution of 4-methoxy benzenethiol (0.7 g, 5 mmol) and 2,6-lutidine (1.9 g, 17.7mmol) in acetonitrile (10 mL) and stirred for 1 h at room temperature. Resulting mixture was then acidified with 1 M HCl and extracted with diethyl ether. The organic layer was dried with sodium sulfate and diethyl ether was removed by rotary evaporation. Crude product was purified by silica gel column chromatography (Hex / EtOAc) to give viscous yellow oil (15% yield).



$^1\text{H-NMR}$ (270 kHz; CDCl_3): δ 7.15-7.09 (m, 2H), 6.98-6.88 (m, 2H), 6.72-6.78 (m, 3H)

$^{13}\text{C-NMR}$ (270 kHz; CDCl_3): δ 158.45, 144.15, 143.85, 130.53, 126.34, 125.56, 120.73, 119.09, 116.70, 114.84, 55.25

IR (neat NaCl v/cm^{-1}) 3410, 2980, 2930, 2830, 1700, 1595, 1495, 1455, 1360, 1325, 1285, 1245, 1175, 1025

HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{S}$ 248.0507, found 248.0515