**Supporting Information for:**

**High Yield and Selective Electrocatalytic Reduction of Nitroarenes to Anilines using Redox Mediators**

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**SI-1: General Experimental Remarks:** Nitrobenzene (99%), ethyl 2-nitrobenzoate (97%), 2-nitroacetophenone (97%) and phosphoric acid (85%) were purchased from Alfa Aeasar. 4-nitrophenol (99%), 1-iodo-2-nitrobenzene (97%) and 1-iodo-4-nitrobenzene (98%) were supplied by Sigma Aldrich. Phosphotungstic acid (reagent grade) was supplied by both Sigma Aldrich and Alfa Aesar. Chloroform (99.8%), acetone (99.5%) and sulfuric acid (95%) were purchased from Fisher Scientific. Dichloromethane (99.5%) and magnesium sulfate (99.2%) were purchased from VWR while the diethyl ether (99.5%) was purchased from Scientific Laboratory Supplies Ltd. Deuterated chloroform (99.8%), dimethyl sulfoxide (99.9%) and methanol (99.8%) were supplied by Cambridge Isotope Laboratories. 254 µm-thick Nafion N-1110 membrane, used in H-cell, was purchased from Fuel Cell Stores and soaked in 1 M sulfuric acid solution overnight prior to use. All chemical reagents and solvents were used as purchased. Carbon felt, used as a high surface area electrode, was purchased from Alfa Aesar (3.18 mm thick, 99.0%).

All electrolyte solutions were prepared with ultrapure deionised water (18.2 MΩ-cm resistivity), obtained froma Sartorius Arium Comfort combined water system. All NMR data were collected using a Bruker AV 400 instrument, at a constant temperature of 300 K. pH determinations were made with a Hanna HI 9025 waterproof pH meter. All other materials were obtained as stated in the text. Experiments performed at “room temperature” were carried out at 25 °C.

**SI-2: General Electrochemical Methods:** Electrochemical studies were performed in a three-electrode configuration (unless otherwise stated) using either a CH Instruments CHI600D potentiostat or a BioLogic SP-150 potentiostat. A glassy carbon button electrode or carbon felt were used as the working electrodes, a graphite rod or a piece of carbon felt were used as the counter electrode, and an Ag/AgCl (NaCl, 3 M) reference electrode was used as specified. Glassy carbon working electrodes (area = 0.071 cm2) were polished using polishing powder and then washed with acetone and deionized water prior to use. Carbon felt electrodes were not re-used.

**SI-3: Experimental**

**SI-3.1: Cyclic Voltammetry:** Cyclic voltammograms were collected in single chamber cells using a three-electrode set-up at room temperature at a scan rate of 10 mV/s (unless otherwise stated) in 1 M aqueous H3PO4 electrolyte. The solvent (10 mL) was thoroughly degassed with N2 prior to the experiments and kept under inert atmosphere throughout the process. To this was added 1.9 × 10–4 mol of the relevant nitroarene substrate and subsequently, when needed, 1 equivalent of the phosphotungstic acid mediator relative to the nitroarene. For the cyclic voltammograms of the substituted nitroarenes a higher amount of starting material (9.74 × 10–4 mol) was used, with the rest of the conditions to remaining as above. A glassy carbon button electrode was used as the working electrode (area = 0.071 cm2), a graphite rod was used as the counter electrode and an Ag/AgCl reference electrode was used. Measurements were conducted without stirring and with *i*R compensation enabled.

**SI-3.2: Bulk electrolysis set-up:** Bulk electrolysis was performed in both three-electrode and two-electrode configurations in a two-compartment electrochemical cell or H-cell (Figure S1), unless otherwise stated. Cell resistances were measured by the *i*R test function available on the CH or BioLogic potentiostats, using the general method developed by He and Faulkner.S[[1]](#endnote-2) The two compartments of the H-cell were separated by a Nafion N-1110 membrane, with the phosphotungstic acid solution in the working compartment with a carbon felt working electrode and an Ag/AgCl reference electrode. The counter compartment was filled with 1 M aqueous H3PO4 of a comparable pH (~0.5) to that of the phosphotungstic acid to prevent a pH gradient forming. A large area piece of carbon felt was used as the counter electrode for the three-electrode configurations, while a Pt mesh was used for the counter electrode in the two-electrode setup. Solutions were stirred at around 450-500 rpm, keeping the same stirring rate for all experiments and bubbled constantly with nitrogen (unless otherwise stated) to prevent the oxidation of the solution by the air (two-electron reduced phosphotungstic acid is slowly re-oxidized by air).



**Figure S1:** Graphic representation of the two-compartment electrochemical cell (or H-cell) that was used during the bulk electrolysis experiments. The left side of the cell is the working side, where the reaction takes place and the right is the counter side where the counter electrode is placed. The two compartments are separated by the Nafion membrane.

**SI-3.3: Electrocatalytic studies:** Electrocatalytic studies were performed as follows. Unless otherwise stated, 9.74 × 10–4 mol of the relevant nitroarene was added to 30 mL of a 3.3 mM aqueous solution of phosphotungstic acid (i.e. a 10 mol% ratio of phosphotungstic acid relative to the nitroarene). This solution (although typically the nitroarene substrate did not dissolve completely at this stage) was then placed in the working electrode compartment of the H-cell, with a 1.8 × 2 cm carbon felt electrode. For the less soluble nitroarenes (ethyl-2-nitrobenzoate, 2-nitroacetophenone, 1-iodo-2-nitrobenzene and 1-iodo-4-nitrobenzene) half this amount of starting material was used, *i.e.* 4.87 × 10–4 mol, but still with a 10 mol% ratio of phosphotungstic acid relative to the nitroarene. The counter side of the cell was filled with 1 M aqueous H3PO4 electrolyte solution. Typically, bulk electrolysis was then carried out at –0.38 V vs. Ag/AgCl until substrate reduction was complete, as judged by the falling off of the current to background levels (see example in Figure S2).

**Figure S2:** Bulk electrolysis of the nitroarene ethyl-2-nitrobenzoate, where 0.095 g (4.87 × 10–4 moles) of the starting material were used together with 4.86 × 10–5 moles (10 mol%) of the polyoxometalate mediator in 30 mL electrolyte.

After electrolysis for a given time, the (now dark blue) solution was removed from the working electrode compartment of the H-cell. The pH of this solution was then raised above the p*K*a value of the anticipated product using 1 M NaOH in order to deprotonate the R-NH3+ salt and form the neutral R-NH2 state. This in turn allowed the reduced organic product to be extracted into organic solvents for isolation. The pH values in question for the various conversions were: nitrobenzene to aniline, pH = 5.6, ethyl 2-nitrobenzoate to ethyl 2-aminobenzoate, pH = 3.2, 4-nitrophenol to 4-aminophenol, pH = 6.0, 2-nitroacetophenone to 2-aminoacetophenone, pH = 9.0, 1-iodo-2-nitrobenzene to *o*-iodoaniline, pH = 2.6 and 1-iodo-4-nitrobenzene to *p*-iodoaniline pH = 2.34 .

Aniline, *o*-iodoaniline and *p*-iodoaniline were extracted using chloroform, 4-nitrophenol was extracted using dichloromethane and the other aromatic organics were extracted using diethyl ether. In all cases, after extraction, magnesium sulfate was added to the organic phase in order to remove any remaining water. The organic phase was then filtered and concentrated under reduced pressure using a rotary evaporator to give the isolated reduced aniline derivatives.

In the case of the 4-aminophenol, special treatment of the reaction medium was needed. The very polar nature of the compound made its extraction from the aqueous phase very difficult and significantly less efficient than for the other aniline derivatives. For this reason, the aqueous phase was first concentrated in the rotary evaporator until it reached a volume of about 5 mL. The pH was then adjusted using a solution of 5 M NaOH to keep the volume lower than 7-8 mL. The NaOH solution was added very slowly to a round-bottom flask which was kept in ice. After the pH adjustment, an acetone/dry ice bath, with a temperature of –78 ˚C was prepared. The round-bottom flask containing the aqueous solution was put into the acetone/dry ice bath for a few seconds, and just before freezing, the contents of the flask were transferred to a separating funnel and extracted with dichloromethane. This process was repeated 3-4 times, allowing most of the organic product to be extracted from the aqueous phase. The combined organic extracts were then dried over magnesium sulfate as described above.

For the larger scale experiments, a larger H-cell and larger carbon felt electrodes were used (3.2 × 4.5 cm). 1.23 g (10 mmol, 1.025 mL) of nitrobenzene was added to 100 mL of a 10 mM aqueous solution of phosphotungstic acid (i.e. a 10 mol% ratio of phosphotungstic acid relative to the nitrobenzene). The isolated amount of aniline was 766 mg (82%).

For the two-electrode setup the regular H-cell and starting material/mediator quantities were used while the carbon felt counter electrode was replased with a Pt mesh. The applied potential was –2.2 V. The internal resistance of the cell was calculated to be 58-60 Ohm.

**SI-3.4: Ex-cell studies:** For the *ex-cell* studies, a 0.3 M solution of phosphotungstic acid was prepared. This solution was then placed in the working compartment of the H-cell and reduced by two-electrons at –0.4 V *vs.* Ag/AgCl under a nitrogen atmosphere with constant stirring. A large area piece of carbon felt was again used as the counter electrode. Portions of the relevant substrates for reduction were placed into 50 mL round-bottom flasks, each of which was equipped with a magnetic stirrer bar and a rubber septum to seal the flask. The flasks were all flushed with nitrogen to remove any oxygen. Various aliquots of the two-electron reduced phosphotungstic acid were then injected into these flasks, depending on whether the aim of the experiment was to obtain a series of ratios of mediator to substrate, or simply to ensure that excess two-electron reduced mediator was present. For example, 9.7 × 10–4 mol of azoxybenzene or azobenzene were placed in round-bottom flasks into which 35 mL of 0.22 M two-electron reduced phosphotungstic acid were added (providing an excess of electrons at the more cathodic position of the second redox wave of the mediator). Each flask was then stirred overnight (12-18 h) at room temperature and under an N2 atmosphere in order for the reaction to complete. After this time, the pH of the reaction mixtures was adjusted above the p*K*a of the expected aniline product and the reaction mixture was then extracted into organic solvent as per the methods described above for the electrocatalytic studies.

**SI-3.5: Aerial re-oxidation of the reduced mediator:** To gauge the rate of spontaneous aerial re-oxidation of the reduced mediator, 0.280 g of H3[PW12O40] were dissolved in 35 mL of 1 M aqueous H3PO4 and added to the working side of the H-cell, which was equipped with a 1 × 1 cm carbon felt working electrode and a Ag/AgCl reference electrode. Other details of the cell were as described in Section SI-3.2. Then, a potential of –0.4 V *vs.* Ag/AgCl was applied across this cell under a nitrogen atmosphere with constant stirring in order to fully reduce the mediator by two electrons. Once fully reduced, the nitrogen purge line was removed from the H-cell, and the two-electron reduced mediator solution was allowed to stir at room temperature open to air. After a defined period of time, the purge line was re-inserted and the solution was then electrochemically re-oxidised at +0.2 V *vs.* Ag/AgCl until completely re-oxidised. Through varying the length of time that the solution was allowed to stir open to air before electrochemical re-oxidation, a curve such as that shown in Figure S3 was obtained, whereby a charge state of 100% corresponds to a fully two-electron reduced mediator solution, 50% corresponds to a a fully one-electron reduced mediator solution and 0% corresponds to a fully oxidised mediator solution. Hence a “half-life” for aerial re-oxidation of the reduced mediator of just over 30 minutes can be estimated.



**Figure S3:** Aerial re-oxidation of the reduced mediator over time. The red line is provided as a guide to the eye.

**SI-3.6: 1H NMR determination of conversions:** After extraction into organic solvent and concentration under reduced pressure, the conversion of the starting material was determined *via* the integration of the relevant 1H NMR peaks. After the 1H NMR peaks in any given sprectrum had been identified and assigned, peaks corresponding to the same number of protons in both the starting material and the various products were compared, allowing the percent of starting material converted to each product (or not converted, and hence still present as starting material) to be determined.

**SI-4: Cyclic Voltammograms**

**Figure S4:** Cyclic voltammogram of nitrosobenzene (the first two-electron reduced intermediate of the reduction of nitrobenzene), collected under the general conditions described above. The scan was started at +0.8 V and was then swept cathodically (reducing). Scan rate: 100 mV/s.

**Figure S5:** Cyclic voltammogram of *N*-phenylhydroxylamine (the product of four-electron reduction of nitrobenzene), collected under the general conditions described above. The scan was started at +0.8 V and was then swept cathodically (reducing). Scan rate: 100 mV/s.

**Figure S6:** Cyclic voltammogram of the starting material nitrobenzene, collected under the general conditions described above. The scan was started at 0 V, sweeping first to +0.8 V and then sweeping cathodically. Scan rate: 100 mV/s.

**Figure S7:** Cyclic voltammogram of the starting material 4-nitrophenol, collected under the general conditions described above. The scan was started at 0 V, sweeping first to −0.8 V and then sweeping anodically. Scan rate: 100 mV/s.

**Figure S8:** Cyclic voltammogram of 2-nitroacetophenone, collected under the general conditions described above. The scan was started at 0 V, sweeping first to −0.8 V and then sweeping anodically. Scan rate: 100 mV/s.

**Figure S9:** Cyclic voltammogram of ethyl-2-nitrobenzoate, collected under the general conditions described above. The scan was started at 0 V, sweeping first to −0.8 V and then sweeping anodically. Scan rate: 100 mV/s.

**Figure S10:** Cyclic voltammogram of 1-iodo-2-nitrobenzene, collected under the general conditions described above. The scan was started at 0 V, sweeping first to −0.8 V and then sweeping anodically. Scan rate: 100 mV/s.

**Figure S11:** Cyclic voltammogram of 1-iodo-4-nitrobenzene, collected under the general conditions described above. The scan was started at 0 V, sweeping first to −0.8 V and then sweeping anodically. Scan rate: 100 mV/s.

**SI-5: Ex-cell reactions between phenylhydroxylamine and 1-electron reduced phosphotungstic acid**

One-electron reduced phosphotungstic acid was prepared according to the method described in Section SI-3.4, with the exception that the potential on the working electrode was restricted to –0.16 V *vs.* Ag/AgCl in order to prevent reduction by more than one electron per mediator molecule. This one-electron reduced phosphotungstic acid was then added to aliquots of phenylhydroxylamine in a purely non-electrochemical reaction step as described in Section SI-3.4. After this time, the pH of the reaction mixture was adjusted to 5.6 before extraction into organic solvent and subsequent isolation according to the general methods in Section SI-3.3. The conversion to aniline was then quantified and plotted against the equivalents of reduced phosphotungstic acid as shown below.



**Figure S12:** Ex-cell reduction of phenylhydroxylamine with one-electron reduced phosphotungstic acid (“[PW12O40]4–”).

**SI-6: NMR characterisation of reaction products**

**Figure S13:** Reduction of nitrobenzene.1H NMR spectra of the nitrobenzene starting material (A), a sample of pure aniline (B), the spectrum of the electrocatalytic reaction medium after extraction and concentration (C) and the spectrum of the extracted and concentrated reaction medium from a direct (i.e. non-mediated) electrochemical reduction of nitrobenzene (D). All spectra were obtained in CDCl3.

**Figure S14:** 1H NMR spectrum of the obtained product, aniline, from the mediated process (spectrum C from Figure S13) including the integrations. The spectrum was obtained in CDCl3. The signal at δ = 7.26 is due to residual CHCl3.

**Figure S15:** 13C NMR spectrum of the obtained product, aniline, from the electrocatalytic reaction medium after extraction and concentration. The spectrum was obtained in CDCl3. 13C NMR (100 MHz, CDCl3) δ = 146.5, 129.4, 118.7, 115.3. The signal at δ = 77.2 is due to CDCl3. Data for this compound were in agreement with those reported for aniline in [S2].

**Figure S16:** Reduction of 2-nitroacetophenone. 1H NMR spectra of the 2-nitroacetophenone starting material (A), a sample of pure 2-aminoacetophenone (B), the spectrum of the electrocatalytic reaction medium after extraction and concentration (C) and the spectrum of the extracted and concentrated reaction medium from a direct (i.e. non-mediated) electrochemical reduction of 2-nitroacetophenone (D). All spectra were obtained in d4-methanol.

The main product of the direct electrochemical reduction (spectrum D) is the hydroxylamine derivative (i.e. incomplete reduction has occurred). As this compound (pictured below) has hitherto not been reported in any detail, we give here the following characterisation:

Mass spectrum: ESI-QTOF (acetonitrile/water 70/30% with 0.1% formic acid): *m/z* = 152.0712 [M+H]+ (calcd. for C8H10NO2; 152.07115).

1H NMR (400 MHz, MeOD) δ = 7.58 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.02 – 6.90 (m, 1H), 2.80 (s, 3H).

13C NMR (100 MHz, MeOD), δ = 167.9, 158.1, 132.7, 124.0, 121.3, 116.8, 114.9, 11.6.

**Figure S17:** 1H NMR spectrum of the obtained product, 2-aminoacetophenone, from the electrocatalytic reaction medium after extraction and concentration (spectrum C from Figure S16) including the integrations. The spectrum was obtained in d4-methanol. The signals at δ = 3.31 and 4.78 are due to residual MeOH.

**Figure S18:** 13C NMR spectrum of the obtained product, 2-aminoacetophenone, from the mediated process. The spectrum was obtained in d4-methanol. 13C NMR (100 MHz, MeOD) δ = 202.6, 152.6, 135.6, 133.2, 118.8, 118.2, 116.2, 27.8. The signal at δ = 49.2 is due to MeOD. Data for this compound are in agreement with those reported for 2-aminoacetophenone in [S3].

**Figure S19:** Reduction of ethyl-2-nitrobenzoate. 1H NMR spectra of the ethyl-2-nitrobenzoate starting material (A), a sample of pure ethyl-2-aminobenzoate (B), the spectrum of the electrocatalytic reaction medium after extraction and concentration (C) and the spectrum of the extracted and concentrated reaction medium from a direct (i.e. non-mediated) electrochemical reduction of ethyl-2-nitrobenzoate (D). All spectra were obtained in d4-methanol.

**Figure S20:** 1H NMR spectrum of the obtained product, ethy-2-aminobenzoate, from the electrocatalytic reaction medium after extraction and concentration (spectrum C from Figure S19) including the integrations. The spectrum was obtained in d4-methanol. The signals at δ = 3.31 and 4.78 are due to residual MeOH. The broad signal at around 6.2 ppm is attributed to the NH2 protons.

**Figure S21:** 13C NMR spectrum of the obtained product, ethyl-2-aminobenzoate, from the mediated process. The spectrum was obtained in d4-methanol. 13C NMR (100 MHz, MeOD) δ = 169.6, 152.7, 135.0, 132.0, 117.8, 116.6, 111.5, 61.2, 14.7. The signal at δ = 49.2 is due to MeOD. Data for this compound were in agreement with those reported for ethyl 2-aminobenzoate in [S4].

**Figure S22:** Reduction of *p-*nitrophenol.1H NMR spectra of the *p-*nitrophenol starting material (A), a sample of pure *p-*aminophenol (B), the spectrum of the electrocatalytic reaction medium after extraction and concentration (C) and the spectrum of the extracted and concentrated reaction medium from a direct (i.e. non-mediated) electrochemical reduction of *p-*nitrophenol (D). All spectra were obtained in d6-DMSO.

**Figure S23:** 1H NMR spectrum of the obtained product, *p*-aminophenol, from the electrocatalytic reaction medium after extraction and concentration (spectrum C from Figure S22) including the integrations. The spectrum was obtained in d6-DMSO.

**Figure S24:** 13C NMR spectrum of the obtained product, *p*-aminophenol, from the mediated process. The spectrum was obtained in d6-DMSO. 13C NMR (100 MHz, DMSO) δ = 148.2, 140.7, 115.6, 115.3. Data for this compound were in agreement with those reported for 4-aminophenol in [S5].

**Figure S25:** Reduction of 1-iodo-4-nitrobenzene. 1H NMR spectra of the 1-iodo-4-nitrobenzene starting material (A), a sample of pure 1-iodo-4-aminobenzene (B), the spectrum of the electrocatalytic reaction medium after extraction and concentration (C) and the spectrum of the extracted and concentrated reaction medium from a direct (i.e. non-mediated) electrochemical reduction of 1-iodo-4-nitrobenzene (D). All spectra were obtained in CDCl3.

**Figure S26:** 1H NMR spectrum of the obtained product, 1-iodo-4-aminobenzene, from the electrocatalytic reaction medium after extraction and concentration (spectrum C from Figure S25) including the integrations. The spectrum was obtained in CDCl3. The signal at 7.9 ppm is due to remaining starting material (see Figure S25). The signal at δ = 7.26 is due to residual CHCl3.

**Figure S27:** 13C NMR spectrum of the obtained product, 1-iodo-4-aminobenzene, from the mediated process. The spectrum was obtained in CDCl3. 13C NMR (100 MHz, CDCl3) δ = 146.2, 138.0, 117.4, 79.5. The signal at δ = 77.2 is due to CDCl3. Data for this compound were in agreement with those reported for 4-iodoaniline in [S6].

**Figure S28:** Reduction of 1-iodo-2-nitrobenzene. 1H NMR spectra of the 1-iodo-2-nitrobenzene starting material (A), a sample of pure 1-iodo-2-aminobenzene (B), the spectrum of the electrocatalytic reaction medium after extraction and concentration (C) and the spectrum of the extracted and concentrated reaction medium from a direct (i.e. non-mediated) electrochemical reduction of 1-iodo-2-nitrobenzene (D). All spectra were obtained in CDCl3.

**Figure S29:** 1H NMR spectrum of the obtained product, 1-iodo-2-aminobenzene, from the electrocatalytic reaction medium after extraction and concentration (spectrum C from Figure S28) including the integrations. The spectrum was obtained in CDCl3. The signal at δ = 7.26 is due to residual CHCl3.

**Figure S30:** 13C NMR spectrum of the obtained product, 1-iodo-2-aminobenzene, from the mediated process. The spectrum was obtained in CDCl3. 13C NMR (100 MHz, CDCl3) δ = 146.9, 139.1, 129.5, 120.1, 114.9, 84.3. The signal at δ = 77.2 is due to CDCl3. Data for this compound were in agreement with those reported for 2-iodoaniline in [S7].

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