Physical Chemistry Chemical Physics

ARTICLE

Supplementary Information

AQDS Material Preparation

2,7-anthraquinone disulfonic acid (AQDS)) disodium salt (>97.0% HPLC) was obtained from TCI chemicals. This sodium salt of AQDS was first dissolved in deionized water and then flushed through a column containing Amberlyst® 15(H) ion exchange resin (Alfa Aesar) activated with hydrochloric acid to replace the sodium ions with protons. Details of the procedure can be found in Reference 6. This ion-exchanged AQDS is used for all of the experiments discussed in the main text.

Synthesis of the H_2AQDS disodium salt

To further validate the construction of the UV-Vis calibration curve, AQDS was chemically reduced to $AQDSH_2$. Pd/C (10% dispersion, 1.28 g, 0.1 equivalent) was added to a stirring solution of AQDS disodium salt (5.00 g, 12.1 mmol) in deionized water (10 ml) contained in schlenk tube. The schlenk tube was sealed and purged with a flow of hydrogen gas for 30 seconds, and then filled with a balloon of hydrogen gas. The reaction mixture was placed in an oil bath at 60 °C. After 18 hours, the reaction mixture was filtered under nitrogen using standard schlenk techniques. The filtrate was evacuated to dryness to afford the reduced form $AQDSH_2$ disodium salt as a brown solid (4.95 g, 11.9 mmol) in 99% yield. Full NMR spectra are shown in Figure SI2.

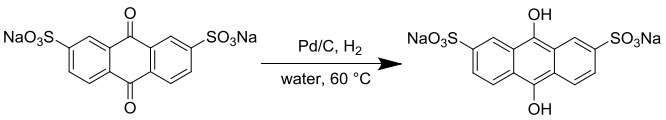

Figure SI1: Chemical reduction of AQDS disodium salt

^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.61 (s, 2H, 2 x ArC**H**), 8.23 (d, 2H, J = 8.5 Hz, 2 x ArC**H**), 7.56 (d, 2H, J = 8.5 Hz, 2 x ArC**H**).

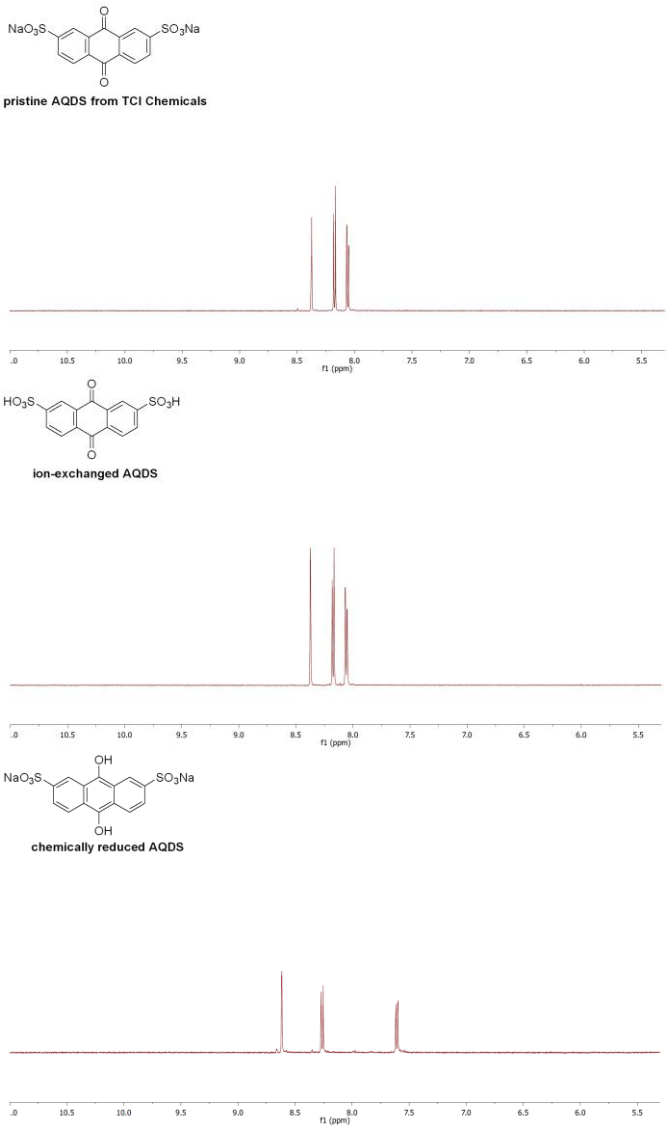

Figure SI2: NMR of (a) AQDS disodium salt, (b) ion-exchanged AQDS, and (c) H_2AQDS disodium salt.

UV-Vis Spectroscopy

UV-Vis spectroscopy of the chemically reduced $AQDSH_2$ disodium salt corresponds to the electrochemically reduced, ion exchanged $AQDSH_2$ described in the text as shown in Figure SI3. The sulfonate counter ion is expected to be fully dissociated and non-absorbing in the UV-Vis region. Because the chemically and electrochemically reduced AQDS have identical UV-Vis spectra and the chemically reduced AQDS NMR shows a single-species, we are confident that the electrochemically reduced AQDS calibration represents complete conversion to H_2AQDS (100% SOC). Full UV-Vis spectra of 1.25 mM and 209 mM AQDS are shown in Figure SI4 and Figure SI5 respectively.

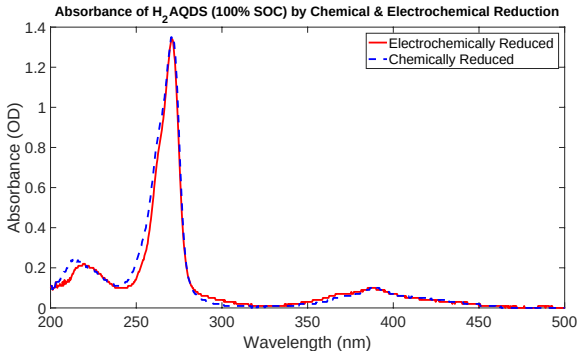

Figure SI3: Absorbance of H_2AQDS chemically reduced (sodium salt form) and electrochemically reduced (protonated form) to show the same, full conversion to the reduced form.

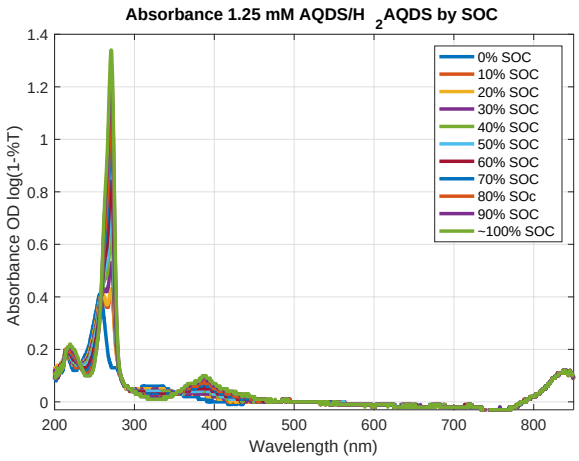

Figure SI4: Full absorbance spectrum of 1.25 M AQDS at intermediate SOCs. The absorption tail above 800 nm is expected to be a calibration artefact.

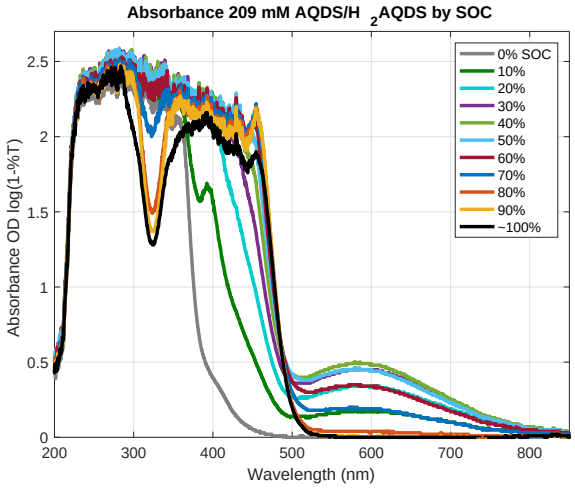

Figure SI5: Full absorbance spectrum of 209 M AQDS at intermediate SOCs. The quinhydrone dimer absorbs uniquely at wavelengths greater than 550 nm, whereas the quinone absorbs strongly in the UV, obscuring the signal in the noise.

Chronoamperometry

Full electrochemical reduction of AQDS to H_2AQDS was validated by chronoamperometry with over 98% of the theoretical charge accessible for a 1 M total quinone solution.

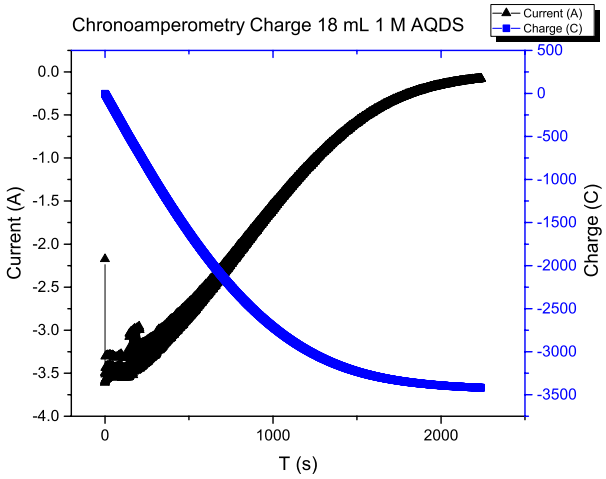

Figure SI6: The chronoamperometry curve when we reduced 18 mL of a 1 M AQDS electrolyte at -0.1 V vs. Pd-H in an AQDS-Bromide cell. 3418 C of charge were used to reduce the AQDS out of a theoretical 3473 C, representing over 98% conversion to $AQDSH_2$ (i.e. 98% SOC).

High-concentration quinone activity

In a non-flow cell as illustrated in Figure SI7, quinone activity as a function of concentration is measured via the open circuit potential (OCP) between two graphite rods placed respectively in a reference solution (10 mM Q + 10 mM HQ in 1 M H_2SO_4) and a working solution (X mM Q + 10 mM HQ in 1 M H_2SO_4) separated by

a Nafion 212 membrane. The starting quinone concentration (e.g. X = 1 M) is diluted by removing an aliquot of the working solution and replacing it with an equal volume of 10 mM HQ in 1M H_2SO_4. Relative activity coefficients correspond to the change in OCP based on deviations from ideal solution behavior.

Figure SI7(b) shows the measured OCP of the X mM Q + 10 mM HQ working electrolyte against 10 mM Q + 10 mM HQ reference electrolyte plotted on a log-linear scale where X begins at 1 M (100 [AQDS]/[H_2AQDS]) and is sequentially diluted to 100 mM (10 [AQDS]/[H_2AQDS]). The slope between 10 and 70 [AQDS]/[H_2AQDS] correlates to the expected potential based on the Nernst equation with the unbound monomer species concentrations (Equation 11) of RT/nF; the slight deviation is attributed to a small change in QHQ concentration based on the equilibrium (Equation 5) and the temporal effect of water crossover changing the liquid volume. In contrast, it is evident that this ideal solution behavior, even corrected for the unbound monomer species concentrations, is not maintained above 70 [AQDS]/[H_2AQDS], corresponding to [AQDS] > 700 mM. As is demonstrated in Figure SI7(b) the OCP plateau above 700 mM AQDS is indicative of a decrease in the activity coefficient. An example of how this could affect the negative half-cell voltage, E_{neg}, can be found as the green line in Figure 6(b) in the main text. The precise origins and quantification of this concentrated solution behavior will be discussed in future work.

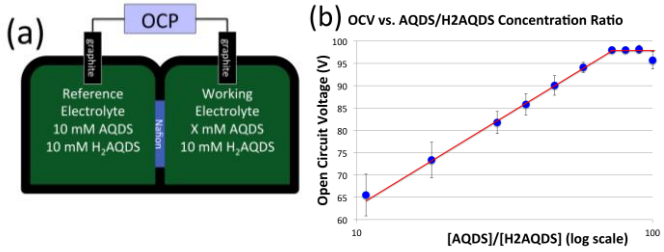

Figure SI7:(a) experimental setup for measuring quinone activity via the open circuit potential. 'X mM' indicates a starting concentration that is subsequently diluted to measure the OCP as a function of the ratio between [AQDS] and [H_2QDS] as shown in (b). It is evident that at high Q concentrations, the voltage increase ceases indicating a change in quinone activity.

Addendum to DFT calculations

There are important cost and accuracy tradeoffs in addressing the ionization of sulfonic groups in quinone-hydroquinone interaction. While it would seem more accurate to model sulfonic groups as ions, this is not the case in practicality: the accumulation of explicit charges is the system results in higher inaccuracies than modelling the protonated sites.

Whereas some or all of the sulfonic groups are ionized in solution, it is unclear how many, as their pKa is likely affected by the quinhydrone environment. In any case, ionized species do not exist as isolated ions, but as electrostatically bound ion pairs, particularly at the high ionic strengths at which the experiments were conducted. In this work, molecular configurations with ionized sulfonates balanced with hydronium ions were observed to converge, after long trajectories, to undissociated sulfonic groups.

In the anhydrous quinhydrone models we observe direct hydrogen bonding among sulfonic groups in quinone and hydroquinone, which are unphysical but they are not a consequence of the ionization degree. In the simulations where we added explicit water molecules, no interaction was observed between sulfonic groups and the opposite monomer in the quinhydrone dimer, only with the surrounding water shell. As a matter of fact, modelling ionized groups only results in increased spurious hydrogen bonding between hydroquinone and sulfonate, which the fully-solvated models confirm to be unrealistic.

The distributions of pi-stacking distances and relative angles within the ensemble of hydrated and non-hydrated hydroquinones are very similar, and less than the variance within each of the classes. The figure below shows the lack of direct hydrogen bonding within any groups in quinone or hydroquinone in the hydrated quinhydrone pair, and the large degree of hydrogen binding in the solvated sulfonic groups by explicit solvent molecules.