Supporting information

1. Relationship between $E_2^{0/}$, $E_5^{0/}$ and $E_1^{0/}$, $E_3^{0/}$, $E_4^{0/}$, $E_6^{0/}$, $E_7^{0/}$, $E_8^{0/}$.

The relationship between the two formal potentials in any 1e1H subsquare is obtained by applying the Nernst equation. For example consider the four-membered scheme MNPR.

$$M + e \rightleftharpoons N(E_3^{0/})$$
$$O + e \rightleftharpoons P(E_2^{0/})$$

Applying the Nernst equation to each redox couple provides,

$$E = E_3^{0/} + \frac{RT}{F}\ln\frac{\Gamma_M}{\Gamma_N}$$
$$E = E_2^{0/} + \frac{RT}{F}\ln\frac{\Gamma_P}{\Gamma_R}$$

and then combining yields

$$E_3^{0/} = E_2^{0/} + \frac{RT}{F}\ln\frac{K_4}{K_3}$$

Similarly:

$$E_6^{0/} = E_5^{0/} + \frac{RT}{F}\ln\frac{K_6}{K_4}$$

$$E_1^{0/} = E_2^{0/} + \frac{RT}{F}\ln\frac{K_1}{K_2}$$

$$E_4^{0/} = E_5^{0/} + \frac{RT}{F}\ln\frac{K_2}{K_5}$$

$$E_7^{0/} = E_2^{0/} + \frac{RT}{F}\ln\frac{K_1 K_7}{K_2 K_8}$$

$$E_8^{0/} = E_5^{0/} + \frac{RT}{F}\ln\frac{K_2 K_8}{K_5 K_9}$$

2. Determination of pathway

For the 2e3H case, there are two 1e3H columns, and each column gives four possible pathways. The weight of each pathway determines the pathway for the whole process. For example, consider the first column (MNOPQRWX) with the assumptions that 1) *O* is the starting species and 2) the electron transfer step is the rate determining step.

$$Rate_{M,N} = Rate_{O,M,N}$$

$$k_{s3}\exp\left(-\alpha_3 f\eta_3\right)\Gamma_M = k_{OMN}\Gamma_O$$

Hence: $$k_{OMN} = \frac{k_{s3}\exp\left(-\alpha_3 f\eta_3\right)\Gamma_M}{\Gamma_O} = \frac{K_3 k_{s3}\exp\left(-\alpha_3 f\eta_3\right)}{[H^+]}$$

A similar procedure can be used to derive k_{OP}, k_{OQR}, k_{OQWX}, k_{PT}, k_{PNS}, k_{PRV} and k_{PRXY}. The expressions for the paths are listed below.

$$path1 = \frac{k_{OQR}}{k_{OMN}+k_{OQR}+k_{OQWX}+k_{OP}} =$$

$$\frac{\dfrac{k_{s1}[H^+]}{K_1}\exp\left(-\alpha_1 f\eta_1\right)}{\dfrac{k_{s3}K_3\exp\left(-\alpha_3 f\eta_3\right)}{[H^+]}+\dfrac{k_{s1}[H^+]}{K_1}\exp\left(-\alpha_1 f\eta_1\right)+\dfrac{k_{s7}[H^+]^2}{K_1K_7}\exp\left(-\alpha_7 f\eta_7\right)+k_{s2}\exp\left(-\alpha_2 f\eta_2\right)}$$

$$path2 = \frac{k_{OP}}{k_{OMN}+k_{OQR}+k_{OQWX}+k_{OP}} =$$

$$\frac{k_{s2}\exp\left(-\alpha_2 f\eta_2\right)}{\dfrac{k_{s3}K_3\exp\left(-\alpha_3 f\eta_3\right)}{[H^+]}+\dfrac{k_{s1}[H^+]}{K_1}\exp\left(-\alpha_1 f\eta_1\right)+\dfrac{k_{s7}[H^+]^2}{K_1K_7}\exp\left(-\alpha_7 f\eta_7\right)+k_{s2}\exp\left(-\alpha_2 f\eta_2\right)}$$

$$path3 = \frac{k_{OMN}}{k_{OMN}+k_{OQR}+k_{OQWX}+k_{OP}} =$$

$$\frac{\dfrac{k_{s3}K_3\exp\left(-\alpha_3 f\eta_3\right)}{[H^+]}}{\dfrac{k_{s3}K_3\exp\left(-\alpha_3 f\eta_3\right)}{[H^+]}+\dfrac{k_{s1}[H^+]}{K_1}\exp\left(-\alpha_1 f\eta_1\right)+\dfrac{k_{s7}[H^+]^2}{K_1K_7}\exp\left(-\alpha_7 f\eta_7\right)+k_{s2}\exp\left(-\alpha_2 f\eta_2\right)}$$

$$path7 = \frac{k_{OQWX}}{k_{OMN} + k_{OQR} + k_{OQWX} + k_{OP}} =$$

$$\frac{\frac{k_{s7}[H^+]^2}{K_1 K_7}\exp\left(-\alpha_7 f \eta_7\right)}{\frac{k_{s3}K_3\exp\left(-\alpha_3 f \eta_3\right)}{[H^+]} + \frac{k_{s1}[H^+]}{K_1}\exp\left(-\alpha_1 f \eta_1\right) + \frac{k_{s7}[H^+]^2}{K_1 K_7}\exp\left(-\alpha_7 f \eta_7\right) + k_{s2}\exp\left(-\alpha_2 f \eta_2\right)}$$

$$path4 = \frac{k_{PRV}}{k_{PNS} + k_{PRV} + k_{PRXY} + k_{PT}} =$$

$$\frac{\frac{k_{s4}[H^+]}{K_5}\exp\left(-\alpha_4 f \eta_4\right)}{\frac{k_{s6}K_6\exp\left(-\alpha_6 f \eta_6\right)}{[H^+]} + \frac{k_{s4}[H^+]}{K_5}\exp\left(-\alpha_4 f \eta_4\right) + \frac{k_{s8}[H^+]^2}{K_5 K_9}\exp\left(-\alpha_8 f \eta_8\right) + k_{s5}\exp\left(-\alpha_5 f \eta_5\right)}$$

$$path5 = \frac{k_{PT}}{k_{PNS} + k_{PRV} + k_{PRXY} + k_{PT}} =$$

$$\frac{k_{s5}\exp\left(-\alpha_5 f \eta_5\right)}{\frac{k_{s6}K_6\exp\left(-\alpha_6 f \eta_6\right)}{[H^+]} + \frac{k_{s4}[H^+]}{K_5}\exp\left(-\alpha_4 f \eta_4\right) + \frac{k_{s8}[H^+]^2}{K_5 K_9}\exp\left(-\alpha_8 f \eta_8\right) + k_{s5}\exp\left(-\alpha_5 f \eta_5\right)}$$

$$path6 = \frac{k_{PNS}}{k_{PNS} + k_{PRV} + k_{PRXY} + k_{PT}} =$$

$$\frac{\frac{k_{s6}K_6\exp\left(-\alpha_6 f \eta_6\right)}{[H^+]}}{\frac{k_{s6}K_6\exp\left(-\alpha_6 f \eta_6\right)}{[H^+]} + \frac{k_{s4}[H^+]}{K_5}\exp\left(-\alpha_4 f \eta_4\right) + \frac{k_{s8}[H^+]^2}{K_5 K_9}\exp\left(-\alpha_8 f \eta_8\right) + k_{s5}\exp\left(-\alpha_5 f \eta_5\right)}$$

$$path8 = \frac{k_{PRXY}}{k_{PNS} + k_{PRV} + k_{PRXY} + k_{PT}} =$$

$$\frac{\frac{k_{s8}[H^+]^2}{K_5 K_9}\exp\left(-\alpha_8 f \eta_8\right)}{\frac{k_{s6}K_6\exp\left(-\alpha_6 f \eta_6\right)}{[H^+]} + \frac{k_{s4}[H^+]}{K_5}\exp\left(-\alpha_4 f \eta_4\right) + \frac{k_{s8}[H^+]^2}{K_5 K_9}\exp\left(-\alpha_8 f \eta_8\right) + k_{s5}\exp\left(-\alpha_5 f \eta_5\right)}$$

3. Cyclic Voltammograms as a Function of Scan Rate.

Representative CVs for the aminobenzoquinone monolayer in pH 5.6 PBS (+0.1M $HClO_4$) are shown in Figure S-1. The CVs have been corrected for the capacitive charging background. Increasing peak currents correspond to 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s, 200 mV/s and 500 mV/s.

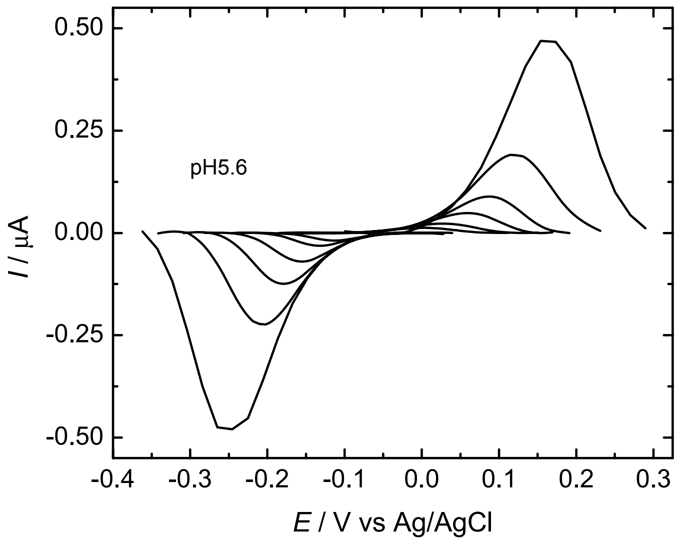

Figure S-1.

4. Chemical Structure Assignment.

Based on our fitting results, the identities of the 12 members of the 2e3H scheme for the aminobenzoquinone system are proposed as follows:

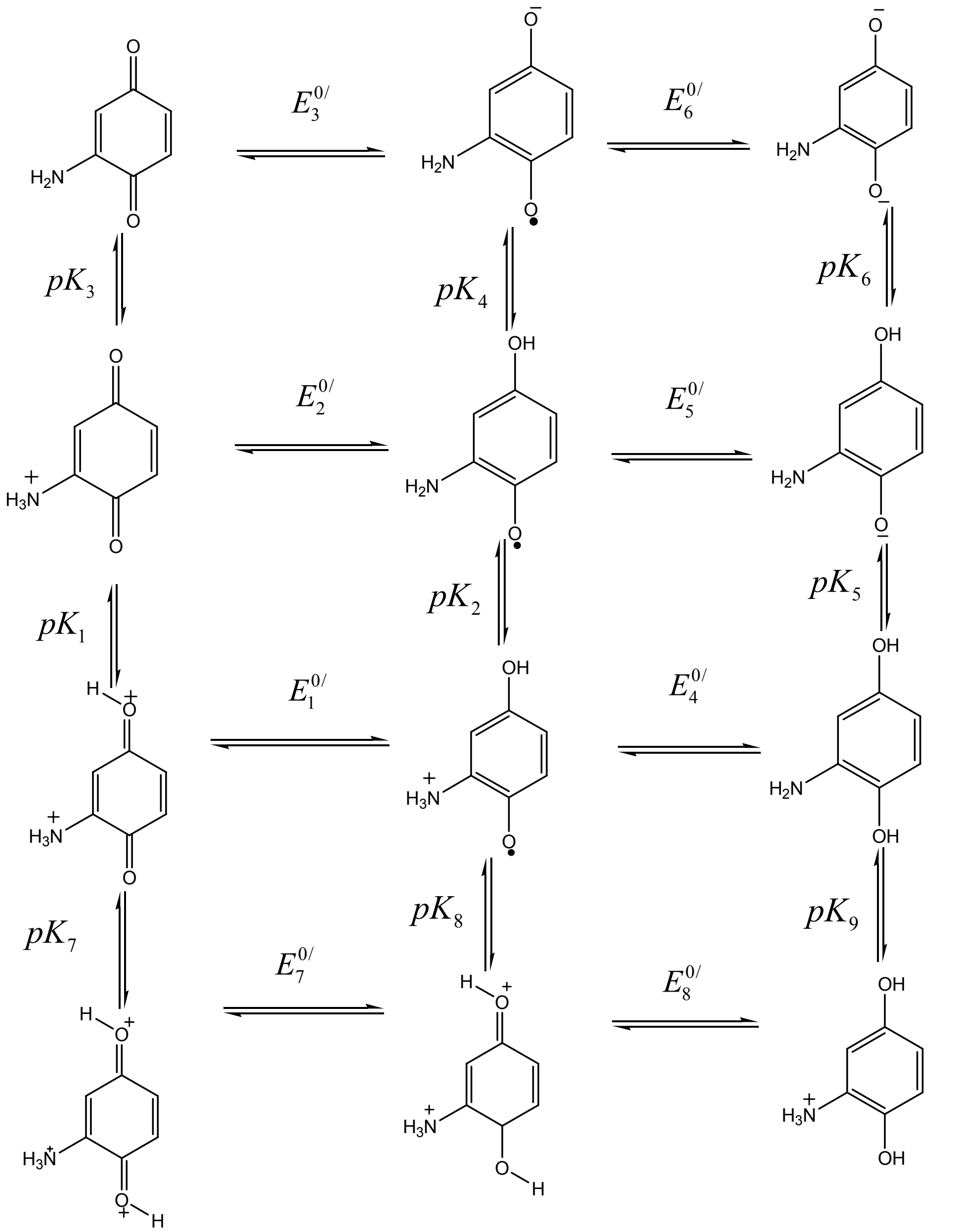

Figure S-2