Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Supporting Information- 'Surface modification imparts selectivity, facilitating redox catalytic studies: quinone mediated oxygen reduction'

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# SI: Section 1

The voltammetric response of the thiol modified gold electrode was recorded in a fully degassed aqueous solution. As can be seen a chemically irreversible surface bound reductive peak is recorded. This voltammetric signal corresponds to the reductive stripping of the thiol from the gold electrode surface. Where the reduction occurs at more negative potentials for the longer chain lengths.[1] For the experimental case where oxygen is present within the solution (as depicted in the main body of the text) the observed voltammetric response corresponds not to the reduction of the oxygen species through the organic layer but alternatively corresponds to the reductive stripping of the modifying layer followed by the direct oxygen reduction at the now bare electrode surface.

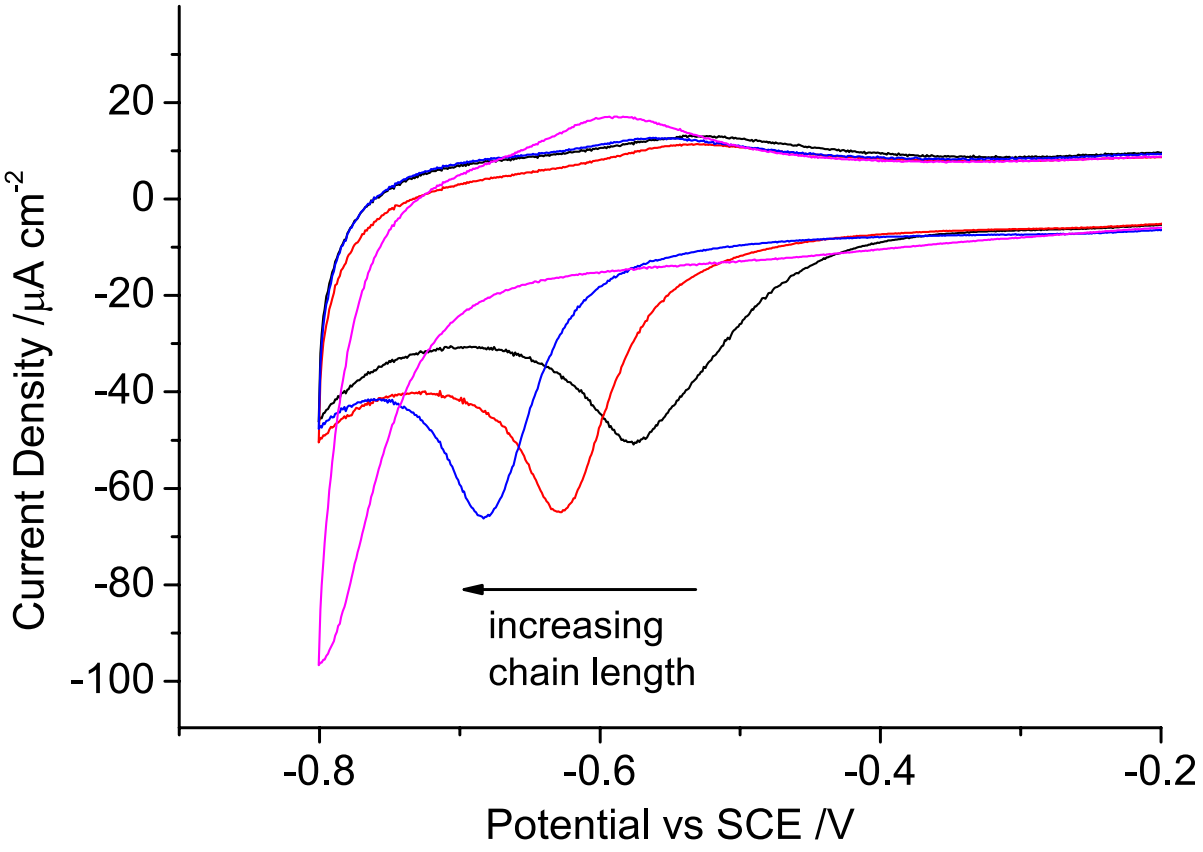


Figure 1: The effect of the alkyl chain length upon the potential of the reductive cleavage of the gold/thiol bond. Voltammetric scan ran at $100 mVs^{-1}$ in pH 6.8 buffer, 1 minute modification of the polycrystalline gold surface with various thiols: black, 1-mercapto-ethanol; red, 3-mercapto-1-propanol; blue, 4-mercapto-1-butanol and pink, 6-mercapto-1-hexanol.

# SI: Section 2

The voltammetric response of AQMS was recorded both at a bare and MCH modified electrode. At the bare electrode surface the voltammetric response is a near ideal reversible response. Conversely for at the modified electrode the electron transfer has been significantly slowed as evidenced by the increase in the measured peak-to-peak separation. For the modified electrode the standard rate of electron transfer ($k^0$) for the AQMS has, on the basis of the peak-to-peak separation been estimated as being approximately $3\times10^{-4}$ cm $s^{-1}$.

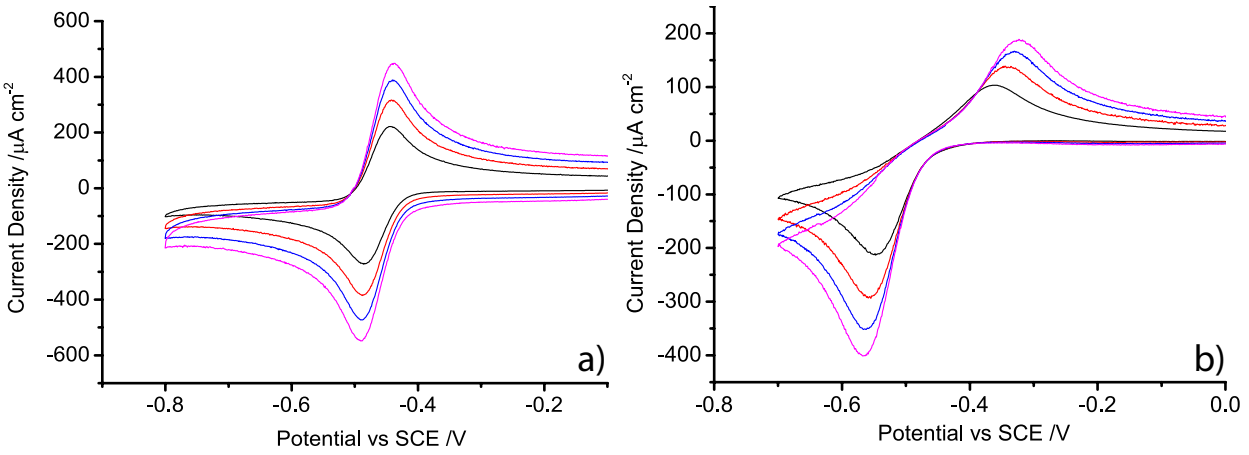


Figure 2: The redox response of 1mM anthraquinone-mono-sulphonate in a pH6.8 buffered de-gassed aqueous solution at variable scan rates (100-400mV$s^{-1}$): a) the response at a bare gold electrode; b) the response at a 6-mercapto-1-hexanol modified electrode.

# SI: Section3

The Matsuda-Ayabe parameter (Λ) for a linear diffusion regime is given as follows;

$$\Lambda = \sqrt{\frac{k^0 RT}{\nu D}} \tag{1}$$

where $k^0$ is the rate of electron transfer (cm s$^-$1), R is the gas constant, T is the temperature (K), $\nu$ is the scane rate (Vs$^{-1}$) and D is the diffusion coefficient (cm$^2$ s$^{-1}$ ). Figure 3 depicts the variation in the forward peak potential for a one electron trasnfer as a function of the Matsuda-Ayabe parameter. This clearly highlights how for a wide range of values the voltammetric system is 'insensitive' to changes in the rate of electron transfer.

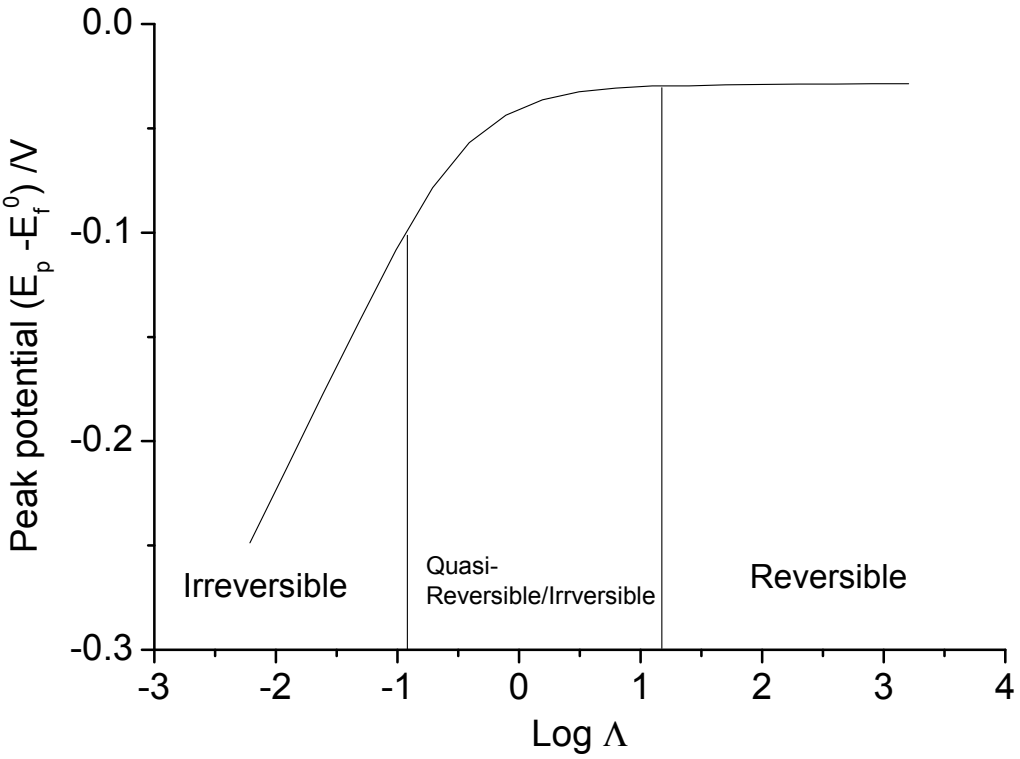


Figure 3: The theoretical variation of the voltammetric forward peak current of a solution phase redox species as a function of the Matsuda-Ayabe parameter

# SI: Section4

The reduction of both 1,4-dihydroxy- (quinizarin) and 1,8-dihydroxy anthraquinone was studied at a MCH modified macro gold electrode. Due to the necessarily low concentration of electroactive species utilised accurate determination of the peak height is subject to a reasonably significant error. During analysis two baselines maybe considered, first, if the response is anticipated to be surface bound then the exponential baseline as depicted in Figure 4 (red line) would be appropriate, this value for the peak height represents the lower limit. Alternatively, if a diffusional response is anticipated then a linear baseline, as depicted in Figure 4 (green line), is more valid. This linear baseline represents the upper limit for the peak current.

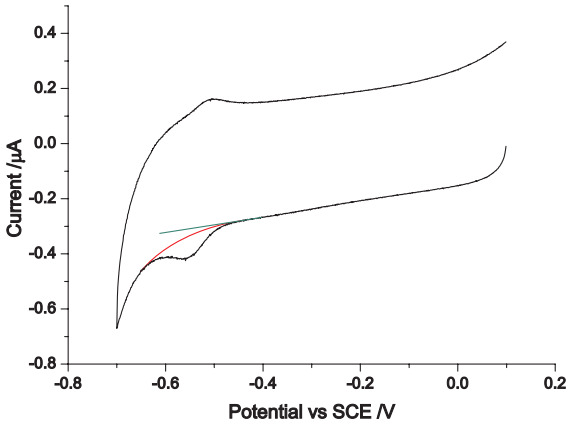


Figure 4: A sample voltammogram showing the reduction of 1,8 dihydroxy-anthraquion at $100 mVs^{-1}$: two possible baselines are shown for calculation of the peak current, green: linear and red: exponential.

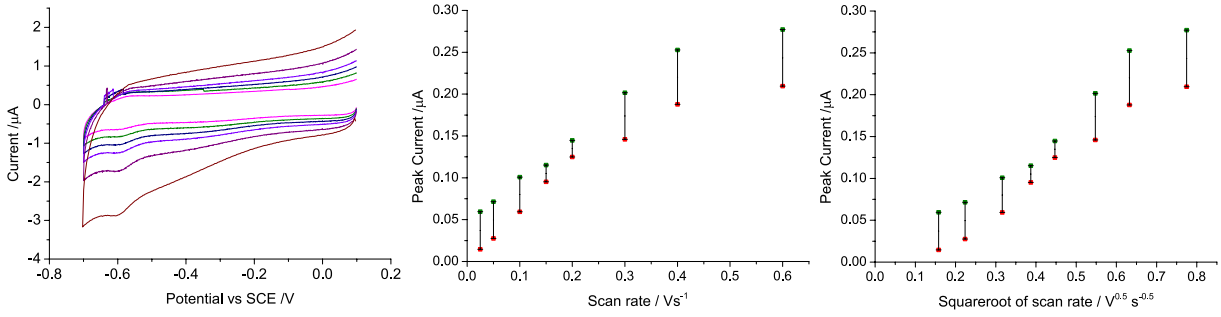


Figure 5: Voltammetry for the reduction of 1,4-dihyrdoxy-anthraquinone and the associated plots of peak current (as measured using a linear [green points] and exponential [red points] baseline) against scan rate and the square-root of scan rate.

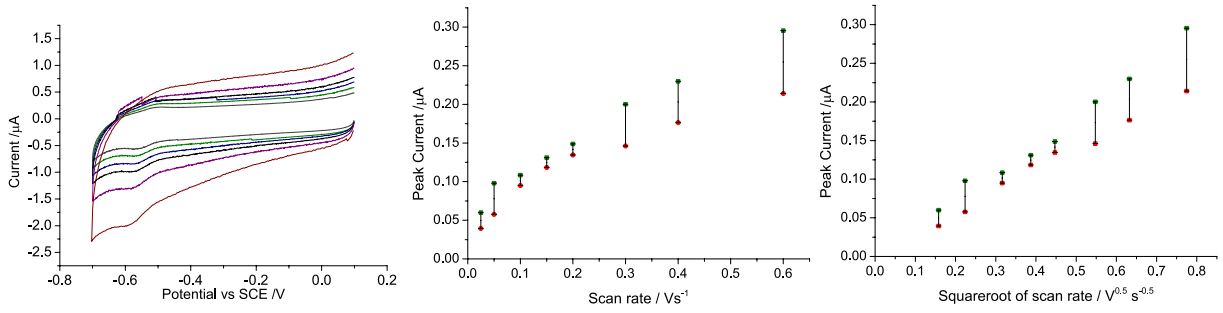


Figure 6: Voltammetry for the reduction of 1,8-dihyrdoxy-anthraquinone and the associated plots of peak current (as measured using a linear [green points] and exponential [red points] baseline) against scan rate and the square-root of scan rate.

Figures 5 and 6 depict the experimental voltammetry for the reduction of 1,4 and 1,8-dihydroxy-anthraquinone (approx 5$\mu$M) in the absence of oxygen (reductive peak at $\sim$ -0.6V). Also shown in Figures 5 and 6 is the variation in the measured peak currents as a function of scan rate. For both cases it seems clear that even if an exponential baseline (red points) is taken to asses the magnitude of the current, the peak is found to vary linearly with the square-root of scan rate, consequently it is concluded that for both compounds the reduction process occurs via a diffusional mechanism i.e. no significant surface adsorption is observed. Moreover, it is of importance that both compounds result in very comparable peak heights hence the observed difference in the mediated oxygen reduction process is not due to the differing diffusion coefficients of the two species.

## References

(1) Kakiuchi, T.; Usui, H.; Hobara, D.; Yamamoto, M. *Langmuir* **2002**, *18*, 5231–5238.