Direct measurement of the local field within alkyl-ferrocenyln-alkanethiolate monolayers: Importance of the supramolecular and electronic structure on the voltammetric response and potential profile

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ABSTRACT

This paper describes the electrochemical behaviour of self-assembled monolayers (SAMs) of n-alkanethiolates with Fc groups inserted at 14 different positions along the alkyl chain (SCnFcC13-n, n = 0–13) studied by cyclic voltammetry. The electronic and supramolecular structures of the SAMs have been fully characterised and all molecules are standing up, allowing for precise control over the position of the Fc unit within the SAM as a function of n revealing the shape of the electrostatic potential profile across the SAMs. The potential profile is highly non-linear due to electronic changes in the nature of the Fc–electrode interaction for small values of n < 5, and supramolecular changes for large values of n = 11–13. For intermediate values of n = 5–11, the potential drop is linear and the data can be fitted to a model developed by White and Smith. The electrochemical behaviour was dominated by a one-step reversible redox-process, but the presence of a shoulder indicates that the Fc units are present in different microenvironments resulting from the mismatch in size between the Fc units and the alkyl chains. Other features, including peak splitting, peak broadening, and peak shifts, can be related to changes in the electronic and supramolecular structure of the SAM revealed by molecular dynamics simulations and spectroscopy. For small values of n < 5, electronic effects dominate and the peak oxidation waves are shifted anodically (~150 mV) and broadened (full width at half maximum of up to 220 mV) because the Fc units hybridise with the Au electrode (for n < 3) or interact with the Au electrode via van der Waals interactions (n = 4, 5). For intermediate values of n = 5–11, supramolecular effects direct the packing structure of the SAMs and clear odd-even effects are observed. For large values of n = 11–13, the top alkyl chains are liquid-like in character and do not block the Fc units from the electrolyte.

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1. Introduction

Redox-active self-assembled monolayers (SAMs) are appealing for applications in molecular electronics [1–4], molecular memory [5–7], and charge storage [8,9]. Besides potential for practical applications, SAMs immobilised on electrodes are attractive model systems to study the mechanisms of charge transfer [10–12] due to their ease of preparation and synthetic modification, and a layer thickness of exactly one molecule [13]. Typically, the charge...
transfer characteristics of these SAMs are investigated using wet electrochemistry with the most widely used method being cyclic voltammetry [13]. Usually, redox-active SAMs consist of an anchoring group (e.g., thiol for anchoring on coinage surfaces), a spacer group (e.g., an alkyl chain, or conjugated backbone), and a redox-active terminal group located at the top of the SAM [14]. Although many factors contribute to the shape of the cyclic voltammogram (CV), including mass and electron transfer rates, defects, and others [see below], the potential drop across the SAM-electrode is also important but, in general, it is not known how the potential drops along the SAM from measurement within the SAM itself [15–25]. Mostly, the potential drop across SAMs are assumed to be linear, but we have shown that this assumption does not hold in solid state molecular tunnelling junctions [17,26] with SAMs of SCnFcC13-n (Cn is the number of aliphatic carbons representing CH2 or CH3 units; see Fig. 1). Here we report the shape of the electrostatic potential profile across the electrode-SAM interface under wet electrochemical conditions of SC5FecC13-n SAMs on Au which can be probed by placing the redox-active group at 14 different positions along the back bone of the SAM, since C13 alkyl chains are sufficiently long to explore effects away from the two electrode interfaces but not too long to be insulating (which can cause irreversible CVs). Our results fit well to a model proposed by Smith and White [27] for n = 5–11, but the potential drop is highly non-linear due to SAM packing effects for n = 12 and 13, and changes in the nature of the Fc—Au electronic structure which changes as a function of n for n < 5. We believe that these results will help to interpret the shapes of CVs and guide future predictive materials design for molecular electronic devices.

One-step reversible redox-active SAMs are characterised by: i) a symmetrical oxidation peak potential, $E_{pa}$, and reduction peak potential, $E_{pc}$, with a peak separation $\Delta E_{\text{peak}} = E_{pc} - E_{pa} = 0$, ii) a ratio of the anodic peak current $I_{pa}$ and the cathodic peak current $I_{pc}$ of unity, and iii) a full width at half-maximum of the anodic voltammetric peak $E_{\text{whm}}$ of 3.53RT/nFE (or 90.6/n mV at 25 °C) where R is the gas constant, F is the constant of Faraday, and nFE is the number of electrons involved in the reaction [28]. One of the most widely studied electrochemically-active SAMs is S(CH2)nFc, i.e., alkanethiols with ferrocenyl (Fc) functional groups. The shapes of the CVs of S(CH2)nFc SAMs are often very complex and, in practice, ideal electrochemical behaviour is rarely observed. Instead, typical non-ideal behaviours, e.g., peak broadening [29,30], peak splitting [31–33], and peak shifting [34,35] are apparent. Various models have been proposed to explain these non-ideal features, such as disordered structures due to the mismatch in size between the bulky Fc group and alkyl chain [36], phase separation [37–40], and electrostatic interactions between Fc groups [41]. In addition, ion-pair formation between adsorbed ferrocum cation, Fc+, and the anion in the electrolyte solution [42–44], and the shape of the interfacial potential drop profile also cause non-ideal electrochemical behaviour [45–48].

We have recently proposed a model to explain the origin of the observed deviations from ideal electrochemical behaviour of SAMs of S(CH2)nFc, with n = 0–15, on gold based on the relative strength of the intermolecular Fc-Fc, Fc-CN, and Cn-Cn interactions, and Fc-Au interactions, and supramolecular structure of the SAMs [49]. We found that these SAMs form dense layers on Au but due to the mismatch in diameters between the Fc and alkyl chains, the Fc units cannot pack well. Consequently, partially buried Fc units are present which causes peak splitting. In addition, we found that defects induced by the surface roughness of the Au electrode and disulphide impurities in the SAM precursor cause significant peak broadening and the appearance of additional redox waves. For values of n < 3, the Fc units hybridise with orbitals from the Au electrode which causes significant peak broadening (up to 174 mV for n = 0) and shifts to higher oxidation potentials (up to 552 mV for n = 0). Although our study [49] gave new insights in how the interplay between supramolecular and electronic structure of the SAMs affects the shape of the CVs, it did not provide conclusive information regarding the shape of the potential profile along these SAMs.

Smith and White [27] modelled the effects of the position of the redox-active moiety within the SAMs (Fig. 1) in terms of the capacitance of the layer between the redox centre and the SAM-electrolyte interface ($\phi_{\text{sol}}$). The potential drop across this so-called “plane of electron transfer” ($\phi_{\text{PET}}$) is given by $\phi_{\text{PET}} - \phi_{\text{sol}}$. By increasing the value of the capacitance between $\phi_{\text{PET}}$ and $\phi_{\text{sol}}$, the peak potential shifts positively and the redox-wave broadens. In this model, the potential drops linearly along the alkyl chain $d_{1}$ between the PET and the metal electrode ($\phi_{\text{PET}}$), and the alkyl chain $d_{2}$ between the PET and solution, and the potential then decays exponentially into the electrolyte solution. Later, Fawcett [50] included the Stern layer and showed this interfacial model reduces the repulsive effect of neighbouring redox centres and makes the local potential less positive than the average potential in the plane. Both models show that burying the Fc group inside the SAM by increasing the thickness of the top layer ($d_{2}$) of the SAM between the redox group and the electrolyte interface significantly influences the electrochemical behaviour resulting in peak shifting by 520–600 mV and peak broadening of up to 200 mV, but the model

Fig. 1. Schematic illustration of alkyl-ferrocenyl-alkanethiolate SAMs on Au. The relative lengths of the alkyl chains below ($d_{1}$) and above ($d_{2}$) the plane defined by the Fc moieties (the plane of electron transfer, PET), determine the position of the Fc units within the SAM. In the model by Smith and White, the potential drops linearly across $d_{1}$ and $d_{2}$, but may do so with different potential decays. The potential then drops non-linearly in solution. $\phi_{\text{PET}} - \phi_{\text{PET}}$ potential at the Fc group, $\phi_{\text{sol}} - \phi_{\text{sol}}$ potential in the bulk solution, $\phi_{\text{PET}}$ potential at the SAM-solution interface, and $\phi_{\text{PET}}$ potential of the metal electrode. Panel a) shows an ideal model of SC5FecC13-n SAM on Au. Panel b) shows a more realistic view of the SAMs where the flexibility of the alkyl chains may reduce the effective lengths of the alkyl chains of a SC5FecC13-n SAM. As discussed in the text, the potential does not drop across very short $d_{2}$ as the boundary of the SAM-electrolyte interface may not be well-defined ($\phi_{\text{PET}}$) due to the flexible nature of the alkyl chains. Note the odd-even tilt angle change between the odd SAM in a) and the even SAM in b).
by Smith and White predicts larger shifts than the model by Fawcett by about 60 mV.

A few experimental studies have attempted [18–23] to map the shape of the potential drops. Creager and Rowe [24] investigated the redox behaviour of \( \text{S(CH}_2\text{)}_n\text{Fc} \) mixed with \( \text{S(CH}_2\text{)}_n\text{CH}_3 \) SAMs with \( n = 4, 6, 8, \) or 10, and observed positive shifts of the formal potential reaching a maximum value of 490 mV for mixed SAMs with \( n = 10 \), along with peak broadening. The authors concluded that their data fitted better to the model by Smith and White than the model by Fawcett. Consequently, they suggested that the charges in the SAM are apparently less efficiently screened than expected from the Fawcett model which could point to phase segregation, or that electrostatic repulsion between the charged ferrocenium cations could not be ignored. These results have been corroborated by Shiota et al. [25] who also studied \( \text{S(CH}_2\text{)}_n\text{Fc:Si(CH}_2\text{)}_n\text{CH}_3 \) mixed SAMs (with \( n = 6 \) or 18) as a function of electrolyte solution and showed that their results followed the model of Smith and White. However, studies involving mixed SAMs may suffer from phase segregation, especially when alkanethiols are used that differ in length [33,51]. Eggers et al. [15] used Fc derivatives with rigid norbornyllogous backbones mixed with \( \text{S(CH}_2\text{)}_n\text{OH} \) (with \( n = 6, 7, 8, 10, \) or 11) that allowed for probing double layer effects above the SAM surface. They used diluted redox active SAMs and could prove that the potential drop above the SAM in the Stern layer is steep followed by a shallow decay in the Gouy-Chapman layer. However, it should be noted that the Smith and White assumes that ions do not penetrate the SAM, and since we have densely packed monolayers we believe this assumption holds in our case (for values of \( n < 11 \)).

In this paper, we map the electrostatic potential profile at the interfaces of the SAM-electrolyte and the SAM-electrode using a redox probe within the SAM as follows. The SAMs were prepared with the Fc groups inserted at 14 different positions along the back bone of the SAM as depicted in Fig. 1, as demonstrated in Ref. [17] (which shows a reversal of rectification of molecular tunnelling junctions in the solid state, whereas in this work we elucidate the complete shape of the potential drop profile under wet electro-chemical conditions in detail). This approach to control the Fc position within the SAM does not rely on mixing two components with each other as was done in previous works and, hence, phase segregation is a non-issue. We note that grain boundaries in the electrode material are still present, however the role of grain boundaries is minimised as template-stripping yields Au surfaces with large grains and thus only a small fraction of the electrode surface exposes grain boundaries at which SAMs cannot pack well (see Ref. [52] for more details). By varying \( n \), we controlled the position of the Fc groups with respect to the bottom-electrode and the electrolyte: for small values of \( n \) the Fc units are located at the bottom of the SAM near the metal surface and shielded from the electrolyte by the alkyl chain (\( d_2 \), Fig. 1) above the Fc units, whilst for large values of \( n \) the opposite is true. In other words, by changing the lengths of two of the alkyl groups at opposite sides of the Fc moiety, we are able to investigate how the spatial position of the Fc units within the SAM affects the shape of the CVs. The electrostatic potential profile across the SAMs can be determined from the CVs, and is found to be non-linear across the SAM. This non-linearity can be explained by Fc–electrode interactions and by considering the supramolecular structure of the SAMs.

2. Experimental section

The details of the synthesis of the SAM precursors, and SAM formation and characterisation can be found in Ref. [17]. Briefly, template-stripped Au electrodes were prepared following a previously reported method (see Supplementary Information for experimental details) [49,53]. Cyclic voltammetry was performed by using a custom built electrochemical cell equipped with a platinum counter electrode, an Ag/AgCl reference electrode and an Au working electrode. The surface area of the Au electrode exposed to the electrolyte solution was \( A = 0.33 \text{ cm}^2 \). The cyclic voltammograms (CVs) were recorded in an aqueous solution of 1.0 M HClO4 between –0.10—0.90 V at a scan rate of 1.00 V/s using an AUTOLAB PGSTAT302N with NOVA 1.10 software. The CV data were analysed using a combination of Gaussian and Lorentzian functions using OriginPro 9.0 software. The anodic peaks were deconvoluted after background correction following a procedure similar to that used in Lee et al. [54] which is described briefly in the supporting information and in Ref. [49]. We characterised the structure of the SAMs using angle resolved photoelectron spectroscopy and near edge X-ray fine structure spectroscopy, supported by molecular dynamics computer simulations using methods described in Ref. [17].

3. Results and discussion

Structure of the SAMs. We minimised defects in the structure of the SAMs by using freshly prepared ultra-flat and clean template-stripped gold substrates and freshly purified thiol precursors to minimise impurities — such as disulphides or from the ambient — that lower the quality of the SAMs [49,55,56]. Fig. 1 shows the structure of the SAMs where the Fc position can be controlled by changing the number of CH₂ units above and below the PET. Here the total alkyl chain length (\( d_1 + d_3 \), Fig. 1) is kept constant at 13 CH₂ units which is long enough to obtain SAMs that are standing up and allows us to study how the shape of the CVs changes as a function of 14 different Fc positions, but, as we show below, the monolayers are not too thick to render the Fc units redox inactive in the applied voltage window (–0.10—0.90 V vs. Ag/AgCl) when \( d_2 \geq d_1 \).

The SAMs have been characterised in detail before using a large number of techniques, and all details are given in Ref. [17]. Molecular dynamics (MD) simulations showed that the SAMs are well behaved with all molecules standing up. Both X-ray photoelectron spectroscopy (XPS) and MD confirmed that all SAMs have a very similar SAM thickness \( d \) and packing density, except for SAMs with \( n < 3 \) where \( d \) slightly decreases from 1.8 nm to 1.4 nm due to steric repulsion between the Fc units. The tilt angles \( \alpha \) of the Fc units with respect to the surface normal were determined with near edge X-ray adsorption fine structure (NEXAFS) spectroscopy. These data revealed an odd–even effect in the Fc tilt angles because the M–S–C bond angle is fixed as explained in detail elsewhere [3,53,57]. The position of the Fc unit within the SAMs, or more specifically the values of \( d_1 \) and \( d_2 \), was determined with angle resolved X-ray photoelectron spectroscopy (AR XPS) and confirmed by MD simulations. Both theory and experiment are in agreement, and show monotonic increase in the value of \( d_1 \) and decrease in the values of \( d_2 \) as a function of \( n \) from which we conclude that we can control the position of the Fc units within the SAM with atomic precision.

We previously determined with ultra-violet photoelectron spectroscopy (UPS) the electronic structure of the SAMs which were confirmed by density functional theory (DFT) calculations [17]. These results show that hybridisation of the HOMO and the d-band of the Au are important for SAMs with \( n < 3 \), while for \( n \geq 3 \) the HOMO is not hybridised with the electrode but is instead localised on the Fc unit. Even though the HOMO is localised on the molecule for \( n = 3–5 \), the Fc units are close enough to the Au electrode to form van der Waals interactions (173 ± 12 meV estimated by dispersion-corrected DFT calculations) that shift the HOMO energy level toward the Fermi-level of the Au electrode, in agreement with UPS data.

Electrochemical Characterisation of the SAMs. We used aqueous 1.0 M perchloric acid as the electrolyte solution and all...
measurements were conducted with an Ag/AgCl reference electrode. The CVs of the SCnFcC13-n SAMs on ultra-flat template stripped Au are given in the supporting information of reference [17] and the electrochemical parameters are summarised in Table S1. The following four observations are made from these data: i) one oxidation and reduction dominates the CVs, ii) the Epa and Epd values increase with decreasing n, iii) the fwhm values increase with decreasing n, and iv) the capacitive currents are larger on the positive side of the redox peak than on the negative side, and increase with decreasing n.

Peak oxidation and reduction potentials. Fig. 2A shows the Epa and Epd values as a function of n. The values of the Epa and Epd shift from 319 ± 4 to 552 ± 2 mV and from 289 ± 2 to 452 ± 1 mV, respectively, when n decreases from 13 to 0. This observation indicates that the Fc moieties are more difficult to oxidise when n is small (d2 >> d1) than when n is large (d2 << d1). This observation could be explained by ion pairing. When the Fc units are close to the electrolyte solution, ClO4 ions from the electrolyte can readily form ion-pairs with the Fc⁺ cations, but this ion pair formation is sterically hampered by increasing d2. Similar observations have been made by Rowe et al. for mixed Fc SAMs diluted with long aliphatic alkyl chains [51]. For n > 11, the values of Epa and Epd are essentially independent of n. Here, the d2 alkyl chains are too short to form ordered van der Waals structures and therefore do not block the ClO4 ions from pairing with the Fc⁺ ions.

Odd-even effects in the full width at half maximum of the oxidation potential. Fig. 2B shows that the fwhm values increase with decreasing n from 112 mV for n = 13 to 226 mV for n = 2. For n = 13, fwhm is reasonably close to that of an ideal SAM (fwhm = 90.6 meV at room temperature) and the increase in fwhm implies that disorder is introduced due to steric repulsion between the buried Fc units (with diameter of 0.67 nm vs. CH2 unit diameter of 0.45 nm) resulting in weaker intermolecular interactions in agreement with MD (Fig. 2D). The MD data also show Fc—Fc interactions are independent of n and contribute 4.1 ± 0.2 kcal/mol to the total packing energy of the SAMs (Epack). Likewise, the Fc—alkyl chain interaction strength is also independent of the value of n and contributes 6.4 ± 0.7 kcal/mol on average to Epack. In contrast, the alkyl chain—chain interactions decrease with decreasing n from 12.3 kcal/mol (for n = 13) to 6.7 ± 0.3 kcal/mol (for n < 5) due to the disorder of the top alkyl chains. The buried Fc units slide above and underneath each other due to competing chain-chain and chain-Fc interactions (see Fig. 5 below).

Another important observation is that fwhm vs. n follows a clear odd-even effect where SAMeven have larger values of fwhm than SAModd. This odd-even effect can also be explained by Fc units in different microenvironments as follows. The NEXAFS spectra and MD simulations show an odd-even effect in the average tilt angle α of Fc units where α is smaller for SAMeven than for SAModd by 5° indicating that the Fc units are standing up more for SAMeven than for SAModd [17]. The different microenvironments of the Fc units affects their electrochemical behaviour (see below). We have reported similar behaviour and even more apparent odd-even effects in the electrochemical behaviour for S(CH2)nFc SAMs (n = 0–15) [49] which have been confirmed by others [45,58,59]. For these reasons, we believe that the odd-even effect in the broadening of the CV data is mainly caused by Fc units located in different microenvironments [49,53,60,61].

Shape analysis of the redox-wave. We analysed the CVs in more detail using a previously reported peak deconvolution

![Fig. 2. A) The values of Epa and Epc. B) fwhm, C) d1 and d2 plotted from MD data (red circles and black diamonds) and XPS data (blue triangles and green squares) D) gives computed contributions to packing energies of SAMs of SCnFcC13-n as a function of n. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image)
method of the anodic peak (to allow us to study the SAM structure in the reduced form) by fitting the data to both Gaussians and Lorentzians [54] (see supporting information for more details). Fig. 3A–C shows the results for the SAMs with \( n = 1, 6, \) and 7 (Fig. S1 shows all data; Table S2 summarises the corresponding electrochemical parameters). The CVs consist of two peaks assigned as peak I (at lower potential) and peak II (at higher potential). In case of the SAMs with \( n = 1 \), an additional peak at a lower oxidation potential, peak III, was observed. All peaks were fitted to Gaussians, with fitting results \( R^2 > 0.99 \). Fig. 3D shows the \( E_{pa,I}, E_{pa,II}, \) and \( E_{pa,III} \) values as a function of \( n \). The \( E_{pa,I} \) and \( E_{pa,II} \) values shift to significantly higher oxidation potentials with decreasing \( n \) from \( 318 \pm 1 \) mV to \( 594 \pm 2 \) mV, and \( 382 \pm 3 \) mV to \( 717 \pm 9 \) mV, respectively. The difference in the values of \( E_{pa,I} \) and \( E_{pa,II} \) \( (E_{pa,II} - E_{pa,I}) \) remains nearly constant at \( 113 \pm 18 \) mV (or \( 2.6 \pm 0.4 \) kcal/mol). Fig. 3E shows that the surface coverage of the Fc units \( (\Gamma_Fc, \text{mol/cm}^2) \) increases with increasing \( n \), where \( \Gamma_Fc \) was determined with

\[
\Gamma_Fc = \frac{Q_{tot}}{n_eFA}.
\]

where \( Q_{tot} \) is the total charge determined by integrating the CV, \( n_e \) is the number of electrons per mole of reaction, \( F \) is the Faraday constant and \( A \) is the surface area of the electrode exposed to the electrolyte solution [13]. Below we explain the electrochemical behaviour of the SAMs in the three regimes corresponding to \( n \): regime 1 \( (n < 5) \), regime 2 \( (n = 5–11) \), and regime 3 \( (n > 11) \).

Regime 1 \( (n < 5) \). Since the Fc units are close to the Au electrode, the packing of the SAMs is affected by Fc-Au interactions. The DFT and UPS data show significant hybridisation of the Fc HOMO with the d [5] orbitals of the Au electrode for \( n < 3 \). For \( n = 4 \) and 5, the van der Waals interactions of the Fc units with the Au electrode are still significant [62]. Fc—electrode interactions broaden the HOMO.
level and shift the HOMO level towards the Fermi-level of the Au electrode (see Ref. \[49\]). These effects stabilise the Fc units and cause the gradual anodic shift of $E_{pa,I}$ and $E_{pa,II}$ and broadening of the redox-wave (i.e., increase of $E_{fwhm}$).

In case of the SC1FcC12 SAM, we observed a pre-peak III with $E_{pa}$ 183 mV (4.0 kcal/mol) lower than the main peak I (Fig. 3A). The presence of peak III was also observed in our previous studies \[49,63\], and was ascribed to an Au–S bonding mode of a disordered chemisorbed species where the molecules are lying flat on Au and interacting weakly with neighbouring molecules. We note that the area underneath peak III represents a value of $G_{Fc,pre}$ of $0.19 \pm 0.005$ mol/cm$^2$ indicating that only a small fraction of this SAM is disordered.

Regime 2 ($n = 5$–$11$). In this regime, the value of $E_{Fc,pre}$ remains nearly constant at $3.8 \pm 4.5 \times 10^{-16}$ mol/cm$^2$ and clear odd-even effects in the values of $E_{Fc,I}$ and $E_{Fc,II}$ values can be observed. The values of $E_{Fc,I}$ for SAM$^{odd}$ ($n = 5, 7, 9$) are larger than for SAM$^{even}$ ($n = 6, 8, 10$) and a reversal of the odd-even effect is observed for the value of $E_{Fc,II}$. The ratio of $E_{Fc,II}/E_{Fc,I}$ for SAM$^{even}$ (0.99 $\pm$ 0.10) is about 3 times higher than that for SAM$^{odd}$ (0.31 $\pm$ 0.13). The MD simulations indicate that the alkyl packing structure of the SAMs with $n > 5$ is dominated by Cx-Cx interactions below Fc (Fig. 4). The simulations also show that the alkyl chains collectively show a pro-even odd-even effect in packing energies and by contrast the Fc groups show a pro-odd packing effect summed over Fc-Fc and Fc-alkyl interactions (Fig. 4C and D). These observations reinforce our conclusion that shoulders in the CVs originate from Fc units in different microenvironments and by comparing the CV and MD data we can assign peak I and peak II (Fig. 3E) to Fc and alkyl packing, respectively. In other words, the “sliding” of Fc units underneath each is more relevant for SAM$^{even}$ with stronger packing energies resulting in a $E_{Fc,II}/E_{Fc,I}$ of near unity than for SAM$^{odd}$ with a ratio of 0.31 where the SAMs are more loosely packed and therefore most of the Fc units are in the same microenvironment. Therefore, we assign peak II to partially buried Fc moieties. Of course, more microenvironments will exist in the system which is evident from the computed height population distributions of the Fc units (see Fig. 5G below), but we find that these two populations dominate and assign the peaks accordingly.

Regime 3 ($n > 11$). We note that for $n > 11$ the odd-even effects are not obeyed. Here, the packing energy is dominated by the long alkyl chain underneath the Fc units allowing SAMs to be densely packed, resulting in higher surface coverages (close to the theoretical value of $4.5 \times 10^{-16}$ mol/cm$^2$) than those SAMs in regimes 1 and 2 because the very short top alkyl chains no longer contribute significantly to SAM packing (Fig. 4).

**Proposed structures to explain peaks I, II, and III.** Fig. 5 shows schematic illustrations of the packing structures of the SAMs which could induce the three distinct microenvironments of Fc units resulting in peaks I, II, and III. Peak III is associated with a chemisorbed lying-down phase of the SAM where the molecules are disordered and the surface coverages is low as explained in more detail in Refs. \[49,55\] (Fig. 5A and B). Peaks I and II are associated with the standing-up phase of the SAM, but are split due to the
Fig. 5. (A-F) Proposed local SAM structures explaining the three different CV peaks assigned as peak I, peak II, peak III along with exemplary CVs. The difference in $\alpha$ of the Fc units between SAM$^{\text{even}}$ and SAM$^{\text{odd}}$ is indicated. Gold, sulphur and iron atoms are shown as pale yellow, dark yellow, and orange space-filling spheres, CH$_2$ groups are shown as blue sticks. (G) Histograms of calculated Fc height above the Au surface for n = 5–11. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
differences in diameters of the Fc units and the alkylic chains which causes steric hindrance and induces local disorder (Fig. 5C–F). Therefore, the Fc units cannot be present in the same plane and slide underneath each other resulting in partially buried Fc units which are more difficult to oxidise than the Fc units atop a schematically drawn in Fig. 5C. Depending whether the value of $n$ is even or odd, Peak I or II dominates for the following reasons. Due to the pro-odd even-odd effect in the packing energy of the alkylic chains in SAM_{even}, the Fc units slide underneath each other more than for SAM_{odd} due to the mismatch in the Fc and alkylic chain diameters resulting in large contribution of Peak II (Fig. 5F). Due to the larger value of $a$ for SAM_{odd} than SAM_{even}, the alkylic-alkyl chain interactions are weakened resulting in a pro-odd Fc packing energy and less sliding of Fc units (as schematically drawn in Fig. 5C) and thus the contribution of peak II is small (Fig. 5D). Fig. 5G shows the computed Fc height histograms (the average distance of the Fc units above the Au surface during MD simulations) where the main peak indicates the position of the majority of the Fc units inside the SAM. The main peak shows splitting indicating that the majority of the Fc units populate slightly different positions within the SAM. This peak splitting coincides with the CV data as the peak splitting is larger for SAM_{even} than SAM_{odd} indicating that for SAM_{even} the population of partially buried Fc units is larger than for SAM_{odd}.

The potential drop model. The total double layer capacitance of the SAM, $C_{dl}$ in F/cm [2], is given by

$$C_{dl} = \frac{\varepsilon_0 \varepsilon_r}{d} = \frac{\varepsilon_0 \varepsilon_r}{d_1} + \frac{\varepsilon_0 \varepsilon_r}{d_2}$$

(2)

where $\varepsilon_0$ is the vacuum permittivity ($8.85 \times 10^{-12}$ F/cm), $\varepsilon_r$ is the relative permittivity (dielectric constant) of the SAM, and $d$ is the thickness of the SAM ($d = d_1 + d_2$). The overall $\varepsilon_r$ values of the SAMs can be determined from the charging current $i_{ch}$ obtained from the CVs using

$$i_{ch} = C_{dl} \nu$$

(3)

where $\nu$ is the scan rate (V/s).

As the number of carbons below Fc (n) changes, the physical position of the Fc group changes. Therefore, by calculating the potential for each Fc position (Fig. 1), a complete spatial distribution of the potential from the electrode to the solution can be mapped. Smith and White [27] derived a set of coupled equations to describe the spatial variation in the interfacial potential distribution by calculating the potential drop from the PET to the solution ($\phi_{PET} - \phi_{film}$), which considers the dependence of the molecular structure of the films, electrochemical parameters in the system and the oxidation state on surface concentrations of the electroactive couple. Unlike Smith and White who used calculated CVs, we extract the potential profile from the experimental CV data as follows.

By delineating the system into 4 different potential regimes (as indicated in Fig. 1), a set of four constituent relations can be constructed describing the relationship between the charge densities and interfacial potentials. Smith and White propose a model wherein the potential decays linearly from the $\phi_M$ to $\phi_{PET}$ and then from $\phi_{PET}$ to $\phi_{film}$, thereafter reaching the film and decaying to $\phi_{sol}$ according to the Gouy-Chapman model. The four constituent relations can be written as a function of the charge density of the metal $\sigma_M$, the charge density of the PET $\sigma_{PET}$, charge density in the solution (diffuse layer) $\sigma_{diff}$:

$$\sigma_M + \sigma_{PET} = \frac{\varepsilon_0 \varepsilon_r}{d_2} (\phi_{PET} - \phi_{film})$$

(4a)

$$\sigma_{diff} = -\frac{\varepsilon_0 \varepsilon_r}{2 \kappa} \sinh \left( \frac{\phi_{film} - \phi_{sol}}{\kappa T} \right)$$

(4c)

$$\sigma_M + \sigma_{PET} + \sigma_{diff} = 0$$

(4e)

where $d_1$ is the distance from the electrode to the Fc and $d_2$ is the distance between the Fc and the film edge (the SAM/electrolyte interface), $T$ refers to temperature, $\kappa$ and $F$ are the ideal gas constant and Faraday’s constant respectively, $\varepsilon$ is the charge of an electron, $\kappa$ is the inverse Debye length, $z$ is the atomic number, $\varepsilon_0$ and $\varepsilon_0$ are the charges of the oxidised and reduced form of the redox couple.

The interfacial potentials in Eq. (4) can be expressed as a function of the applied potential and redox parameters [27]:

$$\phi_{PET} - \phi_{PET} = E^0 - EPZC = \left( \frac{RT}{nF} \right) \ln \left[ \frac{1-f}{f} \right]$$

(5)

where $f$ is the fractional degree of oxidation, $n_f = z_0 - z_k E_{pzc}$ is the potential of zero charge, and $E^0$ is the characteristic formal potential of the SAM. Eq. (5) can be integrated into Eq. (4a) to derive $\sigma_M$ as:

$$\sigma_M = \left( \frac{E^0 - EPZC - \left( \frac{RT}{nF} \ln \left[ \frac{1-f}{f} \right] \right) \varepsilon_0 \varepsilon_r}{d_1} \right)$$

(6)

Similarly, the charge density at the PET $\sigma_{PET}$ is purely a function of the redox species and the surface coverage:

$$\sigma_{PET} = \Gamma_f (z_0 f + z_k (1-f))$$

(7)

where $\Gamma_f$ is the total surface coverage (measured by CV), which can be combined with Eq. (6) and in Eq. (4b) (using the capacitance relations $C_1 = \varepsilon_1 \varepsilon_0 / d_1$ and $C_2 = \varepsilon_2 \varepsilon_0 / d_2$ from Eq. (2)) to derive the potential drop between the PET and the film (and thus across the molecule) ($\phi_{PET} - \phi_{film}$):

$$\phi_{PET} - \phi_{film} = \frac{E^0 - EPZC - \left( \frac{RT}{nF} \ln \left[ \frac{1-f}{f} \right] \right) \varepsilon_0 \varepsilon_r}{C_2} \Gamma_f$$

(8)

The model proposed by Smith and White, with Eqs. (5)–(7) reproduced from them here with Eq. (8) subsequently derived above, give a very general model to describe the spatial variation of the interfacial potential distribution, containing no specific information regarding the actual supramolecular properties of the film, nor the nature of the interaction of the redox unit with the bottom electrode. More specifically, the model does not account for disorder in the SAMs caused by the size mismatch between the redox group and the alkylic chains, odd–even effects in the tilt angles of the Fc units, or hybridisation Fc with the Au orbitals. Therefore, although the model assumes a linear potential drop across ideal SAM structures, the measured potential drop may be nonlinear.

Subsequent experiments have built on the general Smith and White model but modified specifically for the experimental conditions to take into account specific effects (such as different polarities of alkylic chains of the SAM and headgroup [64], and for proteins adsorbed at the electrode/electrolyte interface [55]). Additional effects from specific experimental conditions were demonstrated in Ref. [15], where the potential across the Stern layer and Gouy-Chapman layers was probed using a molecular
ruler’ using Fc molecules attached to a rigid norbornyllogous bridge molecule. However, it has also been reported that techniques probing the SAM from the outside (ex situ) may also interact with the SAM, or at least ‘select’ the interaction by introducing an external stimulus that may bias one effect over another, not truly measuring the potential across the SAM\(^{16}\). In this work, we probe the shape potential of the potential profile in situ (that is, directly inside the SAM) by placing Fc redox-probes at 14 different positions along the alkyl chain instead, allowing us to directly observe the contributions of various conditions such as SAM disorder, odd-even effects on Fc tilt angle and hybridisation with the Au electrode.

**Potential drop across the SAM.** With the complete CV characterisation data, it is possible to calculate the potential drop \(\phi_{\text{PET}} - \phi_{\text{film}}\) using Eq. (8). Using the following values: the specific current position at which half of the species are oxidised \(i = 0.5\); SAM permittivities: \(\varepsilon_1 = 2.7\) (from previous impedance spectroscopy measurements\(^{66}\)); \(\varepsilon_2 = 22.6\) (as determined by Fawcett et al. \(^{67}\)); \(A = 0.33\) cm\(^2\); \(z_0 = 3\); \(z_K = 2\) (preferred oxidation states of Fe); \(E_{\text{pzc}} = +0.27\) V \(^{68}\); \(T = 298\) K; \(\Gamma_C, C_\text{B}, E_\text{D}\) from the CV data, and \(d_1\) and \(d_2\) were taken from the MD simulations (see Fig. 2C and Table S1 for all values). The only assumption made in the calculations comes from \(E_{\text{pzc}}\) (the potential of the uncoated electrode) which will not influence the shape of \(\phi_{\text{PET}} = \phi_{\text{film}}\) in Fig. 6. Fig. 6 gives the potential profile \(\phi_{\text{PET}} = \phi_{\text{film}}\) for all calculated for the entire Fc series. Instead of a single linear profile predicted by Smith and White (given by the solid and dashed red line), the potential profile exhibits clear nonlinear behaviour that is consistent with the above discussion of the CV shape analysis. In regime 1 for \(n < 5\), the CV data show significant broadening and the oxidation potential is shifted anodically due to strong Fc–Au interactions causing the deviation from linearity in Fig. 6. In regime 2 for \(n = 5–11\), the potential drops linearly which is reasonable as at this point the interfacial field interactions with the Fc are at their weakest and the potential profile is dominated by the capacitive effects of the electrode and the electrolyte. This is compatible with the SAM packing dominated by supramolecular interactions (Fig. 2D) since the boundary with either the electrode or the electrolyte does not contribute significantly to the local potential in the SAM. This leads regime 2 to exhibit behaviour most closely in agreement with the model Smith & White propose. In Fig. 6 the linear potential fit is indicated by the red solid line (as opposed to the grey-dashed lines for regimes 1 and 3 that merely serve as visual guides) with a calculated linear drop of \(-55\) mV/n. In regime 3 for \(n > 11\) the \(d_2\) alkyl chains are too short to pack together strongly (Fig. 4) and hence they are “floppy” and the ClO\(_4\) counter ions are not effectively blocked and can readily interact with the Fc\(^+\) units. It should be noted that the absolute value of the potential drop depends on the choice of \(\varepsilon_1\) and \(\varepsilon_2\) (which affects both terms in Eq. (8)), as well as the choice of \(E_{\text{pzc}}\) (which only affects the second term in Eq. (8), which is an order of magnitude less that the first term), however the plot shape (curve in Fig. 6) remains robust (see Figs. S5, S6), confirming our conclusions.

**4. Conclusions**

The electrochemical response of redox-active SAMs measured by cyclic voltammetry is complicated by many factors, especially from contributions from the supramolecular and electronic structure which we have elucidated here. All \(SC_n\text{FcCl}_3\) SAMs were in the standing up phase and did not suffer from back bending of the alkyl chain above the Fc units toward the Au electrode. Electronic effects are important for SAMs with values of \(n < 5\) where the Fc units directly interact with the Au electrode in agreement with our earlier findings\(^ {17,49}\). In the case for \(n < 3\) this interaction was sufficiently strong to cause hybridisation of the Fc and Au orbitals while for \(n = 4\) and 5 this interaction was van der Waals in nature. This Fc—electrode interaction resulted in an anodic shift, and broadening, of the peak oxidation potentials. All cyclic voltammograms showed a shoulder which we associate with densely packed SAMs but with Fc units in different microenvironments. In dense monolayers, not all Fc units can be located in the same plane due to steric hindrance as the Fc units have large diameters than the alkyl chain. We ascribe the observed peak splitting to Fc sliding underneath each other where the slightly more buried Fc units are more difficult to oxidise than the Fc units atop. We also observed odd-even effect in the electrochemical behaviour which could be related to the supramolecular structure of the SAMs revealed by molecular dynamics simulations. We found a pro-even SAM packing energy where the Fc units are more upright and therefore the SAMs pack better than SAM\(^{\text{odd}}\). Therefore, more Fc units slide underneath each other in even than odd SAMs resulting in more prominent peak splitting SAM\(^{\text{even}}\) than SAM\(^{\text{odd}}\). These findings are in line with our previously reported findings\(^ {49}\), which were confirmed by others\(^ {58}\), and indicate that the presence of shoulders in the CVs are inherent to densely packed monolayers and do not per se indicate phase segregation or the presence of disordered phase domains. Disordered regions in the SAMs appeared in our data as a distinct pre-peak at low oxidation potentials since loosely packed SAMs are easier to oxidise than dense monolayers.

Our experiments allowed us to probe the potential drop within the SAMs by using the Fc units as probe to measure the local field. Our data indicate that the potential drop profile is linear for SAMs with \(n = 5–11\) with a drop of \(-55\) mV/n and the data can be fitted to the model put forward by Smith and White\(^ {27}\), but the potential drop deviates from linearity for \(n < 5\) and \(n > 11\). For SAMs with \(n < 5\), Fc—Au interactions dominate resulting in anodic peak shifts and broadening. This effect was not included in the model by Smith and White. For SAMs with \(n > 11\) the supramolecular structure is driven by the large packing energy between the alkyl chains underneath the Fc units while the interactions between the short alkyl chains above the Fc units are too weak to block the ClO\(_4\) counterion.

![Fig. 6. Spatial profile of the potential across the SAM (\(\phi_{\text{PET}} - \phi_{\text{film}}\)) as a function of Fc position. The three regimes observed in the CV peaks are also observed in the potential (indicated by the red solid and grey dashed lines). Regime 1 (grey dashed line as a visual guide) sees an increase in potential, heavily dominated by Fc-Au electrode interactions. Regime 2 sees a steady potential drop across the SAM (solid red line) with a linear fit of a slope of \(-55\) mV/n (extrapolated to all n by the dotted red line). Regime 3 sees a lack of contribution to the potential (grey dashed line as a visual guide) as Fc units are no longer buried in the SAM and are now readily accessible to counterions. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
from interacting with the Fe⁺ ions.

To the best of our knowledge, this is the first instance where the potential drop across the molecule has been experimentally determined using a redox-probe within the SAM to directly measure the local field within the SAM under wet electrochemical conditions. Besides potential drops, our results show that the shape of the CV is complicated by both electronic and supramolecular factors which all need to be taken into consideration in the interpretation of the electrochemical response of redox-active monolayers. We hope that our findings will stimulate future studies to investigate the potential profile of redox-active SAMs and to test the assumptions in the theory in more detail.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.04.041.

References


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References
