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# Electron transfer through ferrocene-terminated self-assembled monolayers

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9-Mercaptononyl-5'-ferrocenylpentanoate was found to self-assemble onto gold electrodes forming a surface-confined redox monolayer. The monolayer exhibits high electron exchange rate and is capable of charge transfer mediation between the solution dissolved redox species and the electrode. The variation of the microenvironment of ferrocene head groups from more to less polar leads to a positive shift of the formal potential of the layer. The same shift may be brought about by substituting the anion of the supporting electrolyte from perchlorate (less hydrated) to fluoride (highly hydrated). In both cases, the electrooxidation current peak follows the monolayer potential shift, indicating an interrelation between the surface-confined and interfacial electron transfer processes.

**Key words:** self-assembled monolayers, ferrocene, ascorbic acid, voltammetry, electrocatalysis, electron transfer

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## INTRODUCTION

Ferrocene-terminated self-assembled monolayers (Fc-SAMs) on electrode surfaces have attracted a considerable interest during the past decade. The possibility to systematically vary the distance between the redox moiety and the electrode surface as well as the possibility to change the microenvironment around the electroactive ferrocene group makes these monolayers an attractive object for experimental and theoretical studies of electron transfer [1–8]. Because of fast electron transfer from surface-confined redox center to the electrode, the ferrocene-terminated SAMs might comprise attractive properties of the mediators for biological redox systems and biosensors. Indeed, soluble ferrocene derivatives are known to be effective electron transfer mediators both for small organic molecules and enzyme redox conversion [9, 10]. Recently we have reported on the properties of several new Fc-SAMs, which contain an ester group in the middle of the alkane chain [11] and exhibit relatively high electron exchange rates. This prompted us to investigate the mediatory properties of these new Fc-SAMs towards several soluble redox substrates. In this communication, we present preliminary data on electron transfer through the SAMs formed by the 9-mercaptononyl-5'-ferrocenylpentanoate (MNFP) on a gold electrode.

## MATERIALS AND METHODS

The polycrystalline Au disk (0.2 cm<sup>2</sup> geometrical surface area) pressed into a Teflon sleeve served as the working electrode. The electrode pre-treatment and SAM formation procedure were described earlier [11]. For the Surface Enhanced Raman Scattering (SERS) measurements, the electrode preparation was similar except that polishing operation was replaced with the procedure of electrochemical roughening in 0.1 M KCl solution [12].

The measurements were carried out in a three electrode electrochemical cell at 25 °C. The counter-electrode was a Pt wire and the reference electrode was a saturated calomel electrode (cyclic voltammetry) or a Hg|Hg<sub>2</sub>SO<sub>4</sub>|0.5 M H<sub>2</sub>SO<sub>4</sub> electrode (SERS spectroscopy). In this work, all potentials are referred to the SCE scale. Cyclic voltammograms (CV) were recorded with the EG & G VersaStat computerized electrochemical system. The electrolyte was 0.1M NaClO<sub>4</sub> (unless otherwise indicated) buffered at pH 7.0 by 0.01M phosphate solution, prepared in Milipore-Q water. All solutions were deoxygenated by bubbling ultra pure Ar for about 20–40 min. All chemicals were commercial materials of analytical grade, except for benzylnicotinamide (BNA), which was synthesized and purified in our department.

SERS measurements were carried out with a FT-Raman spectrometer (PerkinElmer, Model Spectrum

GX) equipped with an InGaAs detector operating at room temperature. Excitation was provided by an air-cooled diode-pumped Nd-YAG laser with an emission wavelength of 1064 nm. The laser beam was focused to a spot of  $\sim 1$  mm<sup>2</sup> and the laser power at the sample was set to 500 mW. In order to reduce photo- and thermoeffects, the spectroelectrochemical cell together with the working electrode was moved linearly with respect to the laser beam ( $\sim 20$  mm s<sup>-1</sup>) [13]. The experiments were carried out in a 180° geometry. The spectral resolution was set at 4 cm<sup>-1</sup> and the wavenumber increment per data point was 1 cm<sup>-1</sup>. All spectra were acquired by 200 scans. None of the spectra presented was smoothed.

## RESULTS AND DISCUSSION

Figure 1a shows typical CV curves of a 9-mercaptotononyl-5'-ferrocenylpentanoate monolayer, which indicates the formal potential of the monolayer  $E^{\circ} = 0.33 (\pm 0.01)$  V. The full surface coverage was found to be  $4.2 \times 10^{-10}$  mol cm<sup>-2</sup>, which is in good agreement with the data of other authors [7]. The electron transfer (from ferrocene moiety to the surface) constant estimated by the Laviron method [16] was found to be *ca.* 32 s<sup>-1</sup>, which agrees well with the data for the Fc-SAMs of similar length [2, 5]. Figures 1 b–e present CVs of the Fc-SAM-modified electrode in the solutions containing different dissolved redox species. Three redox species – ferrocyanide anion ( $\text{Fe}(\text{CN})_6^{4-}$ , Fig. 1c), ascorbic acid (AA, Fig. 1d), and benzylnicotinamide (BNA, Fig. 1e) – exhibit irreversible single-maximum CV curves, while

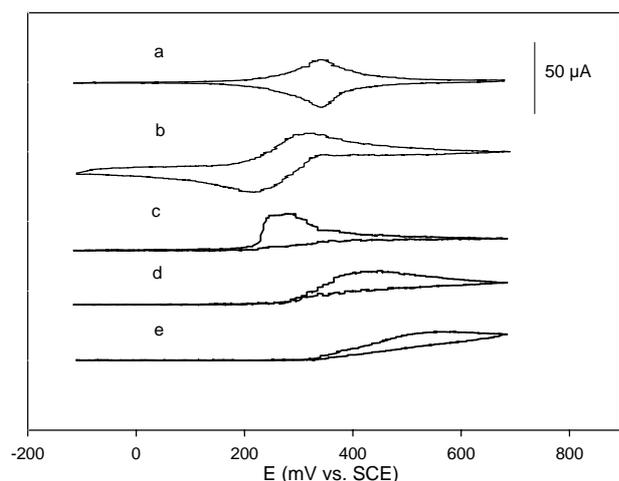


Fig. 1. Cyclic voltammograms of: *a* – 9-mercaptotononyl-5'-ferrocenylpentanoate monolayer, *b* – ferrocene carboxylic acid, *c* –  $\text{Fe}(\text{CN})_6^{4-}$ , *d* – ascorbic, *e* – benzylnicotinamide in electrolyte containing 0.1 M  $\text{NaClO}_4$  and 0.01M phosphate buffer (pH 7.0). Scan rate 100 mV/s. Plots *b* through *e* are background-subtracted cyclic voltammograms

ferrocene carboxylic acid (FCA, Fig. 1b) shows a quasi-reversible response with the peak separation ranging from 60 to 80 mV at the potential scan rate from 10 to 200 mV/s. In the latter case, the difference between peaks [17] yields the heterogeneous electron transfer constant equal to  $0.7 \times 10^{-2}$  cm/s. The midpoint potential  $E^{\circ}$  is close to 0.260 V, which perfectly matches the value of  $E_{1/2} = 0.281$  V ( $E_{1/2} \approx E^{\circ} + RT/nF$ ) for FCA presented in [9]. It is evident that in this case electron transfer in both directions proceeds without a significant overpotential.

Conversely, the oxidation of AA and BNA occurs with significant overpotentials of 0.4V and 0.9V ( $E^{\circ}_{\text{AA}} = -0.16$  V,  $E^{\circ}_{\text{BNA}} = -0.56$  V), respectively. Curiously, ferrocyanide exhibits typical irreversible oxidation, whereas the process occurs with a relatively small overvoltage of 0.03V ( $E^{\circ} = 0.20$  V). At large overpotentials there is a possibility that the oxidation of redox species might occur via direct tunneling of electrons through the SAM, defect pinholes and/or collapsed sites. However, in the case of mediated electron transfer, the redox potential of the surface-confined mediator and the potential of the substrate's electrocatalytic oxidation wave are interrelated [18]. So, the presence (absence) of the correlation between these two features might confirm (reject) the mediator-type mechanism of the electron transfer process.

There are several ways to alter the formal potential of the surface-confined Fc-SAMs. First, the redox potential of the Fc-SAMs is sensitive to the local microenvironment of the ferrocene groups. It shifts positively as the environment becomes less po-

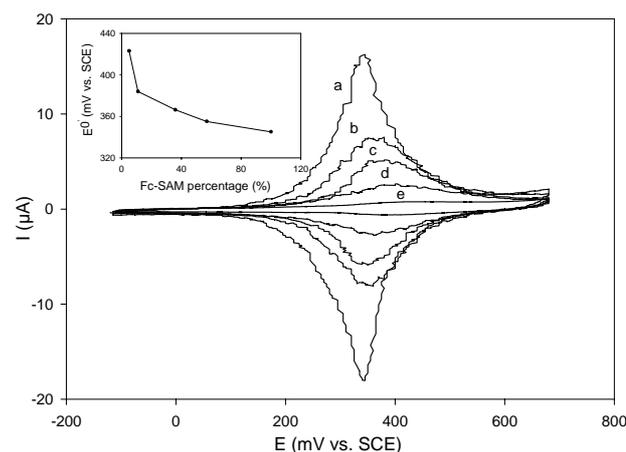


Fig. 2. Effect of octadecanethiol coadsorption on cyclic voltammogram of 9-mercaptotononyl-5'-ferrocenylpentanoate (MNFP) monolayer at 100 mV/s. Percentage of the surface covered with MNFP: *a* – 100%, *b* – 57%, *c* – 37%, *d* – 11%, *e* – 5%. Scan rate 100 mV/s. Inset displays the variation of the monolayer's formal potential with the MNFP content in the monolayer. Electrolyte: 0.1 M  $\text{NaClO}_4$  and 0.01M phosphate buffer (pH 7.0)

lar [7, 8]. Thus, Fig. 2 shows the effect of octadecanethiol (ODT) coadsorption on the MNFP monolayer redox properties. The peak currents of the Fc-SAM decrease and shift positively with increasing the ODT content. The shift reaches  $\sim 80$  mV as the surface concentration of the MNFP decreases to  $\sim 10\%$  (Fig. 2, inset). Simultaneously, as is seen from Fig. 3, the anodic peaks of all the dissolved substrates studied follow the shift of Fc-SAM's redox potential. There are, however, some exceptions. Above 50% of MNFP on the surface, some substrates showed a reverse trend (Figs. 3b and 3d), which we cannot explain at the present moment. Nevertheless, below 50% we always observed a positive shift of the electrooxidation peak-potential with an increase of ODT fraction. This clearly indicates an interconnection between the monolayer and the redox processes of substrates investigated in the present work.

Another possibility to induce the shift of Fc-SAM's  $E^\circ$  is to exploit different affinity of ions towards solvation (hydration). Poorly-solvated ions can readily form ion-pairs with a poorly-solvated ferricenium [7] ion. On the contrary, one might expect that heavily-solvated ions (e.g., fluoride) will less readily penetrate the nonpolar environment. As a consequence, in fluoride-containing buffer solution the redox potential of the Fc-SAM should be shifted positively [7].

Penetration of perchlorate into the MNFP monolayer is clearly seen from the SERS spectrum shown in Fig. 4. At 0.6 V bias, which corresponds to a fully oxidized state of ferrocene moiety in an MNFP layer, one can clearly observe a well-defined band at  $932\text{ cm}^{-1}$ . This band was assigned to the symmetric stretching vibration of a perchlorate anion ( $\nu_s\text{ClO}_4$ ) [14]. The band disappears if the electrode potential is biased at 0.0 V, where the redox monolayer is in a fully reduced form. This observation directly indicates the ion-pair formation between the perchlorate anion and the ferricenium cation in the MNFP monolayer. A similar effect has been recently observed for an 8-ferrocenyloctanethiol monolayer at Au electrode in 0.1 M  $\text{HClO}_4$  solution [15].

The substitution of perchlorate with fluoride buffer leads to drastic changes in the cyclic voltammogram (Fig. 5), which might be tentatively rationalized as the inability of fluoride to penetrate Fc-

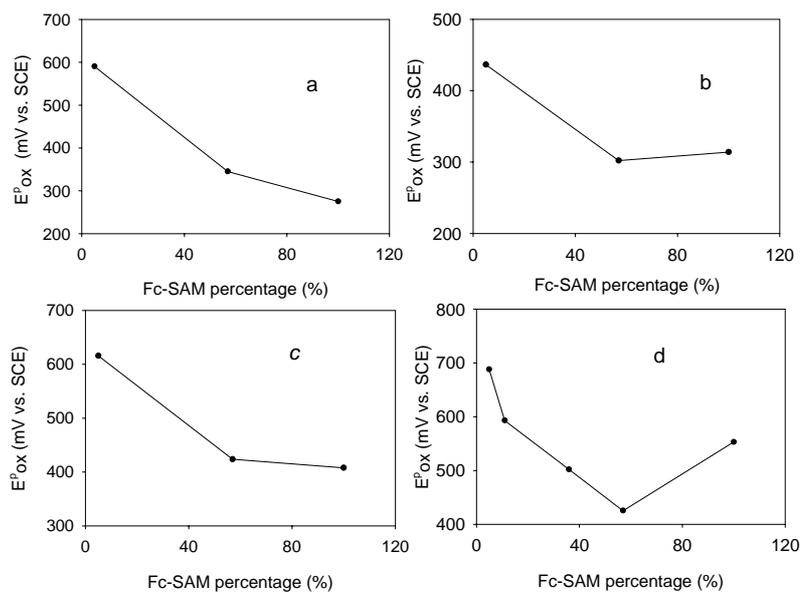


Fig. 3. Anodic peak potential *versus* percentage of MNFP in the monolayer. Redox substrates: *a* – ferrocene carboxylic acid, *b* –  $\text{Fe}(\text{CN})_6^{4-}$ , *c* – ascorbic acid, *d* – benzylnicotinamide. Electrolyte: 0.1 M  $\text{NaClO}_4$  and 0.01 M phosphate buffer (pH 7.0)

SAM and to compensate the positive charge of the  $\text{Fc}^+$  cation. The shift of the formal potential reaches about +180 mV (Fig. 5, inset) and is followed by a synchronous shift of the BNA electrooxidation

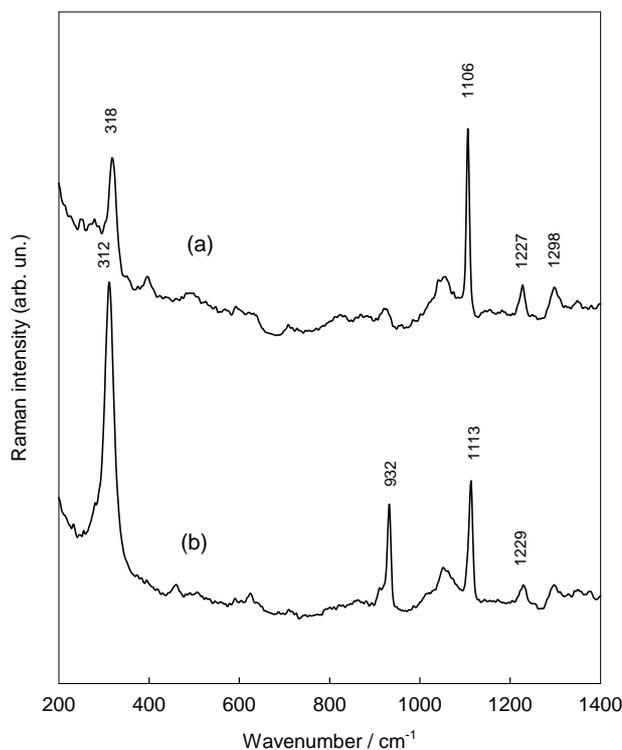


Fig. 4. SERS spectra of the 9-mercaptononyl-5'-ferrocenylpentanoate monolayer on Au electrode at: *a* – 0.0 V and *b* – 0.6 V. Electrolyte: 0.1 M  $\text{NaClO}_4$  and 0.01M phosphate buffer at pH 7.0

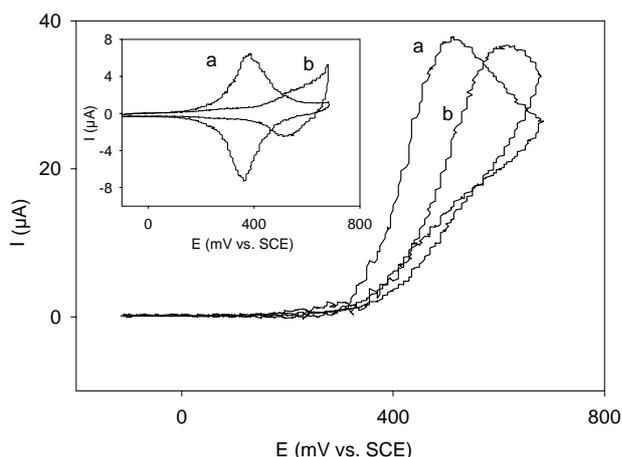


Fig. 5. Effect of anion substitution on the electrooxidation of benzylnicotinamide on Fc-SAM: *a* – 0.1 M perchlorate solution, *b* – 0.1 M fluoride. Both solutions contained 0.01 M phosphate buffer (pH 7.0). The voltammograms are recorded on mixed MNFP/ODT monolayer; percentage of the MNFP in the Fc-SAM – 57%. Potential scan rate 100 mV/s. Background subtracted plots. Inset shows corresponding background voltammograms

wave. This provides a clear evidence that the redox process of the surface-confined Fc-SAM and the process of electrooxidation of soluble redox substrates studied in this work are interrelated.

Summarizing, we conclude that the redox monolayers formed by the 9-mercaptononyl-5'-ferrocenylpentanoate exhibit a fast electron exchange with the gold electrode and shows the ability to mediate electron transfer from various redox substrates.

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## ELEKTRONO PERNAŠA PER FEROCENO SAVITVARKIUS MONOSLUOKSNIUS

### S a n t r a u k a

Nustatyta, jog 9-Mercaptononyl-5'-ferrocenylpentanoatas sudaro savitvarkius monosluoksnius ant aukso elektrodo paviršiaus. Monosluoksnis pasižymi dideliu elektronų mainų greičiu bei geba medijuoti krūvio pernašą tarp tirpale ištirpusių oksidacijos-redukcijos medžiagų ir elektrodo paviršiaus. Feroceno funkcinės grupės mikroaplinkos poliškumo sumažinimas lemia formaliojo monosluoksnio oksidacinio-redukcinio potencialo teigiamumą. Tokį patį efektą galima pasiekti pakeitus foninio elektrolito mažiau hidratuotą anijoną (perchloratas) į labiau hidratuotą (fluoridas). Abiem atvejais elektrolite esančių oksidacijos-redukcijos medžiagų oksidacijos kreivių smailių padėtis atitinka monosluoksnio formaliojo potencialo poslinkius ir patvirtina glaudų ryšį tarp elektrono pernašos monosluoksnyje ir per fazių sąlyčio ribą.