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The structure dependent electrochemical-response of novel 1-(4-mercaptobutyl)-4-(2-ferrocenylvinyl)pyridinium bromide SAMs on an Au electrode

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The 1-(4-mercaptobutyl)-4-(2-ferrocenylvinyl)pyridinium bromide {1-HS(CH$_2$)$_4$-4-[(*E*)-FcCH=CH]C$_5$H$_4$N}$^+$Br$^-$ and its hydrogenated product [1-HS(CH$_2$)$_4$-4-(-FcCH$_2$CH$_2$)C$_5$H$_4$N]$^+$Br$^-$ were synthesized and assembled on an Au electrode to form self-assembled monolayers which showed a structure-dependent electrochemical-response in phosphate buffer aqueous solutions (pH = 7).

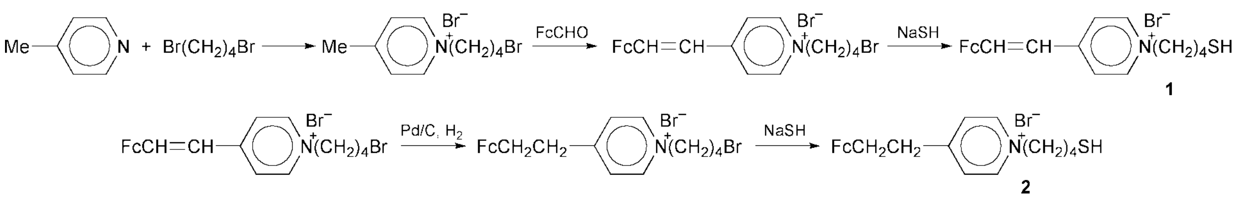
Self-assembled monolayers (SAMs) of alkanethiols and their derivatives with functionalized terminal groups have been studied intensively on gold electrodes due to their stability, organization, and potential application in many fields such as surface chemistry, biochemistry, electroanalytical chemistry, *etc.*[1] Motivated by Chidsey's novel work,[2] many research groups have investigated SAMs of ω-ferrocenylalkanethiols on gold because the ferrocenyl group is expected to exchange electrons readily with gold in the monolayer and the system can be considered as a model for the formation of electronic devices by self-assembly.[3–6] The advantage of electrochemically-active (*e.g.* ferrocene) monolayers is that the redox signal can be used as an internal readout. A linear porphyrin–ferrocene–alkanethiol was recently shown to be both sensitive and electrochemically-active.[7] A mixed acid–ferrocene self-assembled sulfide monolayer on gold shows a pH-dependent electrochemical-response by through-space communication between the receptor and ferrocene readout unit.[8] In addition, Marder reported that the compound incorporating a ferrocenyl moiety as a donor and a pyridinium as an acceptor connected by a CH=CH bridge, which is similar to our compound **1**, has excellent NLO properties.[9]

Here we primarily discuss a novel kind of 1-(4-mercaptobutyl)-4-(2-ferrocenylvinyl)pyridinium bromide and its structure-dependent electrochemical-response in phosphate buffer solution.

Compounds **1** and **2** can be conveniently prepared following the steps shown in Scheme 1.[10,11] Electrochemical measurement was conducted in a three-electrode cell with a CHI660A electrochemical workstation (Covarda, USA). Ag/AgCl and Pt foil were used as reference and counter electrodes, respectively. A gold disk electrode (CHI101) was employed as the working electrode (its apparent area S = 0.0314 cm^2), which was subjected to the same pre-treatment procedure before each experiment. The polished gold electrode (with 0.05 μm Al$_2$O$_3$) was rinsed with water. Thereafter, it was cleaned thoroughly in an ultrasonic cleaner with 1:1 nitric acid, 1:1 alcohol and distilled water, respectively. The cleaned gold electrode was washed with ethanol, dried by N$_2$ stream, then put into 0.1 mmol **1** or **2** ethanol solution and self-assembled in 12 h. After assembling, the monolayers were rinsed with ethanol and dried under a stream of purified N$_2$. The electrochemistry of the SAMs modified Au electrodes was tested by cyclic voltammetry in 0.1 mol L^{-1} phosphate buffer aqueous solution. The scan rates were 50, 100, 200, 300 and 400 mV s^{-1}, respectively.

Fig. 1(A) and (B) show a typical cyclic voltammogram obtained from the SAMs of **1** and **2** modified gold electrodes in 0.1 mol L^{-1} phosphate aqueous solution (pH = 7.0).

In each voltammogram, the electrode potential was cycled between −0.1 and 0.7 V. One electron reversible oxidation of the surface-confined ferrocenyl tail group was observed. The peak currents (i_{pa}, i_{pc}) were found to increase linearly with scan rate (v) as expected for a surface-confined redox system. The currents do not show decrease after repeated cycling in buffer solution, indicating that the ferrocene SAMs are very stable. Hence, it can be considered that the redox centers of these SAMs are fully solvated by aqueous electrolyte and the local environment around each redox center is quite uniform. The surface coverage of each thiolate was estimated from the charge passed for the oxidation of the ferrocene redox center during the anodic sweep. Values of Q_{Fc} were obtained by integration of the area under the anodic wave and were corrected for any charging-current contributions. The surface coverage of **1** was 6.4×10^{-11} mol cm^{-2}, and **2** was 7.1×10^{-11} mol cm^{-2}. This coverage is somewhat lower than the value of *ca.* 4.5×10^{-10} mol cm^{-2}, which is typically reported for a complete monolayer of uncharged ferrocenylalkanethiolates.[2] However, a decrease in packing efficiency is to be expected in this case, considering the steric effects of the pyridinium ion, ethylene band and the cationic charge on the nitrogen. The electrostatic repulsion of the adjacent cationic charges and the need to accommodate a counterion at each positively charged site would necessarily prevent the formation of a tightly packed monolayer. In a study carried out by Creager and co-workers a low monolayer coverage was reported for a charged thiol on gold, and this was



Scheme 1

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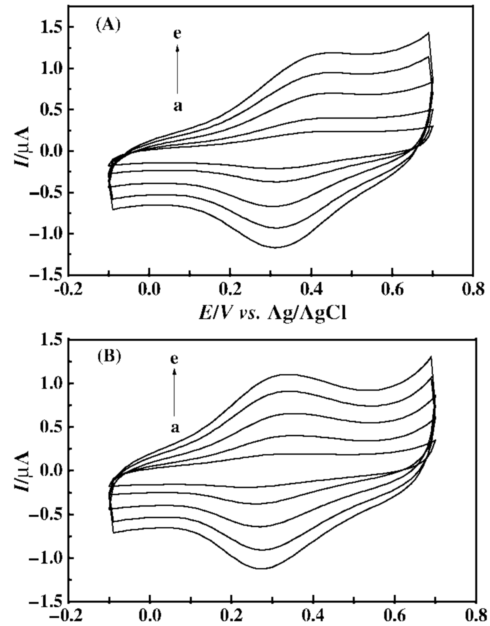

Fig. 1 The cyclic voltammograms of **1** and **2** SAMs modified Au electrode in 0.1 mol L^{-1} phosphate buffer electrolyte (pH = 7). (A) **1**; (B) **2**. The scan rate from **a** to **e** was 50, 100, 200, 300, 400 mV s^{-1}.

attributed to the strength and nature of the coulombic forces relative to dipolar and dispersion of forces within the monolayer.[12]

The location of the electron-withdrawing ethylene band and the electron-donating pyridinum group had a pronounced effect on the formal potential of the modified electrodes. The formal potential for the surface-bound ferrocenyl species was estimated from the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, $E^{0\prime} = 1/2(E_{pa} + E_{pc})$. Monolayers of **1** displayed the more positive formal potential of 0.37 V, whereas monolayers of **2** exhibited the less positive potential of 0.30 V. This can be expected because the electroactive ferrocenyl moiety is located adjacent to the strong electron-withdrawing ethylene band in **1**, thus making it more stable and slightly harder for the ferrocene to undergo oxidation. It is well known that ferrocene monolayers are pH-independent. Fig. 2 shows the redox signal for **1** at pH 5.0, 6.0 and 7.0. The electrochemical response of the **1** monolayer is influenced by the pH of the electrolyte solution.

The electron transfer rate of these SAMs can be estimated from the peak separation ΔE_p. A surface-confined species participating in a reversible electron transfer process would be expected to exhibit a value of $\Delta E_p = 0$ mV. The experimental ΔE_p values obtained from the voltammograms show that the peak potential separation is independent of the scan rate, which implies that the electron transfer is relatively fast. However, the nonzero ΔE_p values (for **1** $\Delta E_p = 120$ mV, for **2** $\Delta E_p = 60$ mV) for separation between the oxidation and reduction peak potentials of Fc/Fc^+ indicated that the presence of the pyridinium ion with positive charge and the ethylene band slowed the electron transfer rate to some extent. The apparent electrochemical reversibility of the monolayers of ferrocene derivatives of the alkanethiolate has been tentatively attributed to the rapid lateral transport of the electrons from one ferrocene unit to an adjacent ferrocene unit, following electron shuttling from the conducting gold surface to the ferrocene plane.[2]. Here, the electron may be entrapped by the pyridinium ion, so the ΔE_p values became large.

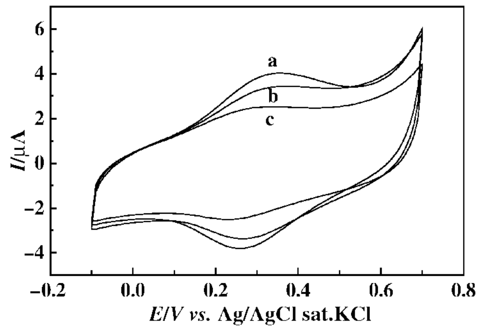

Fig. 2 Electrochemical response of **1** in phosphate electrolyte: (a). pH = 7.0; (b). pH = 6.0; (c). pH = 5.0.

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Notes and references

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10 Data for **1**: ^{1}H NMR (200 MHz, $CDCl_3$), δ: 9.17 (s, 2H, C***H***N), 7.91 (s, 2H, C***H***CHN), 7.70 (d, J = 16.0 Hz, 1H, (η-C_5H_4)C***H***), 6.71 (d, J = 15.6 Hz, 1H, (η-C_5H_4)CHC***H***), 4.81 (s, 2H, −NC***H***$_2$), 4.66, 4.56 (each s, 4H, η-C_5***H***$_4$), 4.20 (s, 5H, η-C_5***H***$_5$), 2.84 (m, 2H, -C***H***$_2$SH), 2.17–1.68 (m, 4H); MS (FAB) *m*/*e*: 378 (M – Br)$^+$.
11 Data for **2**: ^{1}H NMR (200 MHz, $CDCl_3$), δ: 9.76 (s, 2H, C***H***N), 7.72 (s, 2H, C***H***CHN), 4.96 (s, 2H, -NC***H***$_2$), 4.06–3.93 (t, 9H, η-C_5***H***$_4$, η-C_5***H***$_5$), 2.99 (s, 2H, (η-C_5H_4)C***H***$_2$), 2.81 (s, 2H, (η-C_5H_4)CH_2C***H***$_2$), 2.74 (m, 2H, -C***H***$_2$SH), 2.20–1.83 (m, 4H); MS (FAB) *m*/*e*: 380 (M – Br)$^+$.
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