

Donor/acceptor mixed self-assembled monolayers for realizing a multiredox-state surface

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Abstract: Mixed molecular self-assembled monolayers (SAMs) on gold based on two types of electroactive molecules, i.e., an electron donor (ferrocene) and an electron acceptor (anthraquinone) molecule, have been prepared as an approach to realize surfaces exhibiting multiple accessible redox states. The SAMs have been investigated in different electrolyte media. It has been clearly demonstrated that the nature of this media has a strong impact on the types of redox processes that take place as well as on the redox potential values. In the most optimized conditions surfaces with three redox states have been achieved. Such states are accessible within a relative narrow window potential where the SAMs on gold are stable. This work elucidates the key challenges for fabricating bi-component SAMs as electrochemical switches.

In the last decades, the preparation and exploitation of functional self-assembled monolayers (SAMs) has been a topic of intense research since they have shown appealing properties for a wide range of applications such as interface engineering in electronic devices,^[1] as sensing interfaces^[2] and as molecular switches and motors,^[3] among others. A particular approach in the field of molecular electronics is the use of electroactive SAMs to fabricate charge-storage molecular memories where the different accessible redox states act as memory bits.^[4,5] Typically, these systems are composed of a single electroactive unit that can switch between two redox states.^[6] The processing of higher memory densities in such devices could be achieved by increasing the number of memory states in each cell.^[7] This can be realised by preparing SAMs with molecules that contain two or more electroactive moieties, although the synthesis of these systems can be quite complex.^[8] An alternative route is to employ molecules that exhibit multiple redox states.^[9-11] However, often to read all these states it is commonly necessary to apply relatively high voltage potentials which are in detrimental for the SAM stability. Indeed, it is well known that the application of high voltages to molecular functionalised gold-surfaces through S-Au bonds lead to electrochemical molecular desorption.^[12] For this, the design of hybrid

systems (organic molecule/metal electrode) that can operate in a narrow bias window is crucial. Here, inspired by some recent works on mixed

SAMs composed of electron-donor (D) and electron-acceptor (A) units designed to act as artificial systems for light-harvesting and energy-transfer,^[13-17] we have prepared bi-component mixed-SAMs on gold composed of two redox-active species that can be electrochemically switched achieving a ternary memory that operates in a quite narrow voltage window. In particular, we employ ferrocene (Fc) as electron donor unit and, as electron acceptor, an anthraquinone (AQ).

Specifically, the molecules used in this study are: i) the commercially available 11-(ferrocenyl)undecanethiol derivative (Fc-C11-SH, **1**) that bears a terminal thiol group to be grafted on gold and that can undergo one reversible oxidation process ($\text{Fc} \leftrightarrow \text{Fc}^+$), and ii) the anthraquinone derivative **2** which has a thioctic ester group bearing a disulfide that can react with gold. Generally, AQs exhibit two one-electron redox processes ($\text{AQ} \leftrightarrow \text{AQ}^{\cdot-} \leftrightarrow \text{AQ}^{2-}$) in aprotic media and a single two proton, two electron reduction process ($\text{AQ} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{AQH}_2$) in protic environments (Figure 1a).^[18]

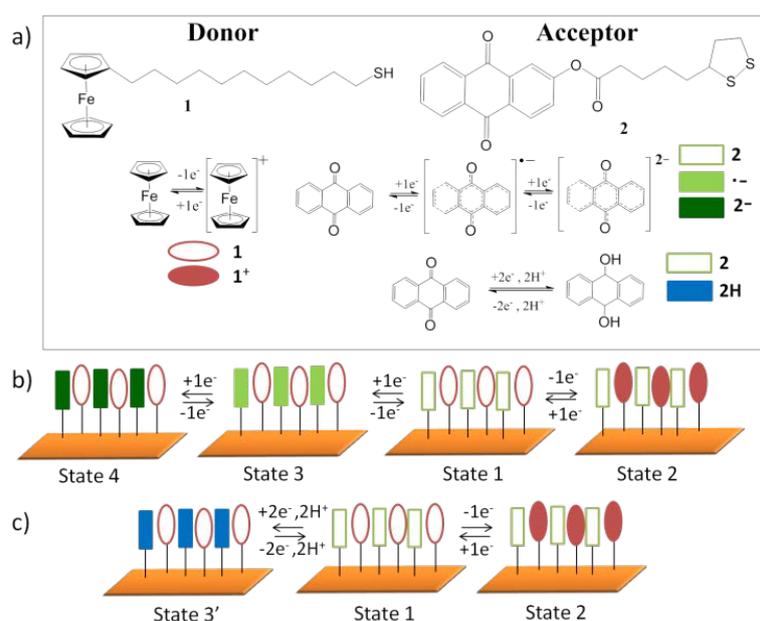
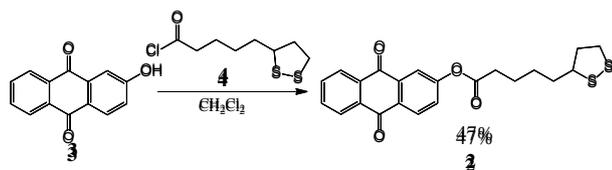


Figure 1. Main Text Paragraph. a) Molecular structure of the Fc donor **1** and the AQ acceptor **2** employed in this study. Colour code for the different redox states is indicated. Scheme of the redox processes that could take place on a mixed Fc/AQ SAM on Au employing as electrolyte b) an aprotic or c) a protic media.

As depicted in Scheme 1, compound **2** is obtained through an esterification reaction between the 2-hydroxyanthraquinone (**3**) and the α -lipoic acid (**4**) (see more details on the synthesis and characterisation in the Electronic Supplementary information, ESI).



Scheme 1. Synthetic route followed to prepare compound **2**.

Cyclic voltammetry (CV) has been used as a tool to characterize the electrochemical properties of the electroactive SAMs and to characterise the redox accessible states shown in Figure 1. As it is known, the type of solvent and the nature and size of the electrolyte ions have a strong influence on the CV response and, hence, on the performance of the electrochemical switch. Therefore, the CV optimum conditions can vary significantly depending on the electroactive system under examination. A clear identified challenge here was to find electrolyte media suitable to switch and stabilise the different redox states of the prepared bi-component SAMs. For this purpose, three different electrolytic solutions have been explored in this study: i) an inorganic salt dissolved in an organic solvent, ii) an aqueous phosphate buffer solution and iii) an ionic liquid. Electrolytes *i*) and *ii*) have been extensively employed for characterizing electroactive SAMs. On the contrary, although the clear advantages that ionic liquids offer for performing electrochemical studies (i.e., low vapor pressure, high thermal stability, high electrical conductivity, and large electrochemical window) their use have been less explored in SAMs.

Prior to the formation of the Fc/AQ mixed SAMs, the preparation and characterisation of the mono-component monolayers was carried out. A commercial substrate consisting of a 50 nm polycrystalline gold film evaporated on glass was used for all the experiments shown here.

First, the SAM based on **2** was prepared by immersing a freshly clean Au substrate, in a 0.5 mM solution of **2** in tetrahydrofuran (THF) for 40 hours under inert atmosphere, at room temperature and light exclusion. The resulting modified substrate was characterized using polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), water contact angle (CA) and CV. The PM-IRRAS spectrum shows three stretching bands, two at 1676 and 1591 cm^{-1} corresponding to the carbonyl groups (-C=O-) of the anthraquinone core and one band at 1760 cm^{-1} corresponding to the ester group (-C-O-C-) (see ESI, Figure S4). The water contact angle measured on the functionalized gold gave a value of $83.1 \pm 1.3^\circ$ which is close to other reported monolayers exhibiting a exposed phenyl group.^[19] Both results indicate the good formation of the AQ-SAM.

For the electrochemical characterisation, we employed a conventional three electrode set-up using the modified gold substrate as the working electrode (with an area of 0.5 cm²), a platinum wire as counter electrode and a silver wire as quasi-reference electrode. The first approach was to use the most common conventional conditions, i.e. using a salt dissolved in an organic solvent as the electrolyte solution. For the AQ-SAM we have combined different solvents (dichloromethane: acetonitrile (DCM:ACN) 9:1 (v/v), ACN, acetone, and THF) with different salts (NBu₄PF₆, NBu₄ClO₄ and LiClO₄). In all of the tested conditions, the peak corresponding to the first reduction process (RP1; AQ→AQ^{•-}) was observed between -0.8 V and -1 V vs Ag(s) but the second reduction process (RP2; AQ^{•-}→AQ²⁻) could not be measured due to the instability of the SAM when increasing the voltage window to more negative potentials. CV registered with the solution of NBu₄PF₆ in acetonitrile gave the lowest value of the E^{1/2}(RP1) in absolute value (-0.8 V vs Ag(s)), i.e. closer to 0 V, and the lowest peak-to-peak potential splitting ($\Delta E_{pp} = E_{cathodic} - E_{anodic} = 0.13$ V at scan rate (SR) 0.3 V/s), indicating that the reduced state is more accessible and the redox process is more reversible in these conditions.

As mentioned in the introduction, it is described that in electrolytic solutions based on protic solvents anthraquinones undergo a two-electron reduction process involving two protons that leads to the hydroantraquinone form: $AQ + 2H^+ + 2e^- \leftrightarrow AQH_2$. This process typically takes place at voltages closer to 0 V than the RP1 process of AQ in an aprotic medium. Furthermore, it has been shown that the redox behaviour depends on the pH. Nagata et al. studied the electron transfer of a quinone SAM on gold and they showed that by increasing the pH of the solution, the peak potential shifts towards a more negative potential and the peak separation becomes smaller.^[20] Taking this into account and in order to optimize the CV response of the herein described monolayer, we proceed to characterize the AQ-SAM using a phosphate buffer solution at different pHs (5.0, 6.9 and 8.9). The measured E^{1/2} vs Ag(s) for increasing pH were -0.31 V, -0.39 V and -0.62 V, respectively, following the trend previously described in the literature. In addition, there is a clear influence on the peak-to-peak potential splitting depending on the pH, which is an indicative parameter of the rate and reversibility of the process. The ΔE_{pp} at pH 5.0 at SR of 0.3 V/s is 0.25 V and at higher pHs this value considerably diminishes to 0.07 V and 0.06 V at pH 6.9 and 8.9, respectively. Considering all above, the buffer solution at neutral pH 6.9 is taken as the optimal one to go forward with the rest of the experiments since in these conditions the redox process occurs at lower $|E^{1/2}|$ and shows higher reversibility.

The electrochemistry of anthraquinone derivatives has also been previously investigated in ionic liquid (IL) conditions.^[21,22] Here, the AQ-SAM was characterized using 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM]⁺[OTf]⁻) as electrolyte. The IL was exhaustively dried prior to its use and the CVs were acquired under nitrogen in a glove box to avoid moisture which could lead to the hydroantraquinone (AQH₂) formation. Interestingly, in the CV of the AQ-SAM in the [BMIM]⁺[OTf]⁻

ionic liquid the two reduction processes of AQ-SAM can be observed at $E_1^{1/2} = -0.31$ V ($\Delta E_{pp} = 0.27$ V, SR= 0.1 V/s) and $E_2^{1/2} = -0.61$ V ($\Delta E_{pp} = 0.19$ V, SR = 0.1 V/s) (Figure 2).

The Fc-SAM was prepared by immersing the gold substrate in a 1 mM solution of compound **1** in ethanol for 20 hours under argon atmosphere, at room temperature and light exclusion. The value of the measured water contact angle was of $78.0 \pm 3.4^\circ$, which is in accordance with previously reported values for similar Fc SAMs.^[23] For this Fc-SAM, also an exhaustive electrochemical characterization was carried out employing the electrolytic optimised conditions found for the above-described AQ-SAM, i.e. ACN/NBu₄PF₆, IL [BMIM]⁺[OTf]⁻ and buffer solution (pH = 6.9). The results show stable and reproducible cyclic voltammograms with one oxidation wave in the three electrolytic media. Remarkably, it was observed that the Fc-SAMs are not stable below -0.8 V vs Ag(s) in ACN/NBu₄PF₆, and therefore this electrolyte was discarded for studying the bi-component monolayer.

Table 1 summarises the $E^{1/2}$ measured for the AQ-SAM and Fc-SAM on gold under the three different electrolytic conditions. It is evidenced that the chemical environment has a huge impact on the voltage at which the redox process is observed, elucidating the importance of correctly choosing the conditions in which a redox active monolayer is studied since it can determine the number of states that can be accessed.

In Figure 2, CVs of both mono-component SAMs acquired in the selected electrolytic conditions for the study of the mixed bi-component SAMs are depicted (i.e., buffered solution at pH 6.9 and [BMIM]⁺[OTf]⁻) (see Fig. S5-S6 in ESI for the CV in ACN/NBu₄PF₆). Noticeable, all the redox processes are observed below |0.8 V| vs Ag(s), a voltage window where the SAMs on gold should be stable. Noticeable, there is a clear shift of the AQ reduction redox peaks towards lower voltages when using the ionic liquid.

Table 1. Values in V of $E^{1/2}$ (versus Ag(s)) obtained from both mono-component SAMs in different electrolytes.

	^a ACN/ NBu ₄ PF ₆	^b Phosphate buffer	[BMIM] ⁺ [OTf] ⁻
Fc-SAM	+0.41	+0.35	+0.41
AQ-SAM	-0.78	-0.39	-0.31 -0.61

[a]0.1 M. [b] pH=6.9

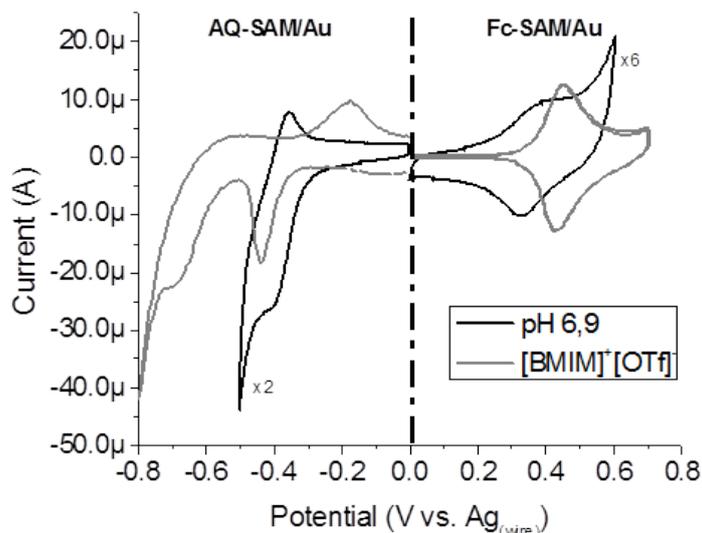


Figure 2. CVs of the mono-component Fc- and AQ-SAMs on gold using as electrolytes: phosphate buffer solution at pH 6.9 (in black) and in the ionic liquid $[\text{BMIM}]^+[\text{OTf}]^-$ (in grey). Scan rate of 100 mV/s. The current intensity is scaled for a more clearly comparison.

The preparation of the mixed SAM was carried out following two approaches: i) from a mixed-component solution (1-step) and ii) sequential immersion in the solution of each component (2-steps). To determine the best methodology and to evaluate the reproducibility, the ratio $\Gamma_{\text{AQ}}/\Gamma_{\text{Fc}}$ of the surface coverage (Γ , mol/cm², See ESI) value was used as indicator. The Γ was extracted from anodic peak of the Fc oxidation wave and from the cathodic peak of $\text{AQ} \leftrightarrow \text{AQ}^{\bullet-}$ process in the ionic liquid $[\text{BMIM}]^+[\text{OTf}]^-$ (Table 2). For the 1-step procedure a freshly cleaned gold substrate was immersed in a mixed solution of the two compounds (in different molar ratios). This route always led to a very low percentage of AQ linked to the surface. This can be attributed to the strongly preferred adsorption of thiols over disulfides, as previously reported.^[24] This is probably due to smaller steric hindrance of thiols to the approach of the molecules to the surface, a lower activation entropy of adsorption, or possibly differences in the rates of conversion of the initially physisorbed species to the chemisorbed thiolate.

For the 2-step procedure, first the freshly cleaned substrate was immersed in a 0.5 mM solution of the AQ **2** in THF for 40 hours, and then, the modified substrate was rinsed and immersed in a 1 mM solution of the Fc **1** in THF at room temperature for 1, 2 and 4 hours under argon. In all cases a good formation of the mixed SAM was observed (see ESI, Figure S7). Importantly, a decrease of the $\Gamma_{\text{AQ}}/\Gamma_{\text{Fc}}$ ratio from 10.0 to 5.0 was observed on increasing the immersion time from 1 to 2 hours. Nevertheless there was not a significant further decrease when the immersion time was increased to 4 hours. Hence, 2 hours was established as the most suitable incubation time for the functionalisation of Fc in the bi-

component SAM preparation. For comparison, the surface coverage values of the mono-component SAM were calculated to be $\Gamma_{AQ} = 2.8\text{E-}10 \text{ mol/cm}^2$ and $\Gamma_{Fc} = 4.0\text{E-}10 \text{ mol/cm}^2$.

Table 2. Surface coverage Γ (mol/cm^2) values calculated for the three mixed-SAMs prepared under different immersion times of the AQ-SAM in the Fc solution.

Immersion time	$\Gamma(AQ)$	$\Gamma(Fc)$	Γ_{AQ}/Γ_{Fc}
1 hour	2.6E-10	2.6E-11	10.0
2 hours	2.4E-10	4.9E-11	5.0
4 hours	2.7E-10	5.2E-11	5.2

The D/A bi-component SAM was also successfully characterized by X-Ray Photoelectron Spectroscopy (XPS) confirming the presence of S2p, Fe2p and O1s (see graphs and assignation in ESI, Figure S8).

Cyclic voltammetry allowed identifying the different accessible redox states in the D/A mixed SAM. The States 1, 2 and 3' (depicted in Figure 1b-c) were electrochemically achieved using the phosphate buffer (pH = 6.9, Figure 3a) and States 1, 2 and 3 employing the ionic liquid $[\text{BMIM}]^+[\text{OTf}]^-$ (Figure 3b). In both cases, we succeed to realise a SAM-based molecular ternary switch using a voltage window below $\pm 0.8 \text{ V}$ (vs Ag(s)), that, as mentioned, is a window voltage where SAMs are stable. Several consecutive voltage sweeping cycles were acquired in both electrolytes without showing a significant decrease of the current intensity in the CVs, which revealed that the SAMs are stable (see ESI, Figure S9). As observed in Figure 3, a shift of the AQ reduction potentials towards more negative values is observed in both electrolytes if compared with the AQ mono-component monolayer which could be attributed to the different chemical environment. For this reason the State 4 depicted in Figure 1b corresponding to coexistence of the dianion form AQ with the neutral ferrocene species (AQ^{2-}/Fc) was not possible to achieve due to desorption of the grafted Fc molecules at the voltage required for the reduction of $\text{AQ}^{\cdot-}$ to AQ^{2-} (see ESI, Figure S10).

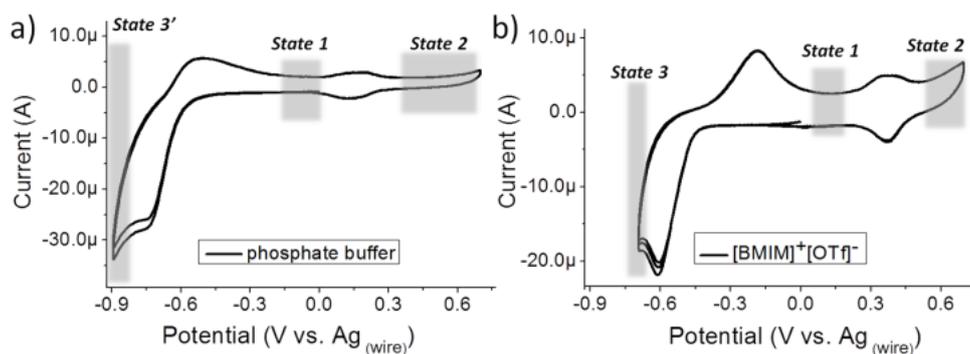


Figure 3. CV of the mixed AQ/Fc SAM on gold using a) the phosphate buffer (pH= 6.9) and b) the IL [BMIM]⁺[OTf]⁻ as electrolyte. Scan rate = 100 mV/s. The shadow areas indicate the different states achieved using the same nomenclature as in Figure 1.

In summary, a mixed electron donor-acceptor self-assembled monolayer has been successfully prepared achieving a 3-state redox molecular switch in a relatively narrow window voltage where SAMs are stable. It has been demonstrated in detail that the choice of electrolyte medium can determine, the potential at which the redox processes occur and, hence, the operational voltage range of the switch. Therefore, this work clearly elucidates the challenges for achieving long-term stable molecular multistate switches employing multiple redox active centres covalently linked to a gold surface.

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