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Abstract

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Keywords

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The detailed characterization of electrochemically switchable molecular assemblies on silicon electrodes†

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In this paper we explore a multi-step synthetic strategy toward fabrication of monolayer-modified Si(100) electrodes that can be electrochemically switched. The synthetic scheme is modular and benefits from an established intramolecular lactonization scheme of benzoquinone analogs. A redox-tagged pendant group can be released from the surface such as to allow for *in situ* monitoring of the switch process. We show that this model system can be used to elucidate chemical and structural events for a surface dynamic system that is rapidly gaining popularity. The influence of polarization times, overpotentials and semiconductor doping type on the kinetic of the switch event is also investigated. In both basic and acidic aqueous electrolytes the release of suitable redox-active markers is found to require unexpectedly large cathodic overpotentials. The release event is accompanied by minor oxidation of the electrode surface and the switched constructs can be regenerated by chemical means with no appreciable deterioration of surface quality.

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1. Introduction

One of the major motivations toward the development of methods to functionalize the silicon surface is the envisioned use of organic/silicon devices in molecular electronics,¹ sensing and optoelectronic applications.² For instance, the ability to modify silicon interfaces with molecular-level control provides access to unprecedented experimental model systems, such as electrochemical devices that can be used in controlling the adhesion and migration of mammalian cells,³ molecular devices that can help in clarifying the role of bacterial binding fibers and antimicrobial peptides,⁴ hybrid heterostructures of organic molecules and semiconductor electrodes for molecular electronic studies,⁵ and interfaces that can clarify the role of surface dipoles on surface hydration.⁶

Being able to provide a chemically stable⁷ interface, without significant defect sites,⁸ is a central requirement of both

molecular electronic devices^{1,9} and sensing interfaces.^{3a,10} In this respect, replacing silicon–hydrogen bonds by silicon–carbon bonds by reactions of 1-alkynes adsorbates with hydride-terminated silicon is a promising chemical route to thermodynamically and kinetically stable interfaces.¹¹ Once protection against oxidative degradation is ensured, orthogonal chemical strategies¹² can be used to precisely adjust the physico/chemical property of these functional surfaces at the same time as retaining the electronic properties of the non-oxidized crystalline silicon surface.^{7c,13}

The dynamic tunability of the chemical properties of an interface is a major target for sensing devices and it has attracted substantial research interest over the last decade.¹⁴ This is largely because relevant biological phenomena, such as cell adhesion or cell migration, involve dynamic environments. An electrode surface where molecular features are controlled by means of an applied bias is greatly desirable in that (i) it will enlarge sensing capabilities; with discrete chemistries available depending on the externally regulated electrode potential, and (ii) it will allow the probing of time-dependent processes triggered by the modulation of molecular features at an interface.^{3b}

Surface-tethered benzoquinone derivatives have played a key role in the development of dynamic model substrates for biological applications,¹⁵ and of particular relevance is the use of a *trimethyl lock*-based lactonization system.¹⁶ The trimethyl lock scheme (Scheme 1)¹⁷ was developed in the 70s to

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Scheme 1 'Trimethyl lock'. Structural requirement for a facile lactonization reaction. The rate of lactonization for **A** is ca. 10^5 times faster than that of **B** (see ref. 17 and 18).

facilitate intramolecular cyclization reactions,¹⁸ and it has more recently seen a renewed interest in the preparation of redox- and phosphatase-sensitive prodrugs.¹⁹ It is also a key component in the preparation of redox-sensitive resins for solid-phase peptide synthesis.²⁰ Yet through quite different approaches, Mrksich and co-workers^{15a,21} and Heath and co-workers²² have used surface-confined trimethyl lock systems to prepare electrochemically-responsive monolayer-modified gold and Si(111) electrodes. Both groups have argued in favor of a very rapid lactonization, *i.e.*, *switch*, in response to modest cathodic potentials; a condition generally compatible with cell culturing. Mrksich and co-workers have shown how the electrochemically-driven release of precise molecular entities from model substrates can be used to probe cellular events such as cell adhesion. The authors draw most of their conclusions on the progress of the electrochemical cyclization reaction in the monolayer from changes in the shape of adherent cells and from mass spectroscopy data. Adherent cells, with typical extended features, were reverted to a rounded morphology if the underlying gold substrate was biased to -700 mV (*vs.* Ag pseudo-reference electrode) for *ca.* 4 min.^{15a} Heath and co-workers have used trimethyl lock amide derivatives as a redox-labile protection for primary amine functions on a surface. They demonstrated the electrochemical removal of the protection by means of reaching sufficiently negative potentials (up to -800 mV *vs.* Ag|AgCl reference electrode, *ca.* -600 mV *vs.* normal hydrogen electrode) in cyclic voltammetry scans. The release of the lactone moiety into the electrolyte solution was intended to leave a putative amine-terminated Si(111) electrode surface. This event was probed indirectly *via* subsequent functionalization with ferrocene carboxylic acid derivatives. As the authors noted, the quality of iron-related emissions in the X-ray photoelectron spectra does not allow for quantification of the iron on the surface. From the Faradaic signal due to immobilized ferrocene units only a very low (*ca.* 0.5%) surface coverage of reactive sites was estimated. More recently, our group has developed a modular and switchable Si(100)-based monolayer system for cell biology studies with at its core a heterobifunctional linker based on the trimethyl lock system.^{3a} We have, however, in contrast with the findings of Mrksich and co-workers and Heath and co-workers, required significantly more cathodic potentials (-1.8 V *vs.* Ag|AgCl|3 M NaCl reference electrode, *ca.* -1.6 V *vs.* NHE) to prompt a complete switch over comparable reaction times.

While several studies now display the scope of the trimethyl lock in dynamic surfaces, the chemical and structural details of

the switch event for the lactonization reaction at surfaces is much less clear. In the majority of published work on this model switchable system only limited kinetic data are available and chemical/structural details on the fate of the underlying films are generally lacking. The purpose of this paper is to report an implementation of the trimethyl lock system on Si(100) electrode surfaces that is primarily aimed to elucidate in detail the release of a surface tethered redox probe. Systematic experiments toward a better understanding of the requirements for this particular switchable system are discussed. The synthesis and application of a modular interface incorporating a synthesized bi-functional redox linker displaying the core trimethyl lock features are detailed by means of X-ray photoelectron spectroscopy, X-ray reflectometry, spectroscopic ellipsometry, cyclic voltammetry and electrochemical impedance spectroscopy. The design of the interface is such that the electrochemically switchable moiety is not released upon the switching event (Scheme 2), and therefore the passivated electrode is amenable to further regeneration.

2. Results and discussion

2.1 Assembly of surface constructs

The modularity of the surface modification strategy depicted in Scheme 2 allows for different surface chemistries to be achieved starting from a common coumarin-derivative, **SAM-2**.^{3a} For this reason the spectroscopic characterization data for both **SAM-1** and for **SAM-2** will be discussed in the context of the properties of **SAM-3**, **SAM-4a/b**, and **SAM-5a/b** samples.

2.1.1 Passivation of the Si(100) surface with monolayers of 1,8-nonadiyne. As reported previously, the thermally-assisted hydrosilylation reaction of diyne **1** by hydrogenated silicon leads to an acetylene-terminated alkenyl-bound monolayer (**SAM-1**). Specular XRR data (Fig. 1a) and XPS (Fig. 2a, Fig. 3a and Fig. S1, ESI†) are in agreement with previous reports.^{6b,11b,23} In brief,²⁴ on the basis of both the refined values of monolayer thickness and electron density, an estimate of the molecular coverage of the silicon surface of $20(3) \text{ \AA}^2$ per grafted molecule of diyne **1** is proposed. This is comparable to the density of *ca.* $21 \text{ \AA}^2$ that can be achieved for SAMs on gold substrates in close-packed Langmuir-Blodgett films.²⁵ Both the refined silicon-organic (σ_{Si}) and monolayer-air (σ_{ML}) interfacial roughnesses were found to be *ca.* 3–4 Å, which reflects a high quality monolayer.

Thickness measurements by ellipsometry are *ca.* 10 Å for **SAM-1** and are comparable with XRR data (Fig. S2, ESI†). In contrast to the complex and debated case of light-promoted hydrosilylation reactions,²⁶ the nature of the dopant appears to have negligible effects on the process of 1-alkynes monolayer formation at hydrogenated Si surfaces by the thermal reactions. No statistically significant differences in monolayer thickness are found between monolayers prepared on either n- or p-type substrates, therefore, only the latter series will be discussed here.

From the refined atomic composition data derived from XPS (Table S1, ESI†) it is possible to calculate the fractional surface

Fig. 1 X-ray reflectometry spectra for organic-modified Si(100) surfaces. (a) Acetylene-terminated monolayers (**SAM-1**), (b) films after the CuAAC reaction of azide **2** with **SAM-1**, (c) ethynylferrocene **4**-functionalized layers (**SAM-5a**), and (d) electrochemically switched **SAM-5a** samples. Refinement of a structural model is shown as a solid line.

Fig. 2 High-resolution XPS spectra of the Si 2p region of surfaces prepared by the thermal reaction of H-terminated Si(100) with diyne **1** (a), after CuAAC reactions with azide **2** (b) and after attachment of 3-azidopropylamine **3a** (c). Si 2p of the electrochemically switchable and redox-tagged **SAM-5a** sample is shown in (d). The takeoff angle between the surface and the analyzer is 90°. The peak fit residuals are shown below the XPS trace.

2.1.2 'Click' attachment of the redox-sensitive linker molecule **2 (**SAM-2**).** The use of an alkyne-terminated Si(100) or Si(111) surface in Cu(I)-catalyzed alkyne-azide cycloaddition reactions (CuAAC or 'click') for the grafting of azide-tagged molecules bearing a range of functional end groups has been detailed extensively in previous works.^{4a,11b,23,29} Si 2p narrow scans acquired from the functionalized surface show no evidence of oxidation of the substrate (Fig. 2b) and preliminary spectroscopic

Fig. 3 High-resolution C 1s XPS narrow scans for the stepwise derivatization of acetylenyl layers. (a) 1,8-Nonadiyne **1** passivated surface (**SAM-1**). (b) Coumarin **2**-modified acetylenyl layers (**SAM-2**). (c) Azide-decorated surface as upon the reaction of 3-azidopropylamine **3a** with the NHS-activated benzoquinone acid surface (**SAM-4a**). (d) Ferrocene-derivatized Si(100) electrodes (**SAM-5a**).

data of **SAM-2** films on Si(100) electrodes have been reported in a previous communication.^{3a} As expected, an increase in nitrogen and oxygen content accompanies the CuAAC procedure (Fig. S3, ESI†). High-resolution XPS scans were acquired and all relevant features for the C 1s and N 1s functions, namely mean binding energies, dispersions (fwhm) and atomic ratios are summarized in Table S1 (ESI†). High resolution N 1s data (Fig. 4a) demonstrate the presence of more than one bonding configuration and are consistent with the formation of a triazole moiety, indicating the fusion of the azido species **2** to the acetylene functionalized surface. As previously reported for immobilized triazoles,^{4a,7c,11b,30} the best fit to the experimental N 1s signal is obtained with a linear combination of two Gaussian curves centered at 401.7 and 400.3 eV and with a 1:2 ratio of the integrated areas (N-N=N and N-N=N ,³¹ respectively). The absence of a peak at *ca.* 404–405 eV, which corresponds to the central electron-deficient nitrogen atom in the azide group,³² suggests that no appreciable quantities of physically adsorbed **2** are present after modification on **SAM-2**.

High-resolution spectra of the C 1s core levels (Fig. 3b) in combination with the N 1s data offer a method to estimate reaction yields for the triazole formation.^{11b} After CuAAC reactions the XPS signature of the functional trimethyl lock group carried by the azide molecule **2** becomes apparent in the C 1s and O 1s narrow scans (Section 3 and Fig. S4, ESI†). Combined quantitative N 1s and C 1s XPS data (C:C:N in Table S1, ESI†) obtained for the clicked **SAM-2** suggest an approximate 55% conversion of surface acetylenes to the corresponding triazoles. Further, from the comparison of XPS- and stoichiometrically-derived O-C=O:N and $\text{O-C=O:(C-O/N, C(O)C)}$ ³³ atomic ratios (Table S1, ESI†) it is possible to infer

Fig. 4 High-resolution N 1s XPS spectrographs for (a) **SAM-2**, (b) azide-decorated **SAM-4a**, and (c) ferrocene-functionalized **SAM-5a** samples. The residuals to the fits are shown beneath each XPS trace.

that the molecular nature of **2** is not appreciably altered upon its immobilization.

Qualitative considerations on the increase of the C 1s/Si 2p atomic ratio (0.38 ± 0.02 for **SAM-1**, 0.76 ± 0.26 for **SAM-2**) indicate an increase in the monolayer thickness after the CuAAC reaction. The attenuation of the silicon signal scales according to the law $\exp(-d_{\text{ML}}/\lambda_{\text{Si,ML}})$ and it can be used to estimate the film thickness after the two-step procedure for the grafting of azide **2**:

$$-d_{\text{ML}}/\lambda_{\text{Si,ML}} (1/\cos \theta) = -\ln(\text{Si } 2p_{\text{ML}}/\text{Si } 2p_{\text{clean}})$$

where Si 2p_{ML} is the integrated area of the Si 2p peak, Si 2p_{clean} is the Si 2p peak area of an unmodified and clean Si substrate, d_{ML} is the thickness of the grafted organic layer, $\lambda_{\text{Si,ML}}$ is the mean free path of Si 2p electrons travelling across the organic film (41.5 Å), and θ is the photoelectron take-off angle with respect to the surface normal. The thickness of the organic layer found by this method is *ca.* 22 Å,³⁴ and is in good agreement with refined XRR data (Fig. 1b, d_{ML} *ca.* 23 Å). Ellipsometric data, on the other hand, would suggest a thinner film (Fig. S2, ESI†, d_{ML} *ca.* 17 Å). Small systematic differences between XRR and ellipsometry data have been previously reported,³⁵ and do not constitute a reason of concern.³⁶

2.1.3 Derivatization of SAMs incorporating the redox-switchable molecule 2. Reactions of activated benzoquinone acid samples with nucleophiles. As an intermediate synthetic step toward **SAM-5**, 3-azidopropylamine **3a** was grafted onto the NHS-activated benzoquinone acid surface (**SAM-3**, Scheme 2). The electron-deficient nitrogen atoms in azido groups of the surface product, **SAM-4a**, is generally a well resolved feature in the N 1s XPS narrow scans with a *ca.* 3 eV separation from the signal due to carbon-bound nitrogen.³² Visible in high resolution N 1s scans (Fig. 4b) is a 404.6 eV peak absent in the lactonized precursor (**SAM-2**). This finding is consistent with the immobilization of the azide **3a** onto **SAM-3**. Curve fitting of the complex N 1s envelope was applied and relevant features of the refined functions are presented in Table S1 (ESI†). The peak area ratio of the 405 eV curve (here referred to as N₄₀₅) to the main contribution in the *ca.* 400–402 eV region (simply indicated as N for clarity) is 0.7:6, close to the stoichiometric ratio of 1:6 expected for an homogeneous array of surface bound molecules. Non-quantitative yields for the stepwise procedure

used in the construction of the interface may account for this minor discrepancy.

The C 1s regions of the XPS spectra is also important in confirming that the alkyl azide **3a** is successfully immobilized onto the oxidized linker derived from **2** (see Section 3, ESI†). In part by using XPS data for **SAM-2** as reference for the carbonyl and nitrogen-bonded carbon assignments, the C 1s peak (Fig. 3c) of **SAM-4a** is fitted to five different contributions: (i) carbon in a carbide configuration (Si–C) at 283.9 eV,³⁷ (ii) a main C 1s signal at 285.0 eV from carbon atoms in an alkyl chain (C–C),³⁸ (iii) oxygen-, nitrogen- and carbonyl-bonded carbon (C–O–N and C(O)C) at 286.3 eV,^{11b,39} (iv) a high energy contribution at 287.7 eV for carbon atoms in carbonyl groups (C=O)⁴⁰ and (v) electron-deficient amide carbons (N–C(O)) at 289.3 eV.⁴¹ Quantitative considerations of the C 1s and N 1s regions support the formation of a **SAM-4a** and representative peak area ratios, such as the N–C(O):N₄₀₅, showed experimental values in very good agreement with those predicted by the stoichiometry of atoms on the surface (Table S1, ESI†). The N:C=O experimental value of 3.1:2 is significantly lower than the stoichiometric 6:2 value and may in fact suggest a non-negligible amount of unreacted NHS-activated intermediates (**SAM-3**).

Despite all the chemical derivatization steps following the passivation of the Si(100) surface with diyne **1** being carried out in aqueous environments, and despite the extensive handling of the samples in air between synthetic steps, essentially no silicon oxide signals were observed in the 102–104 eV region of the Si 2p XPS emission (up to *ca.* 0.06 SiO_x fractional layers, Fig. 2c).^{8b} Again this highlights the effectiveness of the base surface chemistry (*i.e.*, **SAM-1**) in protecting the Si(100) surface from oxidation.

2.1.4 Coupling of ethynylferrocene 4 onto azide-terminated surfaces (SAM-5). In order to devise an experimentally simple tool to quantify, in real-time, the progression of the benzoquinone reduction/hydroquinone lactonization switch sequence we immobilized the redox probe ethynylferrocene **4** onto the distal azide group of **SAM-4a** (Scheme 2). Ferrocene-terminated monolayers are one of the most studied redox-active monolayers systems on metal and semiconductor surfaces,^{13,42} and have been shown to give almost ideal electrochemistry on silicon electrode surfaces.^{30,43} It is central to the design of this

work that any decrease in the number of surface confined ferrocene units does correlate unambiguously with the progress of the switch reaction.

2.1.4.1 Redox constructs incorporating amide links (SAM-5a).

From XPS survey spectra the successful formation of SAM-5a is supported by a set of satellite peaks at *ca.* 715 eV ascribed to the Fe 2p emission, together with carbon-, silicon-, and nitrogen-related signals (Fig. S5, ESI†). Detailed investigation of the N 1s, Fe 2p, and C 1s regions of XPS the spectra (Fig. 3d, 4c and 5a, respectively) further supports successful triazole formation. As evident in Fig. 4c, attenuation at noise levels of the N₄₀₅ emission that was observed in narrow scans of the starting material (SAM-4a, Fig. 4b) is diagnostic of a successful CuAAC reaction, where terminal azide functions are fused with the acetylene of ferrocene 4 (SAM-5a). The experimental N:Fe atomic ratio is 9.1:1 and in satisfactory agreement with the molecular structure of SAM-5a (Table S1, ESI†). While N 1s spectra provide information on the loss of free azido groups, Fe 2p spectra provide information on the attachment of ferrocene 4 onto the same samples. Curve fitting of the experimental XPS Fe 2p signal (Fig. 5a) shows two well-resolved Fe 2p_{3/2} and Fe 2p_{1/2} spin-orbit-split components at 708.2 and 721.0 eV attributed to confined Fe(Cp)₂ species in the product, and suggests predominantly Fe(II) species on the surface with no evidence of high-binding energy satellite signals at *ca.* 711 and *ca.* 724 eV due to Fe(III)-related compounds.⁴⁴

Fig. 3d shows a C 1s narrow scan for the ferrocene-modified SAM, which was deconvoluted into five components and demonstrates the successful attachment of the ferrocene 4 onto SAM-4a to yield SAM-5a. The peak at 285.0 eV can be attributed to aliphatic C–C carbons and carbon atoms from the cyclopentadienyl rings.³⁰ The peak at 283.6 eV results from Si–C carbons. Signals at 286.2 and 287.9 eV are assigned to C–N, C–O, carbonyl-bonded (C(O)C) carbons, and to C=O carbons in benzoquinone carbonyls, respectively. Amide carbons (N–C(O)) appear at 289.3 eV. The experimental C=O:C–N/C(O)C and C=O:Fe ratios were respectively 2.1:6 and 5.2:1, higher than the stoichiometric ratios of 1:6 and 3:1 for the intended product. An explanation for this discrepancy is the presence of unreacted NHS intermediates. Not affected by the presence of NHS derivatives is the N–C(O):Fe ratio, which is 0.8:1 and close to unity as predicted from stoichiometry.

Fig. 5 High resolution XPS Fe 2p scans (a) and cyclic voltammograms (b) for SAM-5a samples.

As substrate oxidation is likely to start at defects in the organic layer,^{7a,45} the absence of a sizable Si 2p band in the 102–104 eV region (SiO_x) is again indicative of an high quality monolayer (Fig. 2d).⁴⁶ The absence of SiO_x signals is despite the fact that all of the surface modification steps downstream from SAM-1 are done in the presence of water; even though oxygen has a key role in the oxidation reaction of the surface it is water molecules that are known to catalyze this reaction.⁴⁷ This is a very encouraging result for future applications of these surfaces.

Fig. S6 (ESI†) shows overlaid cyclic voltammograms (CVs) for the first and 100th cycles (scan rate ν , 0.5 V s^{−1}; potential range, −0.10/0.75 V) in aqueous electrolytes. The figure illustrates a remarkable stability for the ferrocene construct after a minor initial loss.⁴⁸

As displayed in Fig. S7 (ESI†) a linear dependence of the anodic peak current (*I*_{pa}) on ν is diagnostic of a thin-film behavior and supports the formation of SAM-5a. For a diffusionless redox system the peak-to-peak separation (ΔE_p) is expected to approach zero for $\nu = 0$ V s^{−1}.⁴⁹ Presumably due to minor space-charge effects and/or monolayer defects ΔE_p is still 14 ± 3 mV for $\nu = 5$ mV s^{−1} (Fig. 5b).⁵⁰ The dependence of ΔE_p on ν values is shown in Fig. S8 (ESI†). At higher scan rates the peak splitting becomes large in a symmetrical manner; with increasing scan rates both the anodic peak (*E*_{pa}, *i.e.*, the value of *E* at the maximum current value) and the cathodic peak (*E*_{pc}) movements are indistinguishable within experimental uncertainty. This data is indicative of quasi-metallic response of the Si(100) electrode, with a negligible difference in the rates of holes injection and holes extraction between the valence band and tethered ferrocene units.

The apparent formal potential, *E*'₀, extrapolated from voltammograms taken at low scan rates ($\nu = 5$ mV s^{−1}) in 1.0 M perchloric acid solutions is 359 ± 4 mV, a value close to the *ca.* 370 mV that we and others have recently reported for other ferrocene-modified Si(100) and Si(111) electrodes.^{7c,44c} In 1.0 M perchloric acid solutions the fwhm of the oxidative wave at the lowest sweep rate studied (5 mV s^{−1}) is 110 ± 4 mV (121 ± 3 mV for the cathodic wave⁵¹) and indistinguishable, within uncertainty, to the 115 ± 4 mV value observed for shorter constructs previously prepared from Si(100) acetylenyl layers by immobilization of azidomethylferrocene.^{7c} The closeness of the experimental fwhm to the theoretical value of 90.6 mV for identical and isolated ferrocene molecules,⁵² supports the formation of a well-behaved redox film despite the multi-step procedure depicted in Scheme 2. The minor peak broadening is attributed to the repulsion among the positively charged ferricinium moieties upon the oxidation of ferrocene.⁵³

Modular schemes offers great synthetic versatility, however, one of the potential drawbacks of this multi-step chemistry (Scheme 2) is a reduction of the electronic coupling between the redox element and the substrate. For this reason we measured kinetic parameters for the electrode reaction of SAM-5a using both electrochemical impedance spectroscopy (EIS)⁵⁴ and CV methods.⁴⁹ Impedance data are interpreted by fitting the data to equivalent circuit models using the complex

Fig. 6 Representative EIS Nyquist (a) and Bode plots (b and c) for **SAM-5a** samples at either an applied potential $E_{dc} \sim E'_0$ or $E_{dc} = 0$ V. Frequency range was from 100 kHz to 10 mHz. EIS data at $E_{dc} \sim E'_0$ was interpreted by curve fitting the data to the equivalent circuit shown in figure inset. All symbols are experimental data and solid lines are best fits to the data ($\chi^2 < 0.0015$). The rate constant for the electron transfer, k_{et}^o , was 0.65 ± 0.09 s $^{-1}$ ($R_s = 10.7 \pm 0.2$ Ω , $C_{dl} = 0.45 \pm 0.01$ μ F ($\phi = 0.97$), $C_{ads} = 30.10 \pm 3.05$ μ F ($\phi = 0.98$), $R_{ct} = 25416 \pm 3750$ Ω , electrode area was 0.24 cm $^{-2}$).

non-linear least-squares technique included in the frequency-response analysis software.⁵⁵ Fig. 6 shows Nyquist and Bode representations of the impedance data for **SAM-5** at either $E_{dc} \sim E'_0$ in Fig. 6a–b, or at $E_{dc} \sim 0$ V vs. reference in Fig. 6c (E_{dc} , dc offset).⁵⁶ The equivalent circuit used to fit the experimental EIS data at $E_{dc} \sim E'_0$ is shown as an inset in Fig. 6a. For strongly adsorbed electroactive species the relationship between the circuit elements (C_{dl} , double-layer capacitance; C_{ads} , adsorption pseudo-capacitance; R_{ct} , charge-transfer resistance) of the model in Fig. 6a and the kinetic parameters characterizing a redox system has been described in literature.^{43a,57} Both C_{dl} and C_{ads} showed a frequency-dependent

capacitive behavior and were therefore treated as constant-phase elements (CPEs), a mathematical formalism used to model an imperfect capacitor in an electrical circuit. For a CPE the impedance is equal to $1/(j\omega)^\phi Q$, in which ω is the angular frequency, Q is a parameter with the units of $\Omega^{-1} \text{cm}^{-2} \text{s}^\phi$, and ϕ is an exponential term with values between 0 and 1. CPE defines inhomogeneity in the electrochemical system; however, the exact physical origins of the capacitive and conductive components of the CPE element have proven elusive. It is common in literature to correlate the dependence of the CPE capacitance on frequency with increasing roughness of the electrode surface,⁵⁸ or with a resistivity distribution in the film.⁵⁹ We note, however, that in our redox monolayer systems the CPEs behave very similar to a capacitor, as the power-law modifiers have values $0.95 \leq \phi \leq 0.99$, where ϕ equal to unity indicates an ideal capacitor. This ideality is visually evident from Nyquist plots (imaginary vs. real part of the Faradaic impedance, Z'' vs. Z' in Fig. 6a) where plots in the Z'' – Z' plane approach a vertical line in the low-frequency region as C_{ads} and C_{dl} dominate the impedance spectra.⁵⁴ It is likely that both the convenient positioning of E'_0 in a region where ionic permeability is limited,⁶⁰ together with the high monolayer quality are contributing to the remarkably low-leakage character of the SAM. The EIS results can also be presented as Bode-plots (Fig. 6b), which allow for a relative rapid visualization of the kinetic data. At an ac frequency, f , that approaches the time constant of the redox reaction, the slope of Z vs. f plots goes to zero and the value of phase angle reaches a minimum. By approximating the value of C_{ads} by the corresponding Q value, the apparent electron-transfer rate constant, k_{et}^o , can be simply expressed as $k_{et}^o = (2R_{ct}C_{ads})^{-1}$. Using the refined R_{ct} and C_{ads} values, we obtained a k_{et}^o value of 0.7 ± 0.1 s $^{-1}$. This value indicates electron transfer kinetics that are 10- to 200-fold slower than observed for thinner ferrocene films on Si(100) substrates;^{7c,30,61} a difference which can be accounted for in terms of monolayer thickness.⁶² Values of k_{et}^o estimated from peak divergence with ν in CV are no different from those based on EIS measurements.⁶³

At a sufficiently cathodic dc potential ($E_{dc} = 0$ V, Fig. 6c) the phase angle of the Bode plots adopts a sigmoid shape that starts near 0° at high frequency and shifts close to 90° at frequencies of < 100 Hz. An ideal series RC circuit would have the lower-frequency points at 90° because the response is dominated by the double-layer capacitance charging. The EIS data thus suggest a blocking or insulating monolayer that can be modeled using a circuit that does not model a charge-transfer reaction but describes a polarizing electrode^{57d} (i.e. with two terms R_s and C_{dl} in series). Curve fitting results in an interfacial capacity, C_{dl} , of ca. 1.5 μ F cm $^{-2}$ ($\phi = 0.99$).⁶⁴

From the analysis of the area under the CV's cathodic or anodic peaks, the ferrocene surface coverage, Γ , for **SAM-5a** was also determined and found to be $1.71 \pm 0.27 \times 10^{-10}$ mol cm $^{-2}$.⁶⁵ The obtained Γ value is lower than both the theoretical maximum value of 4.8×10^{-10} mol cm $^{-2}$,¹³ and the ca. 3.5×10^{-10} mol cm $^{-2}$ value that we and others have previously reported for densely packed ferrocene films prepared from Si(100) and Si(111)

SAMs.^{7c,30,66} On the basis of the electrochemical data and from the perspective that surface acetylene groups have a foot print of 17–21 Å² (refinement of XRR structural models for SAM-1^{6b,11b}) we can propose an overall extent of conversion (*i.e.*, from SAM-1 to SAM-5a) of approximately 18–22%.

The X-ray reflectivity data for SAM-5a are shown in Fig. 1c. The solid line is calculated from a single-layer model that gave a satisfactory fit to experimental XRR data. The thickness (d_{ML}) of the organic layer was found to be *ca.* 29 Å. Within uncertainty, ellipsometric d_{ML} values ($d_{\text{ML}} = 24 \pm 4$ Å, Fig. S2, ESI†) are comparable to the value determined from XRR data. The measured thickness is slightly smaller than the calculated length of the putative product (*ca.* 35 Å), thus suggesting a possible tilting of the film or roughness factors (or both).

2.1.4.2 Redox constructs incorporating ester links (SAM-5b). With the intent of optimizing both the extent of conversion to the ferrocene surface and the kinetic data for the switch event we did assess the reaction of SAM-4b with ethynylferrocene 4. The reaction product (SAM-5b) was analyzed by cyclic voltammetry to extract Γ values. A representative cyclic voltammogram is shown in Fig. S9 (ESI†) and it indicates Γ values as low as 7.88×10^{-12} mol cm⁻². This figure translates into an approximate 1% reaction yield for the entire synthetic sequence of Scheme 2. Due to these very modest yields further spectroscopic characterization (XPS and XRR) of this “ester” construct was not pursued.

2.2 Electrochemical switch of ferrocene-terminated constructs

XPS, XRR, spectroscopic ellipsometry and cyclic voltammetry were used to follow surface coupling reactions, as well as a means of monitoring the degree of conversion of SAM-5a to its lactonized precursor SAM-2. Most importantly, ferrocenyl units exposed by SAM-5a and SAM-5b afford a convenient way to rapidly assess Γ data, and therefore enable monitoring in real time *via* routine CV experiments the release of the alkyne-tagged ferrocene 4. The switch performance of the redox-sensitive cleavable constructs was evaluated with respect to polarization times, cathodic reductive potentials and doping type.

The electrochemical modulation of the SAMs structure was initially investigated in 1.0 M perchloric acid under an applied bias of –900 mV. It was expected that the cathodic reduction of SAM-5a and the subsequent switch reaction would occur rapidly in acidic solutions⁶⁷ with the working silicon electrode held at –900 mV (*vs.* Ag|AgCl|3 M NaCl).⁶⁸ The CV results shown in Fig. 7a reveal an unexpectedly small conversion to SAM-2 after ~5 min of total polarization time (<50%).

The possibility that the unexpectedly slow switch kinetics could be attributed to depletion of the majority carriers (holes for the p-type electrodes) at potentials cathodic of the semiconductor flat band (E_{FB}) seemed unlikely because of the high levels of dopant used in this study (0.007–0.009 Ω cm). To unambiguously rule out the possibility of space-charge effects hampering the cathodic switch reaction, samples of SAM-5a

Fig. 7 Representative cyclic voltammograms for the electrochemical switch of silicon electrodes (SAM-5a → SAM-2). A reducing potential was created at the working silicon electrode for a specified polarization time (t). CV waves are plotted against polarization times. Electrolyte was 1.0 M HClO₄ and scan rate was 5 mV s⁻¹. (a) Under a bias of –900 mV the reductive cleavage of the amide link in the ferrocenyl functionalized construct was nearly 44% complete after 270 s of total polarization time (the measured ferrocene coverage, Γ , decreased to 1.12×10^{-12} mol cm⁻² from 1.98×10^{-10} mol cm⁻²). With the cleavage process preceding toward the final product (SAM-2) the electrode performances (ΔE_p , E'_0 and peak dispersion) were unchanged within uncertainty. (b) SAM-5a biased at –1800 mV. After 20 s of total polarization time the measured ferrocene coverage, Γ , decreased to 2.05×10^{-12} mol cm⁻² from 1.64×10^{-10} mol cm⁻². Peak fwhm decreased from 109 mV at ($t = 0$) to *ca.* 99 mV. Peak splitting (ΔE_p) were unaltered with polarization times.

were also prepared and switched on highly doped n-type (n^{++} , 0.0014–0.0018 Ω cm) Si(100) substrates. As shown in Fig. S10 (ESI†) the course of Γ values with polarization times was undistinguishable to that observed for p^{++} electrodes (*e.g.*, ~50% after 240 s). Semiconductor space-charge effects do not therefore play sizable effects against the electrochemical reduction of the tethered trimethyl lock in SAM-5a and p^{++} electrodes remain the system of choice for this study.

Due to the slow kinetics found for the switch of construct SAM-5a, we subsequently investigated SAMs incorporating a hydrolytically more liable ester link (SAM-5b). As depicted in Fig. S11 (ESI†) the electrochemically-driven conversion of SAM-5b into SAM-2, the putative product of the switch reaction, was visibly faster than previously observed for SAM-5a.

Nevertheless, as a direct result of the dramatically different redox performances of the two constructs and due to the significantly lower Γ values for **SAM-5b** (Section 2.1.4.2), a rigorous comparison of kinetic data with the intent of correlating the chemical nature of the link to the switch sequence, was not attempted. However, despite the differences between the two systems, a trend can be inferred and the release of immobilized alcohol derivatives is likely to be faster than for the case of primary amines.

The unexpectedly long polarization times required to complete the benzoquinone reduction–hydroquinone lactonization sequence prompted us to investigate the use of more cathodic overpotentials for a rapid release of the ferrocene **4**. Importantly, when the silicon working electrode was held at -1800 mV, a significantly faster switch was observed.⁶⁹ Based on the integrated area of voltammetric waves a $94 \pm 3\%$ conversion of **SAM-5a** to the lactonized precursor **SAM-2** was achieved after 5 s of polarization time (Fig. 7b). The procedure was repeated until a total polarization time (t) of 20 s was reached ($98 \pm 3\%$ extent of conversion), and a representative collection of CVs acquired at the completion of each 5-second chronoamperometric run is displayed in Fig. 7b.⁷⁰

Quantitative electrochemical data on the course of the switch process are supported by spectroscopic analysis of the reaction product. As expected, no evidence of iron-related signals was found in XPS survey scans (Fig. S14a, ESI†) for electrodes biased at -1.8 V for 20 s, showing only oxygen, nitrogen, carbon, and silicon related signals; this is in good agreement with a successful electrochemical reduction of **SAM-5a**. This finding is supported by a closer investigation of the Fe 2p and Si 2p spectral regions. High-resolution Fe 2p spectrographs in Fig. S14b (ESI†) show that the clear emission evident in the precursor (**SAM-5a**, Fig. 5a) is reduced to below the level of detection as the outermost portion of the film is electrochemically removed. Importantly, the passivating properties of the SAM were not significantly altered upon the switch process. Encouragingly, typical XPS Si 2p narrow scans for the switched electrodes, as those in Fig. S14c (ESI†), show minor emissions associated with silicon oxide species (102–104 eV). Estimated SiO_x fractional monolayer coverage varied from a minimum of *ca.* 0.06 to a maximum of *ca.* 0.15 silica sub-layers. Despite the surface modification reactions being performed in the presence of water, and despite the prolonged electrochemical treatment and conspicuous rinsing procedures conducted on the silicon electrodes, minor silica formation is again indicative of a robust and close-packed monolayer (**SAM-1**) that prevents the ingress of oxygenated species to the underlying silicon substrate,^{7a} and/or disrupts the mechanism of oxidation at the surface.⁷¹

In addition, the cathodic cleavage of **SAM-5a** films was monitored by XRR (Fig. 1d) and spectroscopic ellipsometry (Fig. S2, ESI†). The thickness (d_{ML}) of the switched organic layer was 22 Å by XRR methods and 16 Å by ellipsometry. Attenuation of the Si 2p signal by the carbonaceous film also suggests a decrease in monolayer thickness; d_{ML} values are close to 18 Å after the reduction of **SAM-5a** (C 1s/Si 2p atomic ratio is ~ 0.6 , see Section 2.1.2). The thickness value derived

from XRR data is in good agreement with the calculated length of the coumarin **SAM-2** (*ca.* 22 Å), whereas the refined d_{ML} value for the ferrocenyl SAM precursor was 29 Å (Section 2.1.4.1). The decrease in d_{ML} value of *ca.* 7 Å suggested by XRR data indicates a conversion of **SAM-5a** to the lactonized surface and further reinforces voltammetric and XPS evidence for a successful switch of the benzoquinone-containing **SAM-5a**.

2.3 Regeneration of switched electrodes

To demonstrate that both the disappearance of the ferrocene Faradaic current and spectroscopic data (XPS and XRR) were correctly interpreted in inferring a successful switch sequence we did investigate the regeneration of **SAM-5a** from the putative switch product (**SAM-2**).

As described in the previous section, a reducing potential was applied at the working silicon electrode for *ca.* 20 s and the progress of the lactonization reaction was monitored using voltammetry (Fig. S15, top panel, ESI†). Once the conversion of **SAM-5a** to **SAM-2** was judged to be close to completion by integration of CV waves, the chemical procedure depicted in Scheme 2 was then performed on the lactonized electrode to regenerate the ferrocenyl construct (**SAM-5a**). Representative CVs obtained for regenerated electrodes are presented in Fig. S15 (ESI†) (bottom panel). Most importantly, no significant differences were found by mean of cyclic voltammetry between first (parent), second and third generation electrodes (Fig. S15, ESI†). As shown in Fig. S16 (ESI†) XPS analysis of third generation reconstructed electrodes confirmed a high quality ferrocene-terminated film with all relevant spectral features (namely binding energy and fwhm of fitted functions) from C 1s, N 1s, and Fe 2p high-resolution scans (Fig. S16b–d, ESI† respectively) being identical, within the spectrometer resolution, to what observed for freshly prepared electrodes **SAM-5a**. It should be noted however that a population of Fe(III)-related species was evident as two high-binding energy satellite signals at *ca.* 712 and *ca.* 725 eV in the Fe 2p narrow scans of regenerated electrodes (Fig. S16d, ESI†). Ion pairing between residual perchlorate ions and tethered ferricenium units would support the presence of Fe(III) species,⁷² but given the lack of Cl-related emissions in the survey scan of Fig. S16a (ESI†), this explanation is confidently excluded. It is hypothesized that either Fe(III)-surface silanols interactions, or charging of the samples during XPS analysis, are accounting for the high binding energy Fe 2p XPS signal. As shown in Fig. S16e (ESI†), Si 2p high-resolution scans of second and third generation **SAM-5a** constructs suggested partial oxidation of the underlying silicon substrate (*ca.* 0.1 to 0.3 SiO_x fractional monolayers). This finding might partially support the notion of ferricenium units interacting with surface silanols.

As only minor changes in the N : Fe, C=O : C–N and C=O : Fe atomic ratios were found between parent electrodes and regenerated surfaces the robustness of the chemical/electrochemical strategy described here is further supported. Importantly, the assembly of the dynamic film **SAM-5a**, its switch and its regeneration can be confidently interpreted accordingly to the depiction of Scheme 2.

Conclusions

The results presented in this report have demonstrated a general method for the preparation of an electrochemically-responsive SAM on Si(100). A modular chemical procedure, involving among other more conventional coupling strategies, CuAAC reactions, has been described in detail and the prepared silicon electrodes extensively characterized by spectroscopic and electrochemical techniques. The method is robust and experimentally versatile, allowing for the introduction of a range of chemical functionalities onto a hydrogen-terminated silicon substrate and their subsequent quantitative release by electrochemical means. In all cases, either no or minor oxidation of the underlying silicon substrate was observed even after prolonged exposure of the silicon electrode to aqueous and oxidising environments during wet chemical procedures and cathodic/anodic polarization sequences.

The benzoquinone linker *trimethyl lock* concept initially developed by Cohen and Milstien¹⁶ is here adapted through the synthesis of azido coumarin derivative **2** to serve the surface strategy illustrated in Scheme 2. Using modular procedures it has been possible to attach and release a redox marker which allows to accurately monitoring *in situ* the kinetic of the switch process. In sharp contrast with previous reports, a quantitative switch process does require unexpectedly large cathodic potentials. The surfaces produced using this procedure have potential scope in areas such as biochemical and biological sensing, microfluidics and molecular biology; research areas where functional surfaces with dynamic interfacial properties are of great interest.

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