Electronic Supplementary Information for

Oxidative Acetylenic Coupling Reactions as a Surface **Chemistry Tool**

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Experimental

Materials

Materials All chemicals, unless noted otherwise were of analytical grade. Chemicals used in surface modification procedures and electrochemical experiments were of high purity (>99%). Hydrogen peroxide (30 wt.% sol. in water, Sigma– Aldrich), hydrofluoric acid (Riedel-de Haën, 48 wt.% sol. in water), and sulfuric acid (Fluka) used for wafer cleaning and etching procedures were of semiconductor grade or the highest available commercial grade. 1,8-Nonadiyne (1, Alfa Aesar, 97%) was redistilled from sodium borohydride (Sigma–Aldrich, 99+%) under reduced pressure (79 °C, 8–9 Torr) and collected over activated molecular sieves (Fluka, 3 Å pore diameter, 10–20 mesh beads, dehydrated with indicator), and stored under a dry argon atmosphere prior to use. Ethynylferrocene (2, Aldrich, 97%) was purified using column chromatography (Davisil®LC 60Å, 40–60µm) with elution by hexane. Milli-QTM water (>18 M Ω cm) was used to prepare electrolyte solutions and for surface cleaning. Dichloromethane, pyridine, acetone, acetonitrile, ethanol, for surface cleaning and chemical reactions were redistilled prior to use. Azidomethylferrocene **3** was prepared from ferrocenecarboxylic acid according to literature methods.¹ Prime grade single-side polished silicon wafers, 100-oriented (<100> ± 0.05°), p-type (boron), 525 ± 25 µm thick, <0.01 Ω cm resistivity, were obtained from Siltronix, S.A.S. (Archamps, France).

Surface modification

Assembly of the acetylene (SAM-1), ethynylferrocene 2 (SAM-2) and vinylferrocene (control experiment, see below) functionalized surfaces followed the synthetic procedures depicted in Scheme 1. Scheme S1 depict the preparation of SAM-3 using Cu-catalyzed alkyne-azide "click" cycloaddion reactions of SAM-1 with azidomethylferrocene 3.

Assembly of monolayers of 1,8-nonadiyne (SAM-1): Assembly of theacetylenylated Si(100) surface by covalent attachment of the diyne 1 followed a previously reported procedure.² After modification, the silicon wafers were rinsed several times with dichloromethane, ethanol and water before being either analyzed or further reacted with the alkyne molecule 2. The reaction of SAM-1 with the redox olefin vinylferrocene was intended as a control experiment only. "Click" reactions of azide 3 and SAM-1 were aimed to provide a redox assembly (SAM-3) for a comparative study on the effect of the linkage (1,3-diyne vs. 1,2,3-triazole) on the rate of electron transfer. Surface samples had an average size of $10 \times 10 \times 0.5$ mm.

Oxidative coupling of alkyne 2 to acetylene-terminated surfaces (SAM-2): Reaction conditions for the formation of the 1,3-diyne linker at Si(100) electrodes were optimized by screening procedures (methods A-F) adapted from published reports.³

Method A: To a reaction tube containing the alkyne-functionalized silicon surface (SAM-1) were added: (i) ethynylferrocene (**2**; 42 mg, 0.20 mmol), (ii) copper(1) iodide (3.8 mg, 0.02 mmol), palladium(II) acetate (4.5 mg, 0.02 mmol), 1,4-diazabicyclo[2.2.2]octane (24.7 mg, 0.22 mmol) and acetonitrile (10 mL). The reaction mixture was agitated in the dark under air at room temperature for either 10 or 30 min. The prepared samples were then rinsed consecutively with copious amounts of acetonitrile, dichloromethane, ethanol, and water and then rested for a 1-hour period in a 0.05 % (w/v) ethylenediaminetetraacetic acid (EDTA) solution (pH 7.4). Samples were then rinsed with Milli-QTM water before being analyzed.

Method B: The alkyne functionalized surface (SAM-1) and alkyne 2 (42 mg, 0.20 mmol) were added simultaneously to an agitated solution of copper(I) chloride (5 mg, 0.05 mmol) in pyridine (10 mL). Either air or oxygen was then introduced through a frit connected to the inlet tube at a rate of ca. 10 mL/min. The reaction mixture was agitated in the dark at room temperature for 3 h and the prepared derivatized samples then extensively washed as described for method A.

Method C: A solution of copper(I) chloride (26 mg, 0.26 mmol) and N,N,N',N'-tetramethylenediamine (60 mg, 0.52 mmol) in dry dichloromethane (10 mL) was agitated under argon atmosphere for *ca*. 5 min. The alkyne functionalized surface (SAM-1) and alkyne 2 (42 mg, 0.20 mmol) were added rapidly to the solution while bubbling oxygen through it (*ca*. 10 mL/min). The reaction was stopped after 45 min by removal of the modified sample from the reaction vessel. Modified surface samples were washed as described for method A.

Method D: The alkyne functionalized surface (SAM-1) and alkyne 2 (1.4 mg, 0.007 mmol) were added simultaneously to an agitated solution of copper(I) chloride (2 mg, 0.02 mmol) and N,N,N,N-tetramethylenediamine (10 mg, 0.08 mmol) in acetonitrile (10 mL). Either air or oxygen was then introduced through a frit connected to the inlet tube at a rate of *ca*. 10 mL/min. The reaction mixture was agitated in the dark at room temperature for 45 min. Modified surface samples were washed as described for method A.

Method E: The alkyne functionalized surface (SAM-1) and alkyne 2 (1.4 mg, 0.007 mmol) were added simultaneously to an agitated solution of copper(I) chloride (2 mg, 0.02 mmol), N,N,N,N-tetramethylenediamine

(10 mg, 0.08 mmol) and either 1,4-diazabicyclo[2.2.2]octane (10 mg, 0.09 mmol) or 1,8-diazabicyclo[5.4.0]undec-7-ene (15 mg, 0.10 mmol) in acetonitrile (10 mL). The reaction vessel was kept opened to the atmosphere and agitated in the dark and for the specified reaction time (45-90 min). Modified surface samples were washed as described for method A.

Method F: The alkyne functionalized surface (SAM-1) and alkyne 2 (1.4-42 mg, 0.007-0.20 mmol) were added simultaneously to an agitated solution of copper(I) chloride (2 mg, 0.02 mmol) and 1,4-diazabicyclo[2.2.2]octane (10-25 mg, 0.09-0.22 mmol) in acetonitrile (10 mL). The reaction mixture was agitated in air in the dark at room temperature for the specified reaction time (45 min-24 h). Modified surface samples were washed as described for method A.

"Click" attachment of azide 3 to acetylene-terminated surfaces (SAM-3): The "click" immobilization of azide 3 onto SAM-1 followed minor variations of previously reported procedures.⁴ In brief, to a reaction tube containing the alkyne-functionalized silicon surface (SAM-1) were added: (i) azidomethylferrocene (3; 0.7 mM, 2-propanol/water 2:1); (ii) copper(II) sulphate pentahydrate (0.1 equiv) and (iii) sodium ascorbate (7 equiv). Reactions were carried out in the dark at room temperature without excluding air from the reaction environment and stopped after 1 min by removal of the modified sample from the reaction vessel. Modified surface samples were washed as described for removal of the modified sample from the reaction vessel. Modified surface samples were washed as described for method A.

Surface Characterization

X-ray Photoelectron Spectroscopy: X-ray photoelectron spectroscopy measurements were performed on an ESCALAB 220iXL. Monochromatic Al K α X-rays (1486.6 eV) incident at 58° to the analyzer lens were used to excite electrons from the sample. Emitted photoelectrons were collected on a hemispherical analyzer with multi-channel detector at a takeoff angle of 90° from the plane of the sample surface. The analyzing chamber operated below 10⁻⁹ mbar and the spot size was approximately 1 mm². The resolution of the spectrometer was ~0.6 eV. All energies are reported as binding energies in eV and referenced to the C 1s signal (corrected to 285.0 eV). Survey scans were carried out selecting 100 ms dwell time and analyzer pass energy of 100 eV. High-resolution scans were run with 0.1 eV step size, dwell time of 100 ms and the analyzer pass energy set to 20 eV. After background subtraction using the Shirley routine, spectra were fitted with a convolution of Lorentzian and Gaussian profiles as described previously.² When detected, the monolayer coverage of oxidized silicon was calculated directly from the oxidized/bylk Si 2p peak area ratio according to the method described by Webb and co-workers for very thin oxide oxidized/bulk Si 2p peak area ratio according to the method described by Webb and co-workers for very thin oxide overlayers

X-ray Reflectivity: X-ray reflectivity profiles of self-assembled surfaces on Si were measured under ambient conditions on a Panalytical Ltd X'Pert Pro Reflectometer using Cu Ka X-ray radiation ($\lambda = 1.54056$ Å). The X-ray beam was focused using a Göbel mirror and collimated with 0.2 mm pre- and post-sample slits. Reflectivity data were collected over the angular range $0.05^{\circ} \le \theta \le 5.00^{\circ}$, with a step size of 0.010° and counting times of 10 s per step. In order to obtain the quality of data necessary for this study, highly reproducible instrumentation is required with a stable X-ray source and accurate encoding of the angle of the X-ray beam and detector with respect to the sample. Once exposed to air, alignment of the sample on the X-ray reflectometer took approximately 10 minutes prior to measurement. Structural parameters of the prepared surfaces were refined using the MOTOFIT reflectivity analysis software with reflectivity data as a function of the momentum transfer vector normal to the surface $\Omega =$ analysis software with reflectivity data as a function of the momentum transfer vector normal to the surface $Q = 4\pi(\sin\theta)/\lambda$.⁶ The Levenberg-Marquardt method was selected to minimize χ^2 values in the fitting routines. Singlelayer or two-layer models were used to fit the observed data.

Electrochemical measurements: Electrochemical experiments were preformed in a conventional PTFE three-electrode cell with the modified silicon surface as the working electrode, a platinum mesh (ca. 1200 mm²) as the counter electrode, and silver/silver chloride in 3 M sodium chloride as the reference electrode. A rectilinear cross-section gasket defined the geometric area of the working electrode to 24.6 mm². Ohmic contact between the silicon substrate and a copper plate was ensured by rapidly rubbing a gallium indium eutectic onto a close series of marks (emery paper) aimed to expose the bulk of the silicon electrodes. Measurements were performed in air and using 1.0 M perchloris original measurements. Curlis (emery paper) aimed to expose the bulk of the silicon electrodes. Measurements were performed in air and using 1.0 M perchloric acid electrolytes. The cell was enclosed in a grounded Faraday cage during all measurements. Cyclic voltammetry (CV) measurements were performed using a BAS 100B electrochemical analyzer (Bioanalytical Systems, Inc., W. Lafayette, IN). All potentials are reported *versus* the reference electrode. Impedance measurements were performed with a Solartron 1255B (Farnborough, UK) frequency response analyzer interfaced to a Solartron 1287 potentiostat/galvanostat module. Impedance data were collected at 60 frequencies in the frequency range from 0.1 Hz to 0.1 MHz. An ac potential amplitude of 15 mV root mean square was added to the dc potential of the working electrode (E_{dc}). The impedance measurements were performed at a dc potential equal to the apparent formal potential as determined by ac voltammetry experiments.⁷ Both the in-phase (Z') and out-of-phase impedance (Z'') were extracted at the same time from the data and analyzed with the ZView 3.1 and ZPlot softwares (Scribner Associates Inc.) The formalism developed by Laviron to obtain kinetic information⁸ namely the (Scribner Associates, Inc.). The formalism developed by Laviron to obtain kinetic information,⁸ namely, the apparent electron-transfer rate constant, k°_{et} , for the electron-transfer process between tethered redox groups and the conducting substrate, has been here used to determine the rate constants for all of the redox assemblies examined in this study. Electrochemical experiments were performed at room temperature (23±2 °C).



Fig. S1 XPS spectra of monolayers assembled from the diyne 1 on a hydrogen-terminated Si(100) sample (SAM-1). (a) Survey spectrum. (b) Narrow scan of the C 1s region. (c) High-resolution scan for the Si 2p region. Absent from the spectra is the signal associated with SiOx (102-104 eV).



Fig. S2 XRR data showing Fresnel-like decay of a freshly etched, unmodified, hydrogenterminated Si(111) surface.



Fig. S3 XPS spectrographs of ferrocene-derivatized Si(100) surfaces (SAM-2) prepared *via* Pd-catalyzed acetylenic oxidative coupling conditions (method A). (a) XPS survey spectrum. (b) Narrow scan of the Fe 2p region comprising two spin–orbit-split components 3/2 and 1/2. (c) High-resolution Si 2p spectra. (d) High resolution scans of the C 1s region. A sizable contribution to the carbon emission (*ca.* 3.6% of total C 1s) was attributed to adventitious oxidized carbonaceous material (286.8 eV).

SAM / method	<i>E</i> _{1/2} (mV)	$\Delta E_{\rm p}$ (mV) ^b	$\Delta E_{\rm fwhm}$ (mV) ^c	Γ (mol cm ⁻²)	$k^{\circ}_{et}^{d}$ (s^{-1})
SAM-2 / A^e	364.4 ± 11.9	149.1±90.4	326.1 ± 27.2	$2.1\pm1.6\times10^{-9}$	10 ± 9
SAM-2 / D	368.2 ± 2.8	1.2 ± 0.7	104.7 ± 0.3	$2.5 \pm 0.5 \times 10^{-12}$	364 ± 29
SAM-2 / E	360.3 ± 3.5	0.9 ± 0.9	116.9 ± 1.5	$7.3 \pm 0.9 \times 10^{-12}$	372 ± 49
SAM-2 / F ^f	386.2 ± 3.4	1.4 ± 0.8	134.0 ± 5.2	$1.7\pm 0.3 \times 10^{-11}$	376 ± 58
SAM-2 / F ^g	385.1 ± 7.8	8.8 ± 7.1	151.6 ± 9.1	$4.0 \pm 1.7 \times 10^{-11}$	257 ± 36
SAM-3/"click"	377.3 ± 2.7	2.4 ± 0.7	120.7 ± 2.5	$4.3 \pm 0.6 \times 10^{-11}$	119 ± 17

Table S1 Selected electrochemical properties of ethynylferrocene 2- and azidomethylferrocene 3-modified electrodes (SAM-2 and SAM-3, respectively) prepared from acetylenyl Si(100) surfaces^a

^{*a*}All entries were obtained from a minimum of five independently prepared and analyzed electrodes. ^{*b*}E_{1/2} was taken as the average of the anodic and cathodic peak potentials from voltammograms taken at low scan rates (100 mV s⁻¹). ^{*c*}Data voltammograms taken at a scan rate of 100 mV s⁻¹. ^{*d*}Kinetics of the charge-transfer reaction was studied by electrochemical impedance spectroscopy. ^{*e*}Entry 1 in Table 2. ^{*f*}Entry 10 in Table 2. ^{*g*}Entry 13 in Table 2.



Fig. S4 Electrochemical characterization of SAM-2 samples prepared *via* Pd-catalyzed oxidative acetylenic coupling reactions (method A) of alkyne 2 with SAM-1. Figure shows representative voltammograms ((a), v = 100 mV s⁻¹), EIS Nyquist (b) and Bode plots (c-d) at an applied potential $E_{dc} = E_{1/2}$. Frequency range was from 100 kHz to 100 mHz. EIS was interpreted by curve fitting the data to the equivalent circuit of Figure 4. All symbols are experimental data, and solid lines are best fits to the data ($\chi^2 < 0.0015$). The rate of charge transfer, k^{2}_{et} , was 7.1 s⁻¹ ($R_{s} = 24.7 \Omega$, $C_{dl} = 1.77 \mu F$ ($\phi = 0.92$), $C_{ads} = 0.73 \mu F$ ($\phi = 0.89$), $R_{ct} = 971.2 \Omega$).



Fig. S5 Electrochemical characterization of SAM-2 samples prepared by performing four consecutive times the heterocoupling reaction as of Method F (Entry 10 in Table 2). Data voltammograms were taken at a scan rate of 5120 mV s⁻¹. Electrolyte was 1.0 M HClO4. Coverage of electroactive ferrocenyl units, Γ , was 7.22×10^{-11} mol cm⁻², corresponding to a yield for the heterocoupling reaction of 8.7%.



Fig. S6 Linear dependence of the anodic peak current on the scan rate (v) for ethynylferrocene 2-functionalized Si(100) electrodes (SAM-2, method F).



Fig. S7 Representative voltammograms for prolonged CV analysis ($v = 500 \text{ mV s}^{-1}$) of SAM-2 electrodes. Surface samples were prepared according to method F (entry 10 in Table 2). The measured ferrocene coverage, Γ , decreased only marginally to $1.46 \times 10^{-11} \text{ mol cm}^{-2}$ from $1.50 \times 10^{-11} \text{ mol cm}^{-2}$ ($\Delta\Gamma = -2.8\%$). A negligible increase of $\Delta E_{\rm fwhm}$ upon the CV analysis was found (144.0 mV, initial value; 144.9 mV, final value). Electrolyte was 1.0 M HClO₄. Electrode area was 0.246 cm².



Fig. S8 High resolution Si 2p XPS spectrographs for 5 independently prepared and analyzed SAM-2 samples (method F). Despite the chemical derivatization with alkyne 2 being done under oxidative conditions, prolonged exposure to aqueous EDTA solutions and handling of the sample in air, either no (*i.e.* < 0.06, (a)–(c)) or minor (*ca.* 0.1 SiO_x monolayer equivalents, (f)) silicon oxide related signals were observed in the 102–104 eV region; again highlighting the effectiveness of the base surface chemistry (*i.e.* SAM-1) in protecting the Si(100) surface from oxidation.



Fig. S9 EIS Bode plots for SAM-2 (method F, entry 10 in Table 1) and SAM-3 samples. Frequency range was from 100 kHz to 100 mHz. EIS was interpreted by curve fitting the data to the equivalent circuit of Figure 4. All symbols are experimental data, and solid lines are best fits to the data ($\chi^2 < 0.0015$).



Scheme S1 Acetylenyl monolayers as molecular scaffolds toward ferrocene groups irreversibly confined onto Si(100) electrodes. Hydride-terminated Si(100) surfaces were reacted with the neat (terminal) diacetylene species 1 to afford the corresponding hydrosilylation product (SAM-1). Covalently modified acetylenyl surfaces were further reacted to yield redox-active assemblies (SAM-3) through copper(I)-catalyzed alkyne–azide 'click' coupling reactions with substituted azide 3.



Fig. S10 Representative cyclic voltammograms of azidomethylferrocene 3-functionalized Si(100) electrodes (SAM-3) in 1.0 M HClO₄. The scan rates are (a) 100 mV s⁻¹, (b) 500 mV s⁻¹, (c) 2528 mV s⁻¹, and (d) 5120 mV s⁻¹. Currents were normalized to the electrode area (0.246 cm²).



Fig. S11 Prolonged cyclic voltammetry analysis ($v = 500 \text{ mV s}^{-1}$) of SAM-3 in 1.0 M HClO₄ electrolytes. The measured ferrocene coverage, Γ , decreased only marginally to 3.97 $\times 10^{-11} \text{ mol cm}^{-2}$ from 4.13 $\times 10^{-11} \text{ mol cm}^{-2}$ ($\Delta\Gamma = -5.3\%$), and ΔE_{fwhm} increased slightly to 122.3 from 120.4 mV. Electrode area was 0.246 cm².



Fig. S12 Energy-minimized structures (semi-empirical MOPAC calculation, Chem3D Ultra) for the molecules forming SAM-2 and SAM-3. The direct distance (through-space) between the silicon atom and the C-1 of the cyclopentadienyl ring (Cp) was 1.45 nm for SAM-2 and 1.40 nm for SAM-3.

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