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# Silicon (100) surfaces modified by osmium bipyridine complexes

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## Abstract

Tethered osmium bipyridine-pyridine complexes [Os(bpy)2Clpy-R] were prepared from chemically modified non-oxidized silicon (100) electrodes. Pyridinyl groups at the distal end of self-assembled monolayers (SAMs)-modified silicon surfaces were used to coordinatively bind a representative osmium bipyridil complex precursor [Os(bpy)2Cl2]. SAMs presenting the putative osmium ligand were prepared by a step-wise procedure using click reactions of acetylene-terminated alkyl monolayers and isonicotinic acid azide derivatives. The redox properties of the modified Si(100) electrodes were characterized using cyclic voltammetry. 2010 IEEE.

## Keywords

modified, surfaces, complexes, 100, bipyridine, silicon, osmium

## Disciplines

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# Silicon (100) surfaces modified by osmium bipyridine complexes

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**Abstract**—Tethered osmium bipyridine–pyridine complexes [Os(bpy)<sub>2</sub>Clpy–R] were prepared from chemically modified non-oxidized silicon (100) electrodes. Pyridinyl groups at the distal end of self-assembled monolayers (SAMs)-modified silicon surfaces were used to coordinatively bind a representative osmium bipyridil complex precursor [Os(bpy)<sub>2</sub>Cl<sub>2</sub>]. SAMs presenting the putative osmium ligand were prepared by a step-wise procedure using ‘click’ reactions of acetylene-terminated alkyl monolayers and isonicotinic acid azide derivatives. The redox properties of the modified Si(100) electrodes were characterized using cyclic voltammetry.

**Keywords**—component; Si(100) electrodes; 1-alkyne hydrosilylation; self-assembled monolayers; osmium bipyridil.

## I. INTRODUCTION

The design of chemically well-defined and non-oxidized silicon electrodes is of interest in the fields of bioelectronics [1], biosensing [2-4], and molecular electronics [5-6]. To date most of the research effort has been toward the preparation of either ferrocene- or porphyrin-based redox architectures [7-13]. While on the one hand modular (*i.e.* step-wise) approaches appear to be suitable to producing chemically well-defined silicon-based redox SAMs, only a limited number of “wet-chemistry” coupling procedures, nominally amide chemistry-based [10], or Cu(I)-catalyzed alkyne-azide cycloaddition (*i.e.* “click” [14-15]) reactions [8], have been exploited in the preparation of such architectures [16]. We have recently shown that the modification of hydrogen terminated Si(100) using 1,8-nonadiyne **1** (Scheme 1) forms a highly stable monolayer on the silicon surface, [17-18] which protects the underlying silicon from oxidation even in aqueous electrolytes under the influence of oxidising potentials [8-9]. The acetylene-terminated Si(100) surface may then be readily functionalized with a broad range of aryl and alkyl azides [19].

In the present report we discuss a novel “wet-chemistry” protocol amenable to immobilize metal complexes at SAMs-modified silicon surfaces. The protocol is based on ligand exchange reactions (LER) involving monodentate ligand centres tethered on chemically modified and non-oxidized Si(100) substrates. We note that ligand exchange reactions at a surface are at present largely unexplored, as most often LER are performed prior to the attachment of the redox molecule onto the solid substrate [20-21].

One of the few available studies describing the use of LER at chemically modified electrodes is by Moreira and co-workers and details the post-functionalization of Au-thiol

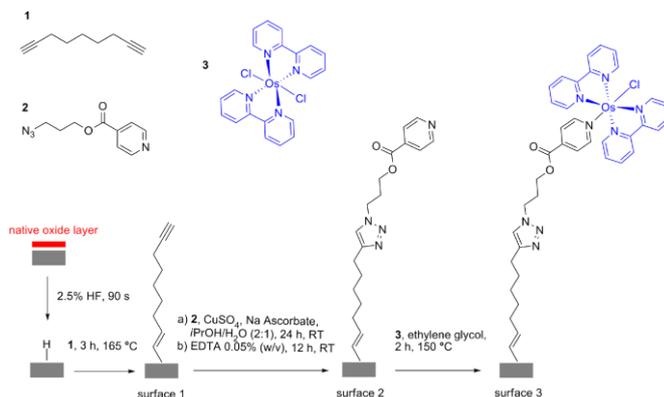


Figure 1. Ligand exchange reactions at Si(100) immobilized pyridine ligands

SAMs *via* the coordination of  $\pi$ -donor transition metal centers [Ru(CN)<sub>5</sub>]<sup>3-</sup> to the nitrogen atom of a pyridine ring in 4-mercaptopyridine SAMs [22]. It is envisioned that analogous chemical approaches would allow for the preparation of a range of redox architectures, based on a multitude of transition metals, derived from a common ligand-modified substrate precursor.

Toward this goal we have recently reported the use of isonicotinic acid-modified Si(100) electrodes for the direct electrochemistry of cytochrome *c* [1], and in the following we detail on the use of these electrodes for the “wiring” of osmium complexes [Os(bpy)<sub>2</sub>Cl<sub>2</sub>] onto the electrode surface by displacement of a chlorine atom and insertion of tethered pyridine ligands (R–py) (Figure 1).

## II. EXPERIMENTAL SECTION

**General:** All chemicals, unless noted otherwise, were of analytical grade and used as received. Chemicals used in surface modification procedures and electrochemical experiments were of high purity ( $\geq 99\%$ ). Hydrogen peroxide (30 wt.% sol. in water, Sigma-Aldrich), hydrofluoric acid (Riedel-de Haën, 48 wt.% sol. in water), and sulfuric acid (J. T. Baker) used in wafers cleaning and etching procedures were of semiconductor 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

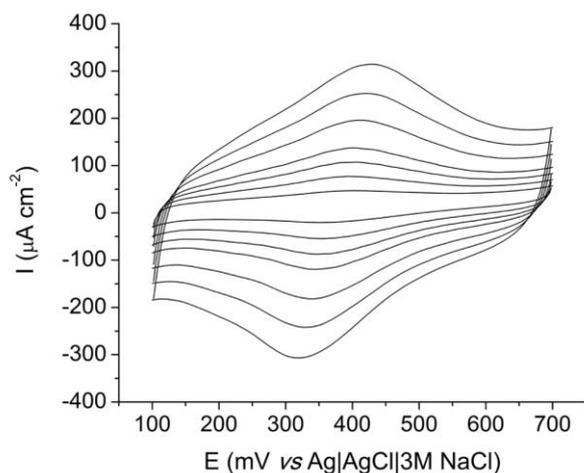


Figure 2. Cyclic voltammetry of Si(100)/isonicotinate ligands/[Os(bpy)<sub>2</sub>Clpy]<sup>+</sup> systems (surface 3). Potential sweep rate was varied from 500 to 5000 mV s<sup>-1</sup>.

argon atmosphere prior to use. Milli-Q™ water (> 18 MΩ cm) was used to prepare solutions and for chemical reactions. Dichloromethane, light petroleum (b.p. 60–80 °C), 2-propanol, ethanol, and ethyl acetate for surface cleaning, chemical reactions and purification procedures were redistilled prior to use. Anhydrous solvents used in chemical reactions were purified as follows: (a) *N,N*-dimethylformamide was distilled under reduced pressure from calcium hydride; (b) tetrahydrofuran was distilled from sodium using a benzophenone indicator. *p*-Toluensulfonyl chloride (Sigma-Aldrich, 98%) was recrystallized from chloroform/hexane. Sodium azide (Sigma-Aldrich, 98%) was crystallized from water by the addition of ethanol. 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). The synthetic procedure for the preparation of the isonicotinic acid derivative **2** in three steps from commercially available isonicotinic acid has been detailed in a previous report. Synthesis of Os(bpy)<sub>2</sub>Cl<sub>2</sub> **3** followed the procedure of Leech and co-workers [23]. Surface modification procedures are schematically depicted in Figure 1.

**Assembly of monolayers of 1,8-nonadiyne **1** (surface 1):** Assembly of the acetylenylated Si(100) surface by covalent attachment of the diyne **1** followed a previously reported procedure. After modification, the silicon wafers were rinsed several times with dichloromethane, ethanol and water before being either analyzed or further reacted with the azide molecules **2** and **3**.

**Attachment of azide molecule **2** to the acetylenyl surface (surface 2):** In a typical ‘click’ procedure, to a reaction vial containing the alkyne-functionalized silicon surface (surface 1) were added (i) the azide molecule (**2**, 10 mM, 2-

propanol/water, 2:1), (ii) copper(II) sulfate pentahydrate (1 mol% relative to the azide) and (iii) sodium ascorbate (10 mol% relative to the azide). Reactions were carried out at room temperature, in the dark without excluding air from the reaction environment and stopped after 24 h by removal of the modified sample from the reaction vessel. The prepared surface-bound [1,2,3]-triazoles samples (surfaces 2) were rinsed consecutively with copious amounts of water, ethanol, dichloromethane and then rested at room temperature for a 12-hour period in a 0.05% (w/v) ethylenediaminetetraacetic acid solution (pH 7.4). Samples were then rinsed with copious amounts water before being further reacted.

**Os(bpy)<sub>2</sub>Cl<sub>2</sub> **3** immobilization (surface 3):** The coordination of Os(bpy)<sub>2</sub>Cl<sub>2</sub> **3** onto the isonicotinic acid modified electrodes followed a procedure analogous to that of Meyer and co-worker for the ligand substitution of a chloride in the complex **3** by 4-(aminomethyl)pyridine in refluxing ethylene glycol solutions of the ligand and complex [24]. In brief, the modified silicon surface (either surface 1 or surface 2) was immersed in a degassed (purged with argon gas) solution of Os-complex (**3**, 10 mM, ethylene glycol). The solution was heated at 150 °C for 2 h. The electrode was then removed from the solution, rinsed with ethanol, Milli-Q™ water, 20 mM sodium phosphate buffer (pH 7.0), and mounted into the electrochemical cell (see below).

**Electrochemical measurements:** All the electrochemical measurements on the putative pyridine-ligated assembly (surface 3) were performed in air in 100 mM potassium chloride electrolyte. All electrochemical experiments were performed in a conventional PTFE three-electrode cell with the modified silicon surface as the working electrode, a platinum mesh 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 mm<sup>2</sup>. 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. The cell was enclosed in a grounded Faraday cage during all measurements. Cyclic voltammetry (CV) was performed using a BAS 100B electrochemical analyzer (Bioanalytical Systems, Inc., W. Lafayette, IN). All potentials are reported versus the reference electrode. Electrochemical experiments were performed at room temperature (23 ± 2 °C).

### III. RESULTS AND DISCUSSION

Detailed spectroscopic characterization of the acetylene-terminated surface (surface 1) and of the ‘clicked’ product (surface 2) have been reported previously [1,17]. With regards to the ability of achieve the coordination of the metal centre in **3** and the tethered pyridine unit of surface 2, initial control experiments were performed on surface 1. Importantly, no Faradaic signal is observed in cyclic voltammograms for the acetylene-terminated electrode reacted with complex **3** under the conditions of section II. The inability to observe a Faradaic response for the acetylene-modified electrode was interpreted as lack of reactivity of **3** toward surface ethynyl moieties.

Figure 2 shows the typical cyclic voltammogram of electrodes functionalized with ester **2** (surface 2) after LER

with precursor **3**. Well-defined redox-waves for the Os<sup>2+/3+</sup> transition were observed at voltage potential sweeps ( $v$ ) in the range 500–5000 mV s<sup>-1</sup> and support the formation of the putative ligated product (surface 3). The apparent formal potential,  $E^{0'}$ , extrapolated from voltammograms taken at low  $v$  values was 375 mV and intermediate between the *ca.* 440 mV  $E^{0'}$  value that Szunerits and co-workers have reported for carboxyl-terminated (R-COOH) boron-doped diamond electrodes functionalized via amide chemistry (R-C(O)NH-R) with amine-terminated Os-complexes [Os(bpy)<sub>2</sub>-Cl(py-CH<sub>2</sub>-NH<sub>2</sub>)<sup>+</sup>], and the  $E^{0'}$  value of 290 mV reported for chemically analogous (R-CO-NH-Os-complex) glassy-carbon-based systems prepared by Leech and co-workers. The surface coverage of electroactive Os-complex was determined by integration of the charge under the anodic peak for background-subtracted CVs. Using this method we estimated the surface coverage to be  $3.5 \times 10^{-11}$  mol cm<sup>-2</sup>, a value close to the  $1.8\text{--}3.3 \pm 0.2 \times 10^{-11}$  mol cm<sup>-2</sup> values reported for different modification of gold electrodes with [Os(bpy)<sub>2</sub>Clpy]<sup>+</sup> complexes [20]. The surface coverage by osmium redox species in all cases is lower than the maximum coverage of *ca.*  $9 \times 10^{-11}$  mol cm<sup>-2</sup> for a closed packed structure on the basis of molecular size [20].

Furthermore, an analysis of the change in peak currents as a function of voltage sweep rate  $v$  allows assessing that the osmium moieties are surface bound rather than physically adsorbed onto surface 2. Figure 3 shows that the anodic peak current scales linearly with the sweep rate  $v$  rather than with  $v^{1/2}$ , indicating a surface redox process and supporting the formation of the surface metal complex [Os(bpy)<sub>2</sub>Clpy-R] (surface 3, Figure 1).

We note that there is clear evidence for electrochemical nonideality of the Os/isonicotinate film/Si redox system, in particular concerning a large dispersion of the voltammetry peaks. The experimental fwhm had an average value of 146 mV, and we hypothesize that the lack of ideality is related to either inhomogeneous attachment of the Os-complex to the pyridine-terminated monolayer or to a weak repulsive interaction between the surface sites leading to a distribution in  $E^{0'}$  values.

Quantitative information on the kinetic of electron transfer for the Os-modified electrode (surface 3) were obtained via cyclic voltammetry using the Laviron treatment [25-26]. An apparent value for the electron-transfer rate constant,  $k_{et}$  was approximated to *ca.* 70 s<sup>-1</sup>. This  $k_{et}$  value was close to the *ca.* 98 s<sup>-1</sup> reported by Fainstein and co-workers for osmium bipyridine-pyridine complexes covalently immobilized onto carboxylic acid-terminated alkanethiol SAMs on gold electrodes [20].

#### IV. CONCLUSIONS

The results presented in this report have demonstrated the step-wise preparation of novel redox devices on Si(100) electrodes using a representative organometallic in ligand exchange reaction between osmium complexes and tethered pyridine ligands. This is the first example of direct reaction between organometallic complexes and immobilized ligands onto non-oxidized silicon surface.

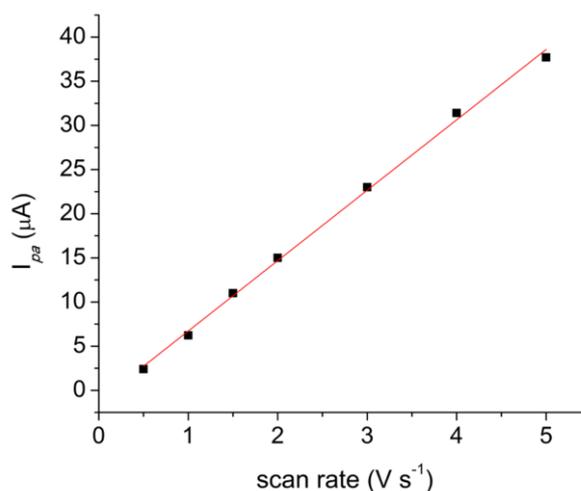


Figure 3. Linear dependance of the anodic peak current on the voltage scan rate for surface 3 electrodes..

The ability to coordinate the osmium centre by pyridine moieties present at the distal end of functional Si(100) monolayers provide a model system to investigate electron-transfer processes at non-oxidized semiconductor surfaces, and open possibilities for envisioned nanoscale bioelectronics devices based on well established organometallic reactions.

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