

Redox-Active Organometallic  $\pi$ -Conjugated Wires and Their Covalent Immobilization on Oxide-Free Hydrogen-Terminated Silicon Surfaces

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The modification of conducting surfaces at the molecular level with redox-active "building blocks" constitutes a powerful approach to the fabrication of such materials, particularly when the goal is integrated systems devoted to information storage or transfer. For such applications, technologically relevant semiconducting surfaces, such as doped silicon, constitute particularly attractive substrates. In this context, oxide-free, hydrogen-terminated silicon (Si-H)<sup>1</sup> surfaces covalently derivatized with redox-active molecules (ferrocene,<sup>2</sup> metal-complexed porphyrins,<sup>3</sup> etc.) have been prepared and examined to determine if molecular memories could result from such electrically addressable hybrid junctions.

In parallel with these studies, there have been relevant developments with redox-active carbon-rich group 8 organometallics. These compounds are ideal candidates for reversible charge storage at the molecular level,<sup>4</sup> and different groups have independently established that both homo- and hetero-polynuclear representatives of this class of molecules can be anchored on conducting silicon<sup>5</sup> or gold<sup>6</sup> interfaces. In complementary studies in the field of optics, we have also demonstrated that electrochemical generation of the various redox congeners of mononuclear Fe(II) **1<sub>n</sub>** (Scheme 1) and dinuclear Fe(II)/Ru(II) **2**  $\sigma$ -aryl acetylides provides a means to modulate the linear and non-linear optical (NLO) properties of these compounds.<sup>7</sup> These studies complement some reports on other electroactive metallic complex-incorporating systems in which the NLO properties can be controlled electrochemically. Taken together, these developments strongly suggest that hybrid junctions incorporating such carbon-rich molecules offer significant potential for realization of a variety of electrochemically controllable optical devices.

In view of these stimulating prospects, we will demonstrate herein that the **1<sub>n</sub>** and **2** complexes can be grafted onto Si-H surfaces through Si-C=C- bonds. The successful covalent assembly of other redox-active dinuclear ferrocenyl/Ru(II) alkynyl complexes (**3** and **4**) on Si(111)-H surfaces using the same alkyne-based hydrosilylation chemistry will be also described.

Compared with **1<sub>n</sub>** and **2** complexes, the use of the ferrocenyl center instead of the organoiron(II) center has been motivated in order to increase the kinetic stability of the first oxidized state in these electroactive assemblies. Furthermore, the ferrocenyl center does not possess the rigidity of the phenylethynyl group as the cyclopentadienyl (Cp) ring can freely rotate around the Fe-Cp axis. This difference might influence both the efficiency of the grafting on Si(111)-H and the electrochemical properties of the resulting modified surfaces. The electron-transfer characteristics of these modified surfaces (Figure 1) will be discussed in connection with available literature data on related ferrocene-based analogous interfaces.

**Scheme 1.** Redox-active mono- and dinuclear organometallic complexes. The terminal unit binding to the Si(111)-H surface is highlighted in bold.

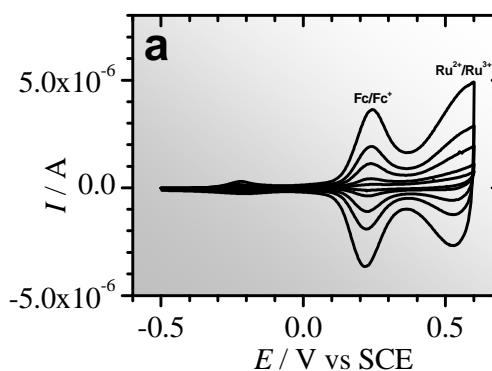
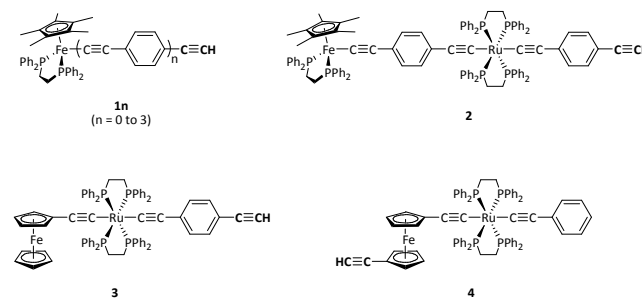


Figure 1. Cyclic voltammograms in  $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NClO}_4$  of **Si-3** at 0.1, 0.2, 0.4, 0.6 and  $1 \text{ V s}^{-1}$ .

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