Electrochemical Oxidation of a Galvinol-Substituted Alkanethiol Monolayer

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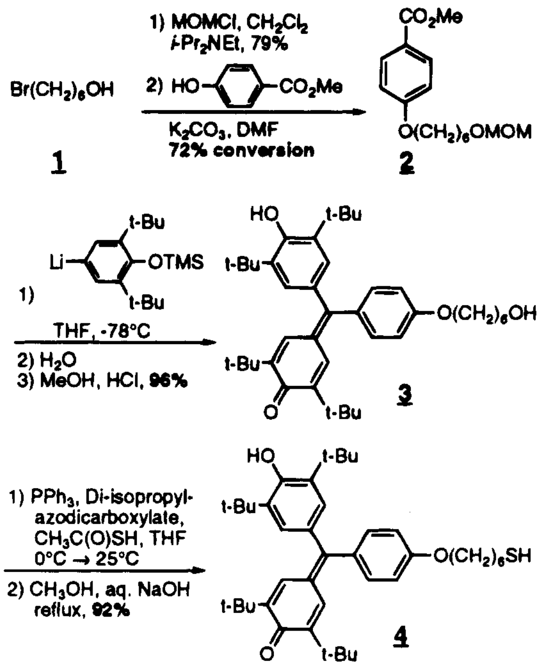
Summary: The preparation of a galvinol-substituted alkanethiol is described. The molecule forms monolayers on gold electrodes and may be oxidized via a one-electron/one-proton process to the corresponding stable free radical.

The preparation of organic-based magnetic materials is a challenge that is important to a number of chemistry-related fields and technologies.[1] The initial focus in the manufacture of organic magnetic materials is the preparation of paramagnetic compounds containing structural features that will induce order among the spins of the molecules. Therefore, design elements must include (1) stable organic species with unpaired electrons and (2) molecular ordering induced by intermolecular interactions. There are several choices for stable, paramagnetic organic species. Galvinoxyl and aryl-substituted galvinoxyls are known, stable organic radicals.[2] Moreover, crystals of galvinoxyl show strong ferromagnetic tendencies.[3] These properties indicate that they may be suitable components for preparing organic magnetic materials. Likewise, there are many vehicles for inducing molecular order. Among these are self-assembled monolayers (SAMs). Indeed, SAMs of alkanethiols on gold films are known to be close-packed, ordered structures.[4]

Our goal is to prepare stable, free-radical-substituted alkanethiol SAMs as molecular magnetic materials. Intermolecular coupling of galvinoxyl radicals has only been observed in the crystalline state. However, the ferromagnetic intermolecular interactions are destroyed by a phase transition near 83 K.[3] It remains to be seen if self-assembly of galvinoxyl-terminated species results in intermolecular coupling similar to (and eventually better than) that observed in the crystalline state. If so, such interactions can be relatively easily altered by changing the length of the methylene chain separating the head and tail groups. That is, engineering of a two-dimensional surface should be easier than three-dimensional crystal engineering. The order of the self-assembled monolayer, coupled with the tendency of galvinoxyl radicals to interact in a ferromagnetic fashion, may yield fascinating new materials. Herein, we report the preparation and electrochemical oxidation of the first stable, organic, free-radical-terminated alkanethiol monolayer.[5]

The preparation of a phenoxygalvinol-substituted alkanethiol is shown below. Commercially available 6-bromohexanol is protected using methoxymethyl chloride. The protected bromide is then used as an alkylating agent for methyl 4-hydroxybenzoate in DMF solvent with potassium carbonate as base. Ester **2** is transformed into galvinol **3** using the modified[6] procedure of Kurreck.[7] Compound **3** is converted to thiol **4** using Mitsunobu conditions[8] followed by alkaline hydrolysis. Using this methodology, several molecules may be prepared with varying methylene chain size. Alternatively, the phenoxy



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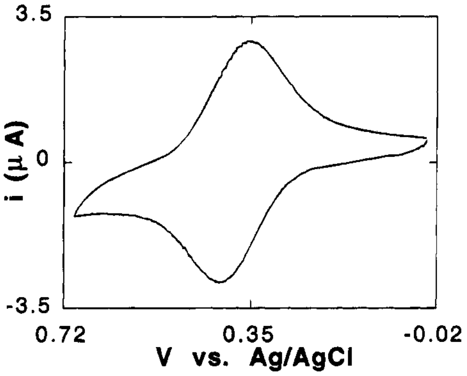

Figure 1. Cyclic voltammogram of thiol **4** adsorbed on a gold film. The voltammogram was recorded in pH 7 phosphate buffer using a platinum auxiliary electrode, a Ag/AgCl/saturated KCl reference electrode, and a scan rate of 200 mV/s.

group can be removed and the alkane chain simply terminated with a galvinol group.

Thiol **4** has been characterized by IR spectroscopy, mass spectrometry, and ^{1}H and ^{13}C NMR spectroscopy. Pertinent features of the IR spectrum include a sharp phenol $-$OH stretch at 3621 cm^{-1} and a weak $-$SH stretch at 2558 cm^{-1}.

Gold substrates consist of polycrystalline gold deposited on glass slides. Monolayer preparation follows standard procedures. First, the gold surface is cleaned by exposing the substrate to hot nitric acid for a few minutes, rinsing with deionized water, and then rinsing with absolute ethanol. Next, a few milliliters of a 20 mM ethanol solution of **4** are pipetted into a clean glass weighing bottle containing a gold substrate. The substrate can also be coated after mounting in an electrochemical cell. After at least 15 min, the coated surface is thoroughly washed with ethanol to remove excess alkanethiol and then dried with a stream of argon. The coated substrate is then ready for characterization.

Cyclic voltammograms of the coated substrates are typical of an adsorbed electroactive species exhibiting quasireversible electron transfer rates[9] (see Figure 1). The voltammetric response is unaffected by (1) rinsing the substrate with ethanol repeatedly, (2) exposing the gold substrate to the alkanethiol solution for longer times, and (3) scanning repeatedly. Also, galvinols without thiol groups do not adsorb onto gold substrates. As for adsorbed species, the peak currents are directly proportional to scan rate. Surface coverage as estimated from the area under the voltammetric curve indicates that a full monolayer is formed. This conclusion is based on a 100 Å^2 area of the phenyl galvinoxyl tail group and on a geometric area of the gold electrode.[10]

The voltammetric response is for the galvinol/galvinoxyl couple.[11] This conclusion is supported by the dependence of the redox potential on pH according to the equation below.

$$\mathrm{GalH} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Gal}^\bullet + \mathrm{H}^+$$

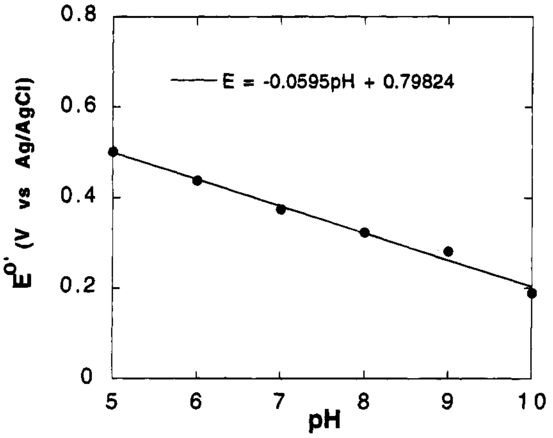

Figure 2. Plot of $E^{0\prime}$ versus pH for thiol **4** adsorbed on a gold film. Voltammograms were recorded using a platinum auxiliary electrode, a Ag/AgCl/saturated KCl reference electrode, and a scan rate of 100 mV/s. We assume $E^{0\prime} = (E_{\mathrm{p,a}} + E_{\mathrm{p,c}})/2$.

According to the Nernst equation, a plot of $E^{0\prime}$ vs pH should give a straight line with a slope of -59 mV/pH unit for a one-electron/one-proton process. The plot in Figure 2 shows this to be the case.

$$E^{0\prime} = E - 0.059 \log \frac{[\mathrm{Gal}^\bullet]}{[\mathrm{GalH}]} - 0.059\mathrm{pH}$$

In summary, galvinol-substituted alkanethiols can be prepared in excellent yield. Electrochemical results suggest that a monolayer is formed upon exposing gold-covered glass slides to ethanol solutions of the alkanethiol. The monolayer is electroactive, and the voltammetric response corresponds to a one-electron/one-proton transfer yielding, after oxidation, a radical-terminated monolayer. Further characterization of this monolayer is underway.

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Supplementary Material Available: Experimental procedures, spectral data, and cyclic voltammograms (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[10] The surface coverage was estimated from the area under the voltammetric curve and corresponds to ca. 2 × 10^{-10} mol/cm^2. The area of the tail group was estimated using molecular models and recent crystal structural data of the isostructural Yang's Biradical: Bock, H.; John, A.; Havlas, Z.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 416. Considering the size of the tail group and the short length of the alkane chain, the monolayer is undoubledly disordered. Characterization of this monolayer as well as the preparation of longer chain galvinol-terminated alkanethiols is underway.

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