

**Synthesis of a Rigid
Dimethoxynaphthalene–Spacer–Dithiol Which
Spontaneously Attaches to Au and Pt Electrodes:
Properties of Monolayer Films in Nonaqueous Solvents**

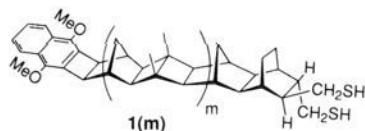
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Self-assembled monolayers (SAMs) of thiolates on metal surfaces, particularly gold, are the focus of intense investigation, partly because electroactive SAMs constitute an important strategy in the modification of electrode surfaces.¹ To date, the majority of studies has been carried out on *n*-alkanethiolates possessing electroactive headgroups such as ferrocene and Ru-(NH₃)₅.² *n*-Alkanethiol chains suffer, however, from conformational mobility which leads to undesirable properties such as structural defects in the SAMs and nonuniform distances between the headgroups and the metal surface. A partial solution to this problem is the use of thiols comprising rigid hydrocarbon chains, and, indeed, SAMs constructed from the rigid *n*-staffanedithiol system have been recently reported.^{2b} If the rigid spacers were to be anchored to the electrode by two or more attachment points, it is conceivable that the goals of distance and orientation control of the electroactive monolayer might be achieved without dependence on neighbor–neighbor interactions, i.e., without the need for “self-assembly”.

An intriguing series of molecules which may serve these needs is **1**(*m*), in which an electroactive group, in this case dimethoxynaphthalene (DMN), and two mercaptomethyl groups are attached to a rigid polynorbonyl bridge of variable but well-defined length.³ Two attractive features of the system **1**(*m*) are



its rigidity and the opportunity provided by the two thiol groups for two-point attachment of the molecule to the metal surface. This should lead to uniform, well-defined, headgroup–metal orientation and separation in the monolayer film, as in **2**.⁴ One might also anticipate an enhanced stability of the film in nonaqueous solvents (most electrochemical studies of SAMs

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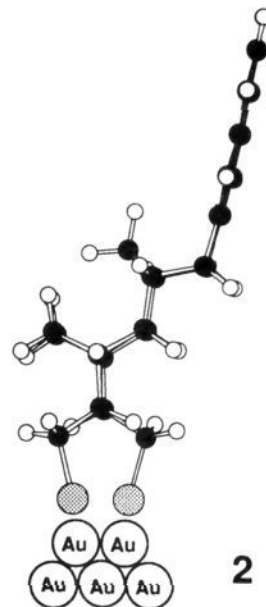
[‡] University of Vermont.

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(4) The geometry of **2** was obtained through MM2 optimization.



carried out to date have used aqueous media⁵). Herein we report the successful synthesis of the first member of the series, namely **1**(0). Monolayer films of **1**(0) attached to Au and Pt electrodes were found to be surprisingly stable in CH₂Cl₂ and THF and to undergo a chemically reversible one-electron oxidation.

The synthetic strategy is shown in Scheme I and begins with Diels–Alder reaction of tetrachlorodimethoxycyclopentadiene to the readily accessible **3**,^{3d} to give the adduct **4**. Reductive dehalogenation (Na, *i*-PrOH), followed by treatment with DDO (to rearomatize the naphthalene ring^{3a}) and deketalization, gave **5**. Ketone **5** readily underwent cheletropic loss of CO (refluxing toluene), and the resulting 1,3-diene was trapped in situ by dimethyl fumarate to give a Diels–Alder adduct which afforded **6** after catalytic hydrogenation. Conversion of **6** into **1**(0) was achieved through reduction to the diol (LiAlH₄), formation of the bis-tosylate (TsCl, pyridine), and conversion of this material into the bis-thioacetate (CH₃COSK, DMSO), followed by reduction (LiAlH₄) to give **1**(0) in 25% overall yield from **3**.⁶

When a polycrystalline gold electrode⁷ is exposed for a brief time⁸ to a 1 mM solution of **1**(0) in CH₂Cl₂/rinsed with the same solvent, and inserted into a new CH₂Cl₂/0.5 M [Bu₄N][PF₆] solution, a chemically reversible oxidation/reduction pair of peaks is observed by cyclic voltammetry (Figure 1a). The *E*_{1/2}, 0.54 V vs Fc, is as expected for one-electron oxidation of the DMN headgroup.⁹ The anodic and cathodic peak currents are both proportional to scan rate from 0.05 to 10 V/s, diagnostic of a surface-confined species.¹⁰ The values of the full width at half-height and Δ*E*_p (at *v* < 0.50 V/s) of ca. 145 and 25 mV, respectively, are somewhat larger than theory¹⁰ for a single-site reversible charge transfer, as has been frequently observed for surface species.^{2a,7a,11}

Surface coverages, Γ, calculated from voltammograms, are in the (3–5) × 10⁻¹⁰ mol/cm² range, consistent with monolayer

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(6) Representative physical data for **1**(0) are in the supplementary material.

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(8) Monolayer coverage is essentially complete within 5 min.

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Scheme I

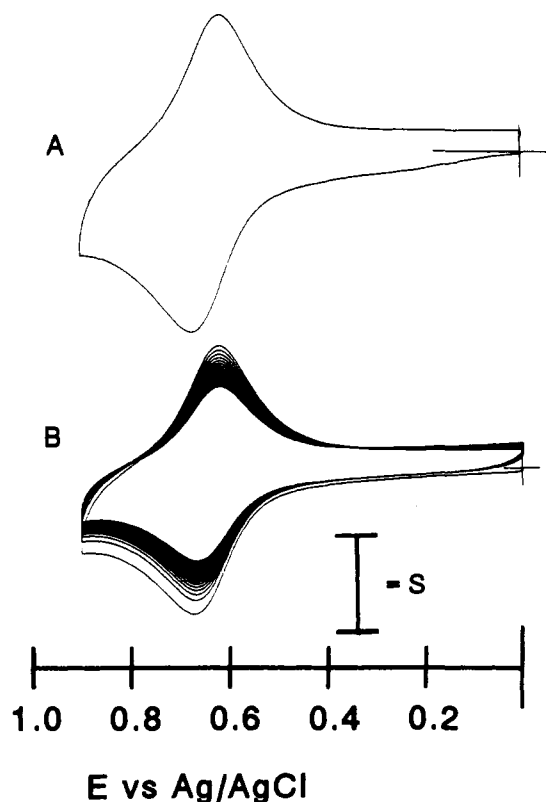
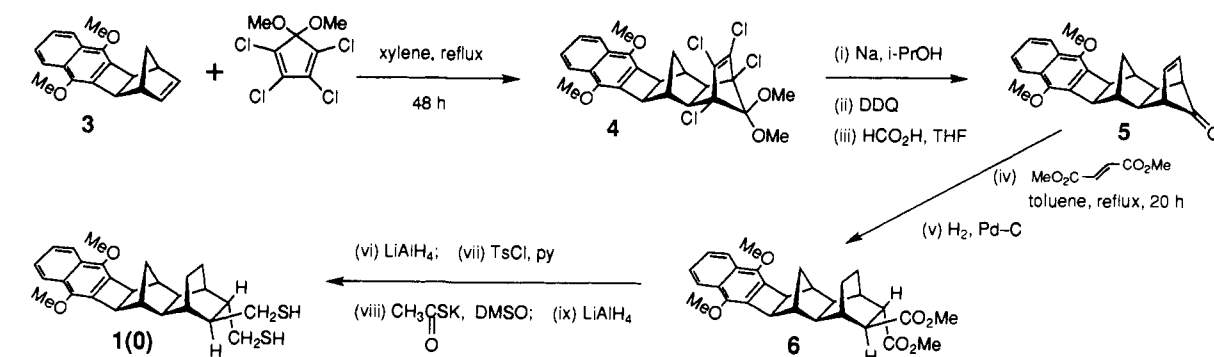


Figure 1. Cyclic voltammograms ($\nu = 0.2$ V/s, $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{Bu}_4\text{N}][\text{PF}_6]$) of a Au electrode with a monolayer of **1(0)**. The electrode had been immersed in a 1 mM solution of **1(0)** in CH_2Cl_2 , followed by rinsing with pure CH_2Cl_2 . Traces of (A) initial scan and (B) continuous scans, $S = 0.2$ μA .

formation.^{7b} Treated electrodes allowed to stand at 0 V in pure $\text{CH}_2\text{Cl}_2/[\text{Bu}_4\text{N}][\text{PF}_6]$ or $\text{THF}/[\text{Bu}_4\text{N}][\text{PF}_6]$ show no diminution of the anodic peak current response over more than 1 h, showing that the molecular film is not readily stripped by nonaqueous solvents. Scanning repetitively through the oxidation wave leads, however, to some loss of electroactivity. A steady-state response (Figure 1b) is reached after ca. 25 scans, with the surface coverage somewhat over half that of the initial value.

Compound **1(0)** shows a higher affinity for Au than does a long-chain alkanethiol, as demonstrated by competitive adsorption experiments. An electrode was first soaked in a solution of 1 mM $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$ in CH_2Cl_2 for 12 h. Once kinetic blockage of the oxidation wave of free ferrocene was achieved, monolayer

C18-thiol coverage was assumed.¹² The electrode was allowed to soak in a separate 1 mM solution of **1(0)** for increasing times. Rapid displacement of the C18-thiol by **1(0)** was monitored by viewing the wave for the latter in a blank CH_2Cl_2 solution. Significant exchange (1×10^{-10} mol/cm²) occurred within 10 min, with maximum coverage (1.6×10^{-10} mol/cm²) after 105 min. The CV of ferrocene was also monitored in a separate solution and became more reversible as the exchange proceeded. If a fully formed film of **1(0)** was allowed to soak in a 1 mM solution of C18-thiol, there was no apparent exchange after 120 min.

Since the geometry of the dithiol tail allows both SH groups to approach the electrode surface (see **2**), it is possible that both sulfurs are involved in the binding of **1(0)** to the metal.¹³ Surprisingly, **1** also forms stable monolayer films on acid-treated Pt electrodes, for which the attachment mode is not as obvious. Although the properties of the films on Pt have not been extensively studied, they appear to be similar to those of films on gold. Literature precedent for attachment of thiols to Pt is limited.^{5,14}

The results of our preliminary studies are clearly encouraging. If attachment of dithiols proves to give films that have generally superior stability in nonaqueous media, then new applications of electrodes with structurally defined chemical modifiers may prove possible, owing to the additional types of electrochemical reactions which are supported by aprotic conditions. We are presently synthesizing analogues of **1(0)** with longer spacers and exploring methods of attaching other redox-active sites, such as ferrocenes and quinones, at the headgroup. These systems may also be of use in the study of distance dependence in heterogeneous charge-transfer reactions.^{2a,15}

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Supplementary Material Available: Representative physical data for **1(0)** (1 page). Ordering information is given on any current masthead page.

(12) The oxidation of ferrocene by C18-thiol is blocked in CH_2Cl_2 if a small amount of free thiol is added to the solution.

(13) Preliminary Raman spectra by Dr. Robin L. Garrell, University of California at Los Angeles, confirm the presence of at least one Au-S linkage per molecule.

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