

Self-Assembled Monolayers of Ferrocenylazobenzenes: Monolayer Structure vs Response

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We report a direct comparison of self-assembled monolayers (SAMs) of a new class of surface-modification reagents, ferrocenylazobenzene compounds **1a**, **b**, on noble metal (Au) and indium-tin oxide (ITO) substrates, Scheme 1. These systems give insight into the role of SAM structure in electron transfer and ion transport processes within SAMs. The structures for SAMs of **1a** on Au and **1b** on ITO, which are controlled by the chemical nature of the substrate and the method for surface modification, dictate the observed electron-transfer processes that occur between the electrode surfaces and the redox-active azobenzene and ferrocene units within these films. For example, under some conditions^{1a} ferrocenylazobenzene compound **1** forms a novel redox bilayer^{1b} on Au, but not on ITO, consisting of an electrochemically inaccessible azobenzene interior layer and an electrochemically accessible ferrocene exterior layer, Scheme 1.²

Thiol compound **1a**³ spontaneously self-assembles into monolayer films on Au substrates, and alcohol-terminated **1b**³ adsorbs onto Cl₃SiCo(CO)₄-modified ITO. The modification of noble metal surfaces with thiol reagents is well known,⁴ and the use of Cl₃SiCo(CO)₄ as a chemical mediator for the modification of oxide surfaces with molecules possessing OH functionality was developed recently by our group.⁵ These methods allow for the direct comparison of SAMs of one molecule type on two dissimilar substrates.

The electrochemical responses for SAMs of **1a** on Au and **1b** on ITO are remarkably different, Figures 1A and 1B, respectively. Furthermore, they differ from the electrochemical responses for solutions of **1a** and **1b** under identical electrochemical conditions. The electrochemical transformations for solution **1a** and **1b** in aprotic and protic environments are comparable to those reported for azobenzene in such environments.⁶ For example, in THF,

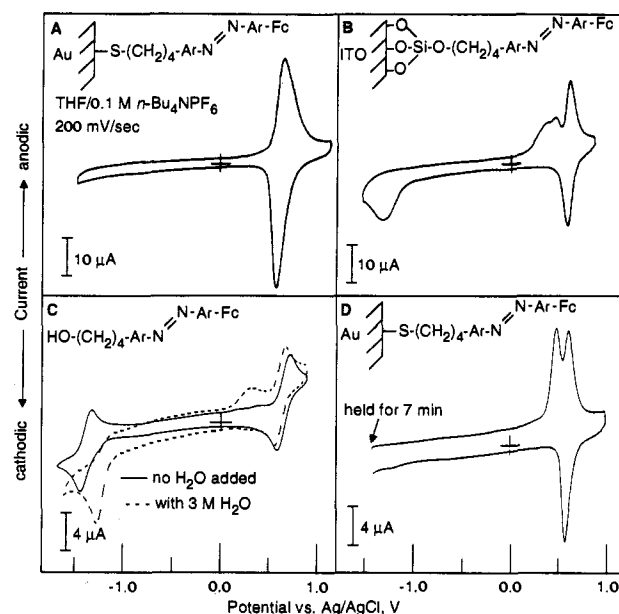
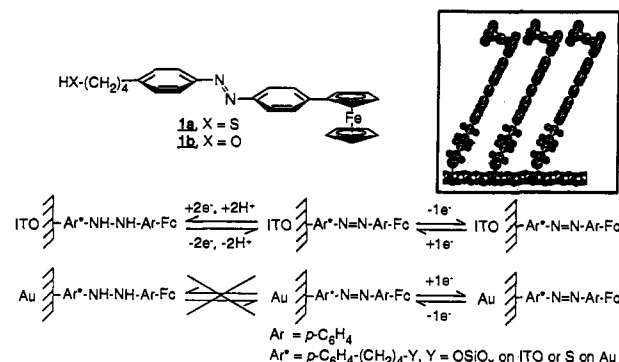


Figure 1. Cyclic voltammetry for (A) a SAM of **1a** (Ar = *p*-C₆H₄) adsorbed onto an Au electrode (0.28 cm²); (B) a SAM of **1b** adsorbed onto a Cl₃SiCo(CO)₄-modified ITO electrode (0.55 cm²); (C) 0.8 mM **1b** in THF/0.1 M *n*-Bu₄NPF₆ at an Au electrode (0.02 cm²) without added H₂O (—) or with 3 M H₂O (---); and (D) a SAM of **1a** adsorbed onto an Au electrode (0.10 cm²) held at -1.5 V for 7 min prior to cycling.

Scheme 1



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(1) (a) Electrochemical conditions: THF/0.1 M *n*-Bu₄NPF₆ at 200 mV/s. (b) Redox bilayer refers to a monolayer film with two layers of redox groups and should not be confused with conventional bilayers consisting of two discrete surface active materials (e.g., lipid bilayer membrane).

(2) The inset is a computer-generated representation of the redox bilayer formed from a SAM of **1a** on Au (111). It is not meant to imply an exact monolayer structure but rather to give the reader a feeling for the relative size of the molecular fragments and their upright orientations with respect to the electrode surface. The hydrogen atoms attached to the cyclopentadienyl rings and the phenyl rings have been omitted for clarity. On Au, **1a** is presumed to be chemically anchored to the surface via Au-S interactions, and on ITO, **1b** is anchored via O-SiO_x covalent bonds. See refs 4 and 5.

(3) **1a**: MS (EI) found 454.1177, calcd 454.1166; ¹H NMR (C₆D₆) phenyl δ 8.16 (d, 2H), 8.13 (d, 2H), 7.44 (d, 2H), 7.04 (d, 2H); Cp 4.49 (t, 2H), 4.15 (t, 2H), 3.88 (s, 5H); Ar-CH₂ 2.29 (t, 2H); CH₂SH 2.10 (quart, 2H); CH₂CH₂CH₂SH 1.25-1.40 (m, 4H); SH 1.05 (t, 1H); UV-vis (cyclohexane) λ_{max} 472, 352, 244 nm. Anal. Calcd for C₂₆H₂₆FeN₂S: C, 68.72; H, 5.77; N, 6.16. Found: C, 68.40; H, 6.00; N, 5.59. **1b**: MS (EI) found 438.1393, calcd 438.1395; ¹H NMR (C₆D₆) phenyl δ 8.15 (d, 2H), 8.12 (d, 2H), 7.43 (d, 2H), 7.07 (d, 2H); Cp 4.48 (t, 2H), 4.14 (t, 2H), 3.87 (s, 5H); CH₂OH 3.27 (t, 2H); Ar-CH₂ 2.38 (t, 2H); CH₂CH₂CH₂OH 1.25-1.50 (m, 4H); OH 0.48 (br, 1H); UV-vis (cyclohexane) λ_{max} 472, 352, 244 nm. Anal. Calcd for C₂₆H₂₆FeN₂O: C, 71.24; H, 5.98; N, 6.39. Found: C, 71.36; H, 6.29; N, 5.95.

(4) Chidsey, C. D. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujscje, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301 and references therein.

(5) Chen, K.; Herr, B. R.; Singewald, E. T.; Mirkin, C. A. *Langmuir* **1992**, *8*, 2585.

(6) (a) Sadler, J. L.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 1979. (b) Boto, K. G.; Thomas, F. G. *Aust. J. Chem.* **1973**, *26*, 1251.

compound **1b** (0.8 mM) undergoes a reversible one-electron reduction to form a radical anion ([FcArN=NAr']⁻, Ar = *p*-C₆H₄, Ar' = *p*-C₆H₄(CH₂)₄OH, E_{1/2} = -1.33 V vs Ag/AgCl) and a reversible one-electron oxidation (E_{1/2} = 0.64 V) to form a ferrocenium species, Figure 1C (—). In a process not shown in Figure 1C, the radical anion of **1b** will undergo a further one-electron, one-proton reduction (E_{pc} = -1.86 V) to form a "monoprotonated dianion" ([FcArNH=NAr']⁻).

In contrast with **1b**'s behavior in aprotic media, **1b** in protic media (THF with ~3 M H₂O) undergoes a two-electron, two-proton reduction (E_{pc} = -1.28 V) to form a ferrocenylhydrazobenzene species (FcArNH-NHAr'), Figure 1C (---). The ferrocenylhydrazobenzene species then may be reoxidized (E_{pa} = 0.31 V) in a reaction that involves the loss of two protons to reform the parent ferrocenylazobenzene **1b**. Significantly, the hydrazobenzene of **1b**, FcArNHNHAr', was independently synthesized and spectroscopically characterized;⁷ it may be oxidized electrochemically in THF/0.1M *n*-Bu₄NPF₆ at E_{pa} = 0.42 V to form **1b**. The potentials at which these processes may

(7) *p,p'*-HO(CH₂)₄C₆H₄NHNHC₆H₄-(*η*⁵-C₅H₅)Fe(*η*⁵-C₅H₅): MS (EI) (M⁺ - 2) 438; ¹H NMR (C₆D₆) phenyl δ 7.32 (d, 2H), 6.96 (d, 2H), 6.67 (dd, 4H); Ar-NH-NH-Ar 4.82 (br, 2H); Cp 4.47 (t, 2H), 4.10 (t, 2H), 3.93 (s, 5H); CH₂OH 3.29 (t, 2H); Ar-CH₂ 2.42 (t, 2H); CH₂CH₂CH₂OH 1.25-1.60 (m, 4H); OH, 0.62 (br, 1H).

be effected are helpful in characterizing the products formed upon oxidation and reduction of monolayer films of **1a** and **1b**.

The cyclic voltammetry of ITO modified with **1b** in THF/0.1 M *n*-Bu₄NPF₆ exhibits a reductive wave at -1.35 V assigned to the reduction of the azobenzene moieties within the monolayer film. Two return oxidative waves are observed at 0.39 and 0.51 V. The large separation between reductive and oxidative waves and the potential(s) at which reoxidation of the reduced azobenzene species may be effected suggests that a chemical reaction occurs upon reduction of the film. On the basis of the peak potentials for reduction/oxidation of surface-confined **1b**, we propose that reduction at -1.35 V leads to formation of a ferrocenylhydrazobenzene, which is reoxidized to the parent ferrocenylazobenzene species at 0.39 and 0.51 V, Figure 1B. Note that a single oxidative wave is observed for the hydrazobenzene compound at a comparable potential, and the two oxidative waves in Figure 1B, which are observed even after repeated cycling, suggest that there are different domains within the monolayer film.⁸ The ferrocene layer in SAMs of **1b** is also electrochemically accessible and exhibits a wave ($E_{1/2} = 0.62$ V) typical of surface-confined species.⁹ The conversion of the azobenzene groups to hydrazobenzene groups in monolayer films of **1b** was unanticipated since under identical conditions and in the same potential window, solution **1b** undergoes a reversible one-electron reduction to form a radical anion, Figure 1C (—). In Figure 1B, the surface species being oxidized at 0.39 and 0.51 V cannot be the radical anion or even the monoprotonated dianion, each of which in solution exhibits oxidative waves at $E_{pa} = -1.29$ V. At present, the proton source in this reaction is unknown and could be trace H₂O, electrolyte, solvent, or a protic surface; it is the subject of current investigation.

In contrast with monolayers of **1b** on ITO, SAMs of **1a** on Au have an electrochemically accessible ferrocene layer and an electrochemically inaccessible azobenzene interior layer, Scheme 1. The cyclic voltammetry of a **1a**-treated Au electrode exhibits one wave assigned to the ferrocene/ferrocenium redox couple and does not exhibit waves associated with azobenzene reduction, even at slow scan rates (1 mV/s), Figure 1A. The surface coverages of **1b** on ITO (2.2×10^{-10} mol/cm²) and of **1a** on Au (5.1×10^{-10} mol/cm²) as determined by the integration of the current associated with the ferrocenyl redox waves are consistent with complete monolayers.^{4,10}

The disparity between electrochemical responses for SAMs of **1a** and **1b** on Au and ITO, respectively, may be attributed to the structures of the SAMs formed from these compounds. Surface coverage, ellipsometric, and interfacial capacitance data for SAMs of **1a** on Au are consistent with those of tightly packed monolayers with a thickness of 21 ± 2 Å, Scheme 1.¹¹ Under these conditions, the incorporation of charge-compensating ions (*n*-Bu₄N⁺ or H⁺) into the azobenzene layer of the SAM is prohibited; we propose that this is responsible for the electrochemical inaccessibility of the azo groups in the film. Monolayers of **1b** on ITO are more loosely packed with more free volume and disorder than films of **1a** on Au, predominantly because there are fewer surface attachment sites on Cl₃SiCo(CO)₄-modified ITO than on Au.¹⁰

(8) For a discussion of domain behavior in electroactive films, see: Smith, C. P.; White H. S. *Anal. Chem.* **1992**, *64*, 2398. The word "domain" is defined as a region with a distinct set of chemical and physical properties.

(9) *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Wiley: New York, 1992.

(10) Based on packing arrangements in crystallographic data for Cl₃SiCo(CO)₄ and a Si...Si distance of 8.56 Å, monolayer coverage is 2.3×10^{-10} mol/cm². For ITO substrates, the surface coverage of the SiCo(CO)₄ groups ultimately dictates the surface coverage of the ferrocenylazobenzene. See: Robinson, W. T.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 1208.

This is reflected by the lower surface coverage for **1b** on ITO compared with **1a** on Au. The coverage of **1a** on Au is comparable to alkythiolferrocenes adsorbed on Au, which form tightly packed monolayers with the ferrocene groups positioned at the exterior of the film.⁴

Significantly, when an Au electrode modified with **1a** is held for 7 min at a potential negative enough to effect reduction of **1a** and moved to a potential positive enough to reoxidize the SAM, an oxidative wave associated with conversion of the reduced species to the parent azobenzene is observed, Figure 1D. Again, the half-wave with $E_{pa} = 0.49$ V (Figure 1D) is consistent with reoxidation of a ferrocenylhydrazobenzene species rather than a radical anion or monoprotonated dianion. Approximately 40% of the azobenzene units within the film are being accessed electrochemically as determined by a comparison of the relative currents associated with the ferrocenylhydrazobenzene and ferrocene redox waves.¹² In a separate study, *in situ* surface-enhanced Raman spectroscopy of a SAM of **1a** on Au confirms reduction of only a fraction of the film and formation of the ferrocenylhydrazobenzene species under similar conditions.¹³

Finally, ~20% of the azobenzene molecules within a SAM of **1a** on Au become electrochemically accessible in a THF/0.1 M *n*-Bu₄NPF₆ solution with ~1 M H₂O. On addition of H₂O to the solution, the H⁺ source is increased, and the film apparently has enough free volume to allow for some H⁺ incorporation and to accommodate the structural changes associated with reduction of the azobenzene groups within the film. A similar effect is observed by the addition of hydroquinone or LiBF₄ to the same electrolyte solution with ~30% or ~20%, respectively, of the azobenzene groups becoming electrochemically accessible.

This study shows that the structures for SAMs of **1** on Au and ITO are significantly different and dictate the observed electron-transfer processes that occur within these novel ferrocenylazobenzene systems. Furthermore, it shows that ion transport, and therefore electron transfer, within SAMs may be regulated by the molecular architecture of the film.

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Supplementary Material Available: Details of the synthesis of **1a,b**, Raman spectroelectrochemistry of **1a,b**, and ellipsometry of **1a** (4 pages). This material is contained in many 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.

(11) X-ray photoelectron spectroscopy: **1a** on Au: S (2p) 163 eV, C (1s) 285 eV, N (1s) 401 eV, Fe(2p_{3/2}) 707 eV, Fe (2p_{1/2}) 720 eV. **1b** on ITO: Si (2p) 104 eV, C (1s) 286 eV, N (1s) 402 eV, Fe (2p_{3/2}) 710 eV, Fe (2p_{1/2}) 723 eV. Ellipsometry: details are given in the supplementary material. Interfacial capacitance: (Helmholtz model: $C_d = \epsilon\epsilon_0/d$; $\epsilon =$ dielectric constant of the medium or n^2 , $n = 1.6$ for ferrocenylazobenzene, $d =$ film thickness, which is 21 Å as determined by ellipsometry) theoretical 1.1 μF/cm², experimental 2.2 μF/cm². C_d for a SAM of **1a** on Au compares well with C_d for a SAM of CH₃(CH₂)₁₇SH on Au and is ~10⁻² C_d for our bare Au. See: Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(12) Note that ~10% of the monolayer is removed from the electrode in this process as evidenced by a decrease in I_{Fc} .

(13) Herr, B. R.; Mirkin, C. A.; Hulteen, J. C.; Van Duyne, R. P., unpublished results.