

## Photon-Gated Electron Transfer in Two-Component Self-Assembled Monolayers

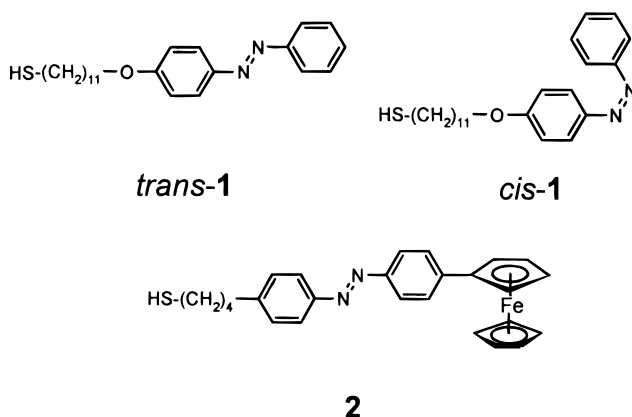
Daniel G. Walter, Dean J. Campbell, and Chad A. Mirkin\*

Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, Illinois 60208

Received: August 26, 1998; In Final Form: October 15, 1998

The preparation and characterization of a photoactive, two-component self-assembled monolayer (SAM) consisting of 99:1 *cis-p*-(C<sub>6</sub>H<sub>5</sub>)N=N(C<sub>6</sub>H<sub>4</sub>)O(CH<sub>2</sub>)<sub>11</sub>SH (**1**) and *trans-p,p*-Fc(C<sub>6</sub>H<sub>4</sub>)N=N(C<sub>6</sub>H<sub>4</sub>)(CH<sub>2</sub>)<sub>4</sub>SH (Fc = C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>; **2**) are reported. With this SAM, electron transfer between solution ferrocyanide and the Au substrate is forced to occur through mediating ferrocenyl sites in the film, resulting in a diode-like response. However, by photochemically converting large “footprint” *cis*-**1** to the smaller footprint *trans*-**1**, the free volume within the film is increased, thereby allowing for direct electron transfer between the solution ferrocyanide and the electrode surface and a normal electrochemical response (i.e.,  $i_{pa} = i_{pc}$ ). All states of the film have been characterized by cyclic voltammetry, FTIR spectroscopy, and differential capacitance measurements. All data from these techniques are consistent with the conclusion that *cis*–*trans* azobenzene isomerization within the monolayer results in increased film porosity, which reduces the film’s ability to block the access of solution redox-active species to the underlying Au electrode surface. This novel two-component structure establishes the concept for a new type of molecule-based electronic device, a “photoswitchable diode” that is capable of amplifying the signal associated with a photodriven event via an electrochemical response. With such a system, a small number of photons can release a relatively large number of electrons from the solution electron reservoir. Significantly, this system shows how one can regulate electron-transfer events involving SAMs through photochemical control over film structure and free volume.

In recent years, there has been a great deal of interest in the preparation and study of “molecule-based electronic devices”.<sup>1</sup> The working components of these structures range from single molecules<sup>1,3</sup> to nanocrystals<sup>2</sup> to a collection of molecules in the form of a monolayer film.<sup>1</sup> Our research in this area has focused on utilizing the collective redox-active and photoactive properties of molecules within self-assembled monolayers (SAMs) to study and control electron transfer between electrodes and surface-confined adsorbates or redox-active molecules in solution.<sup>4,5</sup> Recently, we demonstrated the concept of ion-gated electron transfer in a SAM, where electron-transfer events between an electrode surface and redox-active adsorbates can be regulated by the SAM structure and the size and concentration of available charge-compensating counterions.<sup>4</sup> Herein, we show that electron transfer in a two-component SAM can be modulated by photons, which effect a structural change in a monolayer film that results in a concomitant change in the film’s porosity and, therefore, ability to block the access of solution redox-active species to the underlying Au electrode surface. Specifically, we wish to report the preparation and characterization of a SAM-based “photoswitchable diode”, formed from redox- and photoactive azobenzene alkanethiols adsorbed onto an Au(111) substrate, Scheme 1. A two-component monolayer consisting of a high ratio (99:1) of azobenzenealkane-thiol (*p*-(C<sub>6</sub>H<sub>5</sub>)N=N(C<sub>6</sub>H<sub>4</sub>)O(CH<sub>2</sub>)<sub>11</sub>SH) (**1**) to ferrocenylazobenzene-alkane-thiol (*p,p*-Fc(C<sub>6</sub>H<sub>4</sub>)N=N(C<sub>6</sub>H<sub>4</sub>)(CH<sub>2</sub>)<sub>4</sub>SH, Fc = C<sub>5</sub>H<sub>4</sub>-FeC<sub>5</sub>H<sub>5</sub>; **2**), exhibits diode-like behavior in a solution of potassium ferrocyanide that is dependent upon the isomeric state (*cis* or *trans*) of the adsorbed azobenzenealkane-thiol molecules, Scheme 1. In this system, the molecular footprint of the azobenzenealkane-thiol (**1**), and thus the free volume within the

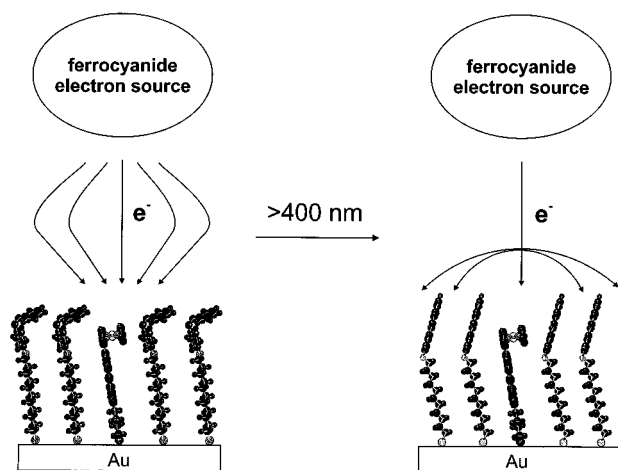


film, can be controlled by a photoinduced *cis*- to *trans*-azobenzene conversion. It is important to note that others have demonstrated that the electrochemical response of a monolayer can be controlled via photochemically induced isomerization reactions involving azobenzene<sup>6a</sup> or stilbene adsorbates.<sup>6b</sup> In these studies, the redox-active properties of the *adsorbates* in single-component SAMs, in the absence of ferrocyanide, are highly dependent on adsorbate packing within the monolayer film.

With two-component films consisting of *cis*-**1** and **2**, electron transfer between solution ferrocyanide and the Au substrate is forced to occur through mediating ferrocenyl sites in the film, resulting in a diode like response, Scheme 1 (left). However, by photochemically converting *cis*-**1** to *trans*-**1**, the free volume within the film is increased, thereby allowing for direct electron transfer between the solution ferrocyanide and the electrode surface, Scheme 1 (right); this results in a normal electrochemical response (i.e., the response typically observed using a bare

\* To whom correspondence should be addressed. E-mail: camirkin@chem.nwu.edu.

## SCHEME 1



electrode,  $i_{pa} = i_{pc}$ ). Note that this is a form of amplification of the signal associated with the photon-driven event; in principle, a small number of photons can release a relatively large number of electrons from the solution electron reservoir. The magnitude of the response can be controlled via the concentration of the redox source (e.g. ferrocyanide, Scheme 1).

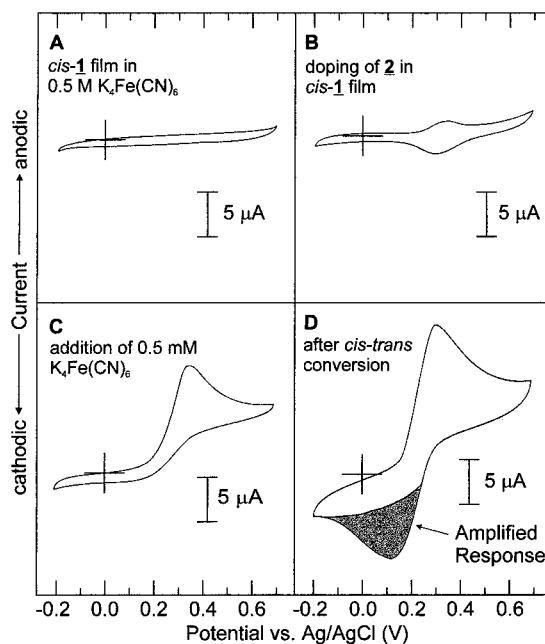
## Experimental Section

**General.** All operations were performed in the absence of light unless otherwise noted. Absolute ethanol was purchased from Midwest Grain Products (Pekin, IL). Potassium ferrocyanide(II) trihydrate, 1,1'-diacetylferrocene, sodium perchlorate, and tetra-*n*-butylammonium hexafluorophosphate were purchased from Aldrich Chemical Co. and used without further purification. Compounds *trans*-1 and 2 were prepared by literature methods.<sup>5</sup> Dichloromethane was dried by refluxing over  $\text{CaH}_2$ , and tetrahydrofuran was dried by refluxing over Na/benzophenone; both solvents were freshly distilled prior to use. Deionized  $\text{H}_2\text{O}$  was purified with a Barnstead Nanopure system (18.3 M $\Omega$ ). All solvents and solutions were deoxygenated by bubbling with prepurified  $\text{N}_2$  for 15 min prior to use. Au wire (0.020 in. diameter, 99.95%) and Ti wire (0.010 in. diameter, 99.95%) were obtained from D. F. Goldsmith Chemical & Metal Corp. (Evanston, IL). Si(100) wafers with a 1  $\mu\text{m}$  thermal oxide coating were obtained from Silicon Quest International, Inc. (Santa Clara, CA).

**Synthesis of *cis*-*p*-( $\text{C}_6\text{H}_5\text{N}=\text{N}(\text{C}_6\text{H}_4)\text{O}(\text{CH}_2)_{11}\text{SH}$  (*cis*-1).** Compound *cis*-1 was prepared by irradiating ( $\lambda = 360 \text{ nm}$ ) *trans*-1 in ethanol at  $0^\circ\text{C}$  for 48 h followed by chromatography on silica gel at  $0^\circ\text{C}$ . Using  $\text{CH}_2\text{Cl}_2$  as the eluent, the first component to be isolated was *trans*-1, as evidenced by  $^1\text{H}$  NMR and UV-vis spectroscopy. Changing the solvent to 1:15 ether/ $\text{CH}_2\text{Cl}_2$  allowed elution of a second band, which was pure *cis*-1.<sup>7</sup>

**Preparation of Au Substrates.** Au wafers were prepared with a Edwards model Auto 306 thermal evaporator operating at a base pressure of  $1.0 \times 10^{-7}$  Torr. Au films were epitaxially grown on Si(100) wafers by first resistively heating Ti wire to a thickness of 50 Å, then resistively heating Au to a thickness of 2000 Å, as monitored by quartz crystal microbalance. Electrodes were stored in vacuo prior to use.

**SAM Preparation.** Au substrates were immersed for 48 h in 0.5 mM solutions of 1 in 99:1 dichloromethane:ethanol (ethanol is used to lower the freezing point of the solution) at  $-40^\circ\text{C}$ . The films were removed from solution, vigorously rinsed with ethanol at  $-40^\circ\text{C}$ , and blown dry with prepurified



**Figure 1.** Electrochemical response for (A) a pure *cis*-1 film in the absence of light and in the presence of 0.5 mM  $\text{K}_4\text{Fe}(\text{CN})_6$ ; (B) the film in A after doping it with 1% 2 (no  $\text{K}_4\text{Fe}(\text{CN})_6$ ); (C) the two-component film (1:99, 2:*cis*-1) after addition of 0.5 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  to the cell; (D) the two-component film, in the presence of 0.5 mM  $\text{K}_4\text{Fe}(\text{CN})_6$ , after irradiation with  $>400 \text{ nm}$  light for 1 h. All measurements were made at  $5^\circ\text{C}$ , and the solutions were purged with  $\text{N}_2$  prior to use. The geometric area of the working electrode was  $0.21 \text{ cm}^2$ . The electrolyte used in all of the above experiments was 0.2 M  $\text{NaClO}_4$  in  $\text{H}_2\text{O}$ . Scan rate =  $100 \text{ mV/s}$ . Counter electrode = Pt gauze, reference =  $\text{Ag}/\text{AgCl}$ . Electrode area =  $0.21 \text{ cm}^2$ .

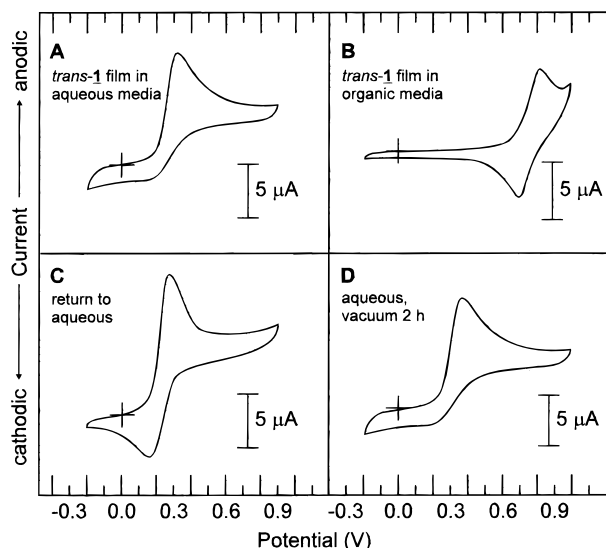
grade  $\text{N}_2$ . Surfaces containing 1 were then immersed for 30 min in a 0.5 mM solution of 2 in 99:1 dichloromethane:ethanol at  $-40^\circ\text{C}$ , rinsed as described previously, and stored at  $0^\circ\text{C}$  until use.

**Electrochemical Measurements.** Cyclic voltammetry was performed with either a Pine AFRDE4 bipotentiostat with a Linseis LY 1400 recorder or a PAR model 273A Potentiostat/Galvanostat operated with model 270 software. Electrochemical experiments were performed under a prepurified  $\text{N}_2$  atmosphere, using a conventional three-electrode cell. Each cell consisted of a Au/Ti/Si wafer working electrode, a Pt gauze counter electrode, and a Ag wire or  $\text{Ag}/\text{AgCl}$  reference electrode. Capacitance measurements are based on the current at  $-0.1 \text{ V}$  vs  $\text{Ag}/\text{AgCl}$  with a refractive index of 1.55.

**Infrared External Reflectance Spectroscopy.** Infrared external reflection spectroscopy was performed using a Nicolet 730 Fourier transform infrared spectrometer with a Spectra Tech FT-85 grazing angle accessory. The refractive geometry of the accessory allowed only p-polarized light to impinge upon the sample with an  $85^\circ$  incident angle. Spectra were taken using 512 scans at  $2 \text{ cm}^{-1}$  resolution.

## Results

Like SAMs formed from *trans*-1<sup>4</sup> or  $\text{C}_{12}$ – $\text{C}_{18}$  linear alkanethiols,<sup>8</sup> SAMs of *cis*-1 form excellent blocking layers in 0.5 mM aqueous solutions of ferrocyanide with 0.2 M  $\text{NaClO}_4$ . Under these conditions, there is no evidence for the ferrocyanide  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple, Figure 1A. Compound 2 can be doped into the film by exchange with surface-adsorbed *cis*-1; cyclic voltammetry and integration of the current associated with ferrocenyl-based oxidation/reduction shows that  $5.0 \times 10^{-12}$

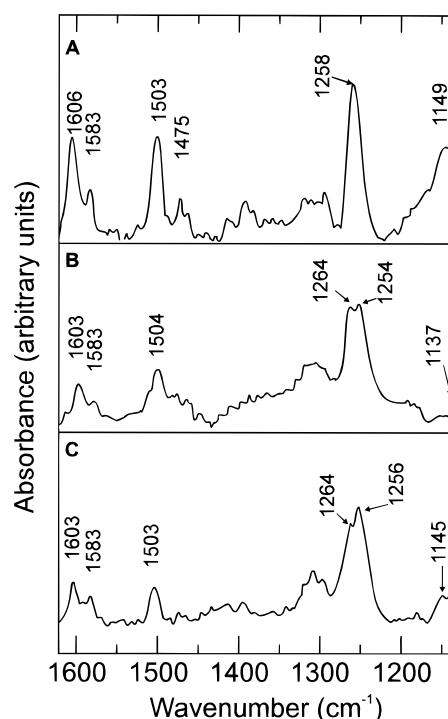


**Figure 2.** Electrochemical response of *trans*-1:2 (99:1) film on Au (A) in 0.2 M NaClO<sub>4</sub> and 0.5 mM K<sub>4</sub>Fe(CN)<sub>6</sub> in H<sub>2</sub>O; (B) in 0.1 M TBAPF<sub>6</sub> and 2.0 mM Fc(C(O)Me)<sub>2</sub> in THF; (C) in 0.2 M NaClO<sub>4</sub> and 0.5 mM K<sub>4</sub>Fe(CN)<sub>6</sub> in H<sub>2</sub>O after exposure to THF, prior to vacuum; (D) in 0.2 M NaClO<sub>4</sub> and 0.5 mM K<sub>4</sub>Fe(CN)<sub>6</sub> in H<sub>2</sub>O after exposure to THF and vacuum. For all experiments: scan rate = 100 mV/s; counter electrode = Pt gauze; electrode area = 0.22 cm<sup>2</sup>. Reference electrode for A, C, and D = Ag/AgCl; reference electrode for B = Ag wire.

mol/cm<sup>2</sup>, or approximately 1% of the film, consists of **2**, Figure 1B.<sup>5</sup> If the above electrode is transferred to a cell containing a solution of 0.5 mM aqueous K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.2 M NaClO<sub>4</sub>, a substantial increase in oxidative current is observed without an increase in reductive current. This electrochemical response is typical of a current rectifying monolayer based on ferrocenyl sites that mediate electron transfer between the metal film and a ferrocyanide electron reservoir,<sup>8</sup> Figure 1C and Scheme 1. This response was highly reproducible and was stable to repeated cycling; no evidence of breakdown of this rectifying layer was observed during 150 cycles at 200 mV/s over the -300 to +800 mV potential window.

Significantly, after the film was irradiated with ambient room light (400–800 nm) under an N<sub>2</sub> atmosphere at 0 °C, a *cis*-1 to *trans*-1 azobenzene conversion is effected within the film and a normal electrochemical response is observed, Figure 1D. Note that thiolate oxidation or desorption<sup>9</sup> does not occur under these conditions (vide infra). Here, an oxidation/reduction wave with comparable cathodic and anodic peak currents is observed. This occurs because the larger footprint *cis*-adsorbates are converted to the smaller footprint *trans*-adsorbates, allowing the ferrocyanide ions direct access to the electrode surface. On the basis of the crystallographic data for *cis*- and *trans*-azobenzene,<sup>10</sup> we estimate that *cis*-1, with its nonplanar azobenzene structure, will occupy approximately 1.5–2 times the cross-sectional area occupied by *trans*-1.

Without SAM structural data it is impossible to directly determine the exact difference in molecular footprints for the two isomeric forms of **1** in a two-dimensional film. However, differential capacitance measurements, which are a measure of film porosity,<sup>8</sup> show that a *trans*-1 film formed from photoisomerizing a *cis*-1 SAM (11.3 ± 0.5 μF/cm<sup>2</sup>) has a higher capacitance than a film of *trans*-1 formed directly from *trans*-1 adsorbate in solution (1.5 ± 0.5 μF/cm<sup>2</sup>) or a SAM of *cis*-1 (1.6 ± 0.5 μF/cm<sup>2</sup>). The differential capacitance of our bare Au substrates is 17.5 μF/cm<sup>2</sup>. These experiments are consistent



**Figure 3.** Infrared external reflectance spectroscopy of: (A) a *trans*-1 film on Au; (B) a *cis*-1 film on Au; (C) a *trans*-1 film formed via photoconversion of *cis*-1 film. Band assignments for a SAM of *trans*-1 (cm<sup>-1</sup>): 1603, 1583 ν(φ 8a and b); 1503 ν(19a φ); 1475 δ(CH<sub>2</sub>); 1258 ν<sub>a</sub>(φ-O); 1147 ν<sub>a</sub>(φ-N). ν<sub>a</sub> = antisymmetric stretch; ν<sub>s</sub> = symmetric stretch; δ = bending. Assignments were made based on a comparison with the spectrum of a Langmuir–Blodgett film of CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>C<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>O(CH<sub>2</sub>)<sub>5</sub>CO<sub>2</sub>H.<sup>10</sup>

with the conclusion that an increase in film porosity accompanies the photoconversion of the *cis*-1 SAM to a *trans*-1 monolayer.

Interestingly, the diode-like behavior of these two-component SAMs is also dependent upon choice of solvent. For example, when a two-component film (consisting of 99:1 **1:2**) that behaves as a rectifier in 0.2 M aqueous NaClO<sub>4</sub> is moved to a THF/0.1 M TBAPF<sub>6</sub> electrolyte, it no longer affords a diode-like response, compare Figures 2A and 2B. 1,1'-diacetylferrocene [Fc(C(O)Me)<sub>2</sub>] was used as the electron source in this experiment because of the poor solubility of ferrocyanide in THF. Note that Fc(C(O)Me)<sub>2</sub> is 280 mV more difficult to oxidize than **2**; therefore, if the two-component SAM forms a passivating layer in THF, one would expect current rectifying behavior. Instead, a response more characteristic of a porous film is observed, Figure 2B. Upon rinsing the two-component SAM vigorously in THF and then ethanol followed by drying with N<sub>2</sub>, the film still exhibits an electrochemical response characteristic of an imperfect blocking layer, even in aqueous media in the presence of 0.5 mM ferrocyanide, Figure 2C. Apparently, trapped solvent disrupts the monolayer structure, allowing access of the ferrocyanide to the electrode surface. Consistent with this hypothesis, after the films are dried under vacuum for 2 h, the original diode-like response returns, Figure 2D. This phenomenon is very reproducible and was observed for films soaked in ethanol or dichloromethane. Importantly, these results demonstrate that organic solvents can significantly and reversibly influence the structures of these films. This observation has significant ramifications not only in developing systems with controlled architectures but also in developing structural models for these films. Indeed, oftentimes scanning probe microscopy techniques are performed on these systems in the presence of organic solvents.<sup>11</sup> From these studies, it is clear that such

solvents can influence monolayer structure and, therefore, the interpretation of such data must be done very cautiously.

Finally, although the external reflectance infrared spectra of *trans*- and *cis*-**1** are quite similar, the surface photoisomerization can be followed by monitoring in the 1100–1650  $\text{cm}^{-1}$  region of the spectrum, Figure 3. Moreover, a monolayer of *trans*-**1** formed via photoconversion of a *cis*-**1** SAM can be differentiated from a monolayer formed directly from *trans*-**1** adsorbate in solution. *Trans*-**1** monolayers, prepared by either method, (Figure 3A and C) exhibit a characteristic  $\nu_a(\phi\text{-N})$  band in the 1145–1149  $\text{cm}^{-1}$  region of the spectrum. The  $\nu_a(\phi\text{-N})$  band for a SAM of *cis*-**1** appears at 1137  $\text{cm}^{-1}$ . The SAM formed via direct adsorption of *trans*-**1** from solution shows a characteristic sharp  $\nu_a(\phi\text{-O})$  band at 1258  $\text{cm}^{-1}$  (Figure 3A), while the analogous bands for the *cis*-**1** SAM (Figure 3B) and the *trans*-**1** film formed via photoisomerization of a *cis*-**1** SAM (Figure 3C) exhibit broader and sometimes multiple bands in this region. Other bands in this region, including the phenyl ring stretching modes and all  $\text{CH}_2$  bands, do not differ significantly for the three types of films, which is consistent with the IR spectroscopy data reported for other monosubstituted azobenzene-containing thin films.<sup>12</sup> Note that in these types of structures, switching back from *trans*-**1** to *cis*-**1** by irradiation with 360 nm light could only be partially effected ( $\sim 20\%$  as evidenced by a decrease in cathodic current). The reverse isomerization is exceptionally slow and inefficient, not only because of the low quantum yields with respect to *trans*-to-*cis* conversion for monosubstituted azobenzenes,<sup>13</sup> but also presumably due to inhibitory steric effects within the film and excited-state quenching by the Au surface.<sup>14</sup>

This system shows how one can regulate electron-transfer events involving two-component SAMs with photoisomerizable adsorbates that differ in shape and footprint. The structures of such adsorbates allow one to regulate access of redox-active molecules to the electrode surface. The device reported herein is by no means a practical one due to the quenching properties of the Au substrate and inefficiency of the photodriven azobenzene isomerization. However, this system is an important illustration of the degree of control one can exert over the structure of a monolayer film and its electron-transfer properties through judicious choice and design of adsorbates. It also is important to note that these studies suggest that organic monolayers have “soft” porous structures in organic media while in aqueous media they have more rigid, charge blocking structures.

**Acknowledgment.** C.A.M. acknowledges the ONR (N00014-97-1-0430) and the NU Materials Research Center (Award No. DMR-9120521) for support of this work.

## References and Notes

- (1) Mirkin, C. A.; Ratner, M. A. *Annu. Rev. Phys. Chem.* **1992**, *43*, 719.
- (2) Storhoff, J. J.; Mucic, R. C.; Mirkin, C. A. *J. Cluster Sci.* **1997**, *8*, 179.
- (3) (a) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690. (b) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
- (4) Campbell, D. J.; Herr, B. R.; Hulteen, J. C.; Van Duyne, R. P.; Mirkin, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 10211.
- (5) (a) Caldwell, W. B.; Campbell, D. J.; Chen, K.; Herr, B. R.; Mirkin, C. A.; Malik, A.; Durbin, M. K.; Dutta, P.; Huang, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 6071. (b) Caldwell, W. B.; Chen, K.; Herr, B. R.; Mirkin, C. A.; Hulteen, J. C.; Van Duyne, R. P. *Langmuir* **1994**, *10*, 4109.
- (6) (a) Wang, R.; Iyoda, T.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. *Langmuir* **1997**, *13*, 4644. (b) Wolf, M. G.; Fox, M. A. *J. Am. Chem. Soc.* **1995**, *117*, 1845.
- (7) Compound *cis*-**1**: MS (EI): exp 384.2227, calcd 384.2235.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  6.7–7.4 (m, 9H, aryls); 2.50 (dt,  $J_{\text{HH}\alpha} = J_{\text{HH}\alpha'} = 7.1$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{-SH}$ ); 3.90 (t,  $J_{\text{HH}} = 6.5$  Hz, 2H,  $\text{O-CH}_2\text{-CH}_2$ ); 1.70 (m, 2H,  $\text{O-CH}_2\text{CH}_2\text{CH}_2$ ); 1.2–1.7 (m, 16H,  $\text{O-CH}_2\text{CH}_2\text{-(CH}_2)_8$ ); 1.15 (t,  $J_{\text{HH}} = 7.1$  Hz, 1H,  $\text{CH}_2\text{-SH}$ ). UV-vis (1:15 ether: $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}} = 236$  nm ( $\epsilon = 12\,000\text{ mol}^{-1}\text{ cm}^{-1}$ ), 276 nm ( $\epsilon = 2600\text{ mol}^{-1}\text{ cm}^{-1}$ ), 348 nm ( $\epsilon = 900\text{ mol}^{-1}\text{ cm}^{-1}$ ).
- (8) (a) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365. (b) Rowe, G. K.; Creager, S. E. *J. Phys. Chem.* **1994**, *98*, 5500. (c) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559. (d) Uosaki, K.; Sato, Y.; Kita, H. *Electrochim. Acta* **1991**, *36*, 1799. (e) Sato, Y.; Itoigawa, H.; Uosaki, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1032. (f) Kunitake, M.; Nasu, K.; Manabe, O.; Nakashima, N. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 375.
- (9) (a) Chadwick, J. E.; Myles, D. C.; Garrell, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10364. (b) Gillen, G.; Bennett, J.; Tarlov, M. J.; Burgess, D. R. F. *J. Anal. Chem.* **1994**, *66*, 2170.
- (10) (a) Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr., Sect. C* **1983**, *39*, 1121. (b) Mostad, A.; R  mning, C. *Acta Chem. Scand.* **1971**, *25*, 3561.
- (11) Jaschke, M.; Sch  nherr, H.; Butt, H.-J.; Bamberg, E.; Besocke, M. K.; Ringsdorf, H. *J. Phys. Chem.* **1996**, *100*, 2290.
- (12) (a) Wang, R.; Iyoda, T.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. *J. Electroanal. Chem.* **1997**, *438*, 213. (b) Ozaki, Y.; Sato, T.; Iriyama, K. *Langmuir* **1994**, *10*, 2363.
- (13) Rau, H. *J. Photochem.* **1984**, *26*, 221.
- (14) *Spectroelectrochemistry: Theory and Practice*; Gale, R. J., Ed.; Plenum Press: New York, 1988.