Monitoring Electron Transfer in an Azobenzene Self-Assembled Monolayer by *in Situ* Infrared Reflection Absorption Spectroscopy

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The redox behavior of the self-assembled monolayer of 4-ethoxy-4′-((*N*-(10′′-mercaptodecyl)amino)-carbonyl)azobenzene ($CH_3CH_2O-Ph-N=N-Ph-C(O)NH(CH_2)_{10}-SH$, abbreviated as $C_2AzoC_{10}SH$ below) on a gold electrode surface has been investigated by electrochemical *in situ* Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS). The bands observed in the potential dependent IRRAS spectra corresponded well to the reduction/oxidation process of the azobenzene group in the monolayer. No bands were found in the *in-situ* FT-IRRAS spectra for the C−H stretch of the methylene group and the N−H stretch as well as the C=O stretch of the amide moiety, suggesting that no orientation change occurs in the polymethylene chain of the monolayer during the redox reaction of the azobenzene group. The band intensity observed in the *in-situ* IRRAS spectra depends on the reaction time, especially in the reduction process of the azobenzene monolayer. Our results provided direct evidence for a slower reduction of azobenzene to hydrazobenzene than the reverse process, i.e., oxidation of hydrazobenzene, thus augmenting the importance of understanding the relationship between monolayer structure and electron transfer.

Introduction

The self-assembled monolayer (SAM) containing the azobenzene moiety has become a frontier subject of interfacial chemistry and materials science research very recently.[1−12] Mirkin and his co-workers investigated the electrochemical redox behaviors of the ferrocenylazobenzenebutanethiol (Fc−Ph−N=N−Ph−$(CH_2)_4$SH, Ph denotes the benzene ring) and the azobenzenebutanethiol (Ph−N=N−Ph−$(CH_2)_4$SH) monolayers on gold electrode

in aprotic and protic solutions.[1−4] A significant effect of the packing structure on the redox behaviors of azobenzene moiety in the monolayer was proposed.[3,4] Liu and his co-workers studied the electrochemical behaviors of the azobenzene self-assembled monolayers with different structures in aqueous solution by electrochemical techniques in detail.[5−9] It was found that the redox reaction of azobenzene group in the monolayer on gold electrode was a $2e^-/2H^+$ process and the redox behaviors were affected greatly by the monolayer structure. Studies on the packing structure and other properties of the azobenzene self-assembled monolayers on gold surfaces have also been carried out by other research groups.[10−12] However, the recognition of the reduction products and the possible molecular conformational change accompanying the reduction/oxidation process have not been clearly addressed for the azobenzene self-assembled monolayer, partially due to the difficulties in spectroscopic measurement of monolayers in electrolyte solutions.

The technique of *in situ* surface infrared and Raman spectroscopy has been applied successfully in interfacial electrochemistry in the last decade.[13−15] It has become one of the most useful methods to obtain information about *in situ* structure and chemical reactivity of adsorbed species on electrode surfaces and is of great importance in elucidating the nature of the interfacial chemical processes. Many spectroscopic investigations have been carried out on the self-assembled monolayers under *ex*

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situ condition.[16−28] Although the *in situ* spectroscopic characterization is expected to give more insight into the role of the monolayer structure in electron transfer process on the interface between the monolayer and the electrolyte solution, its study is still limited.[29−39] The first *in situ* Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS study on the SAM modified electrode was carried out by Popenone et al.[30] for an 11-mercaptoundecyl ferrocenecarboxylate (FcCOOC₁₁SH) monolayer on gold. Uosaki et al. investigated changes in the structure and orientation of the 2-(11-mercaptoundecyl)hydroquinone (H₂QC₁₁SH)[36] and 11-ferrocenyl-1-undecanethiol (FcC₁₁SH)[37,38] monolayers on a gold electrode during the redox reaction of the terminal redox groups by *in situ* FT-IRRAS measurements. Mirkin et al. confirmed the formation of hydroazobenzene in the electrochemical reduction of the azobenzene group in the Fc−Ph−N=N−Ph−(CH₂)₄SH monolayer on gold electrode by the surface-enhanced Raman spectroscopy (SERS) measurement, although no detailed assignment was given in the paper.[4] Wang et al. reported an orientation change of terminal azobenzene group in the 10-[(4-phenylazo)phenoxy]decane-1-thiol (Ph−N=N−Ph−O−(CH₂)₁₀SH) monolayer as the azobenzene group was electrochemically reduced.[34]

This paper introduces *in situ* FT-IRRAS measurement as a probe to investigate the relationship between structure/orientation change and electrochemical behavior of 4-ethoxy-4'-((N-(10''-mercaptodecyl)amino)carbonyl)azobenzene (CH₃CH₂O−Ph−N=N−Ph−C(O)NH(CH₂)₁₀−SH, abbreviated as C₂AzoC₁₀SH below) monolayer at a gold/electrolyte solution interface. As will be shown, potential dependent FT-IRRAS spectra enable us to confirm the redox process of azobenzene to hydrazobenzene, as well as to give insights into the sluggish reduction kinetic behavior of the azobenzene group within highly organized monolayers.

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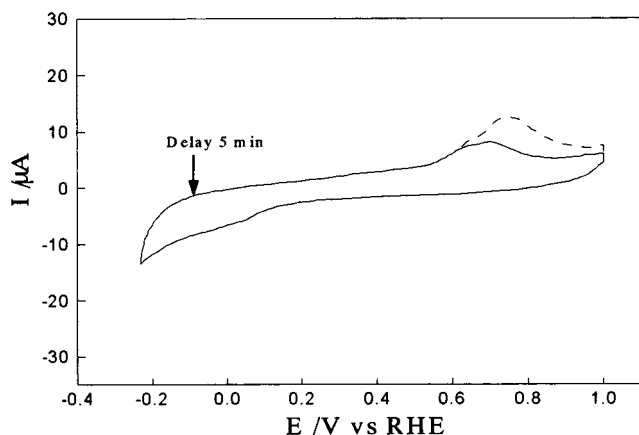(39) Yang, D. F.; Al-Maznai, H.; Morin, M. *J. Phys. Chem. B* **1997**, *101*, 1158.

Experimental Section

4-Ethoxy-4'-((N-(10''-mercaptodecyl)amino)carbonyl)azobenzene (C₂AzoC₁₀SH) was synthesized from 4-hydroxy-4'-carboxylato azobenzene using a previously reported method.[6] The final product was purified by silica gel column chromatography: yield 80%. Proof of its chemical structure was based on: ¹H NMR(DMSO-d_6) δ 1.24−1.39 (m, 15H, −CH₃, −CH₂CH₂-CH₂−); δ 2.68 (t, 2H, CH₂SH); δ 3.42 (m, 2H, NHCH₂); δ 4.16 (m, 2H, CH₂O); δ 7.13 (d, 2H, ArH); δ 7.88−8.02 (m, 6H, Ar**H**); δ 8.60 (t, 1H, N**H**); **SH** was not detectable due to trace water in the solvent. MS (FAB): *m/e* 442 (M + 1). IR (KBr) 3356 (amide A, N−H stretch), 2975 ($\nu_{as\ CH_3}$), 2892 ($\nu_{s\ CH_2}$), 2917 ($\nu_{as\ CH_2}$), 2849 ($\nu_{s\ CH_2}$), 1636 (amide I, C=O stretch), 1553 (amide II), 1256 ($\nu_{Ph−O−C}$), the benzene ring (1603, 1585, 1501, 1396) and 2558 ($\nu_{S−H}$) cm⁻¹.[40−42]

A polycrystalline gold disk (8 mm diameter × 1 mm thick, 99.98% purity) was used as a working electrode in the present study. The surface of the electrode was polished successively with 1.0, 0.3, and 0.05 μm alumina slurry. The electrode was cleaned first with pure water in an ultrasonic bath and then electrochemically by cycling the potential between 0.05 and 1.8 V (vs RHE) in 0.1 M H₂SO₄ solution for about 30 min before the surface modification. The real surface area was determined from the charge for the reduction of the gold oxide layer. The monolayer was constructed by dipping the electrode into 0.1 mM C₂AzoC₁₀SH/ethanol solution for about 24 h. After modification, the electrode was rinsed in an ultrasonic bath with ethanol for about 3 min to remove the physically adsorbed C₂AzoC₁₀SH molecules and then rinsed with pure water several times and dried with purified nitrogen gas before further characterization.

A detailed description of conditions for the *in situ* FT-IRRAS measurements has been given elsewhere.[36,38] A home-made IRRAS cell with a CaF₂ window was used and the gold electrode was pressed against the window so that the thickness of the water layer between the window and the gold electrode surface was minimized. The incidence angle at the electrode surface was approximately 65° with respect to the surface normal. The IRRAS spectra of the monolayer were presented in the form of the normalized change of reflectance, i.e., $\Delta R/R$, which is equal to $(R_s − R_r)/R_s$ where R_s and R_r are the reflectance at sample and reference potentials, respectively. $\Delta R/R$ is proportional to concentration decrease of absorbing species if $\Delta R/R$ is small. The subtractively normalized interfacial Fourier transform infrared reflection−adsorption spectroscopy (SNIFTIRS) was used to improve S/N ratio.[14] A total of 1024 scans (4 cm⁻¹ in resolution) was recorded at each potential with the potential being switched between the reference potential and the sample potential every 128 or 64 scans for four or eight times.

For both electrochemical and spectroelectrochemical studies, a quasi-reversible hydrogen electrode and a Pt wire were used as reference and counter electrode, respectively. All potentials reported in this paper are presented with respect to the reversible hydrogen electrode (RHE). The supporting electrolyte was a phosphate buffer solution at pH 5.0.[43] For *in situ* FT-IRRAS measurements, the potential steps were provided by a personal computer (NEC, PC-8801) via a 12 bit D/A converter and the FTIR spectrometer was controlled by the same computer through a RS-232C interface. All the measurements were carried out at room temperature (23 °C) after the solution was deaerated by bubbling purified nitrogen for at least 15 min. All the measurements have been repeated more than three times.

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(43) Composition of the buffer: 0.1 M Na₂HPO₄ + 0.1 M KH₂PO₄ + 0.1 M NaClO₄. The pH value is adjusted with 1.0 M H₃PO₄ and 1.0 M NaOH. No difference has been found for the electrochemical behavior of the azobenzene monolayer in this buffer compared with our previously used B−R buffer, and the pH value used here is also within the pH = 3−9 range in which the azobenzene/hydrazobenzene redox is typical.[6]

Figure 1. Cyclic voltammograms of the $C_2AzoC_{10}SH$ monolayer modified gold electrode in phosphate buffer (pH 5.0) with a supporting electrolyte of 0.1 M $NaClO_4$. Scan rate was 0.05 V/s (solid line). The dashed line indicates the oxidation wave after the potential was kept constant at -0.1 V for 5 min.

Results and Discussion

The cyclic voltammetry of a $C_2AzoC_{10}SH$ monolayer on gold electrode at a sweep rate of 0.05 V/s yielded a pair of reduction and oxidation peaks around 0 and +0.7 V (Figure 1, solid line). Repetitive cycling from -0.2 to +1.0 V over hundreds of scans did not alter the voltammetric properties, such as peak height, peak position, and shape, demonstrating that the monolayer is stable to the redox process in this potential region. The voltammetric features are similar to those of the C_2AzoC_2SH monolayer[6] except for a larger peak separation ($\sim$0.7 V). When the potential was kept constant at -0.1 V for 5 min, a much larger anodic peak was observed in the next anodic sweep (Figure 1, dashed line). This suggests that all of the azobenzene moieties in the monolayer cannot be reduced completely to the hydrazobenzene form in the potential cycle with a sweep rate of 0.05 V/s.

In situ IRRAS measurements were carried out to investigate the structure/ conformation changes in the azobenzene self-assembled monolayer in contact with an electrolyte solution as a result of the electrochemical redox reaction of the azobenzene moiety. The *in situ* IRRAS spectra of the $C_2AzoC_{10}SH$ monolayer modified gold electrode obtained by using both p- and s-polarization are shown in Figure 2. These spectra are presented in the form of differential reflectance spectra between the sample potential and the reference potential, i.e., $\Delta R/R = (R_{sam} - R_{ref})/R_{sam}$. The reference potential was +0.80 V where the functional group in the monolayer was expected to exist as azobenzene (oxidized form) and the sample potential was selected at -0.1 V where the functional moiety was expected to be in the reduced form, i.e., hydrazobenzene (Figure 1). In this sense, the upward and downward peaks in the IRRAS spectra correspond to oxidized and reduced forms, respectively. A clear difference between the spectra obtained with p- and s-polarization is evident. With p-polarization (Figure 2A), the spectrum showed a number of absorption bands in the regions of 1800–1200 cm^{-1}, while no discernible bands could be found with s-polarization (Figure 2B). According to the "surface selection rule" of infrared reflection measurement on metal surfaces,[44] the bands observed by p-polarization are due to chemisorbed $C_2AzoC_{10}SH$ monolayers on the gold electrode surface rather than species in the electrolyte solution.
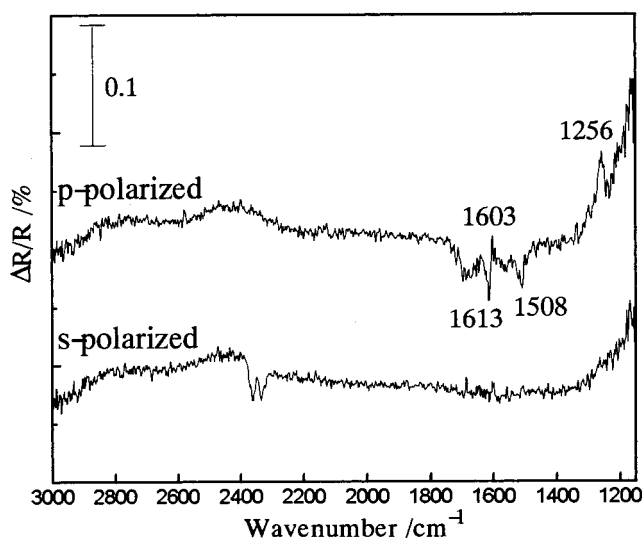

Figure 2. *In situ* IRRAS spectra of the $C_2AzoC_{10}SH$ monolayer on a gold electrode in the 3000–1150 cm^{-1} region. The reference and sample potentials are +0.8 and -0.1 V, respectively. The collection mode is 8 × 128 scans.

Table 1. Peak Positions (cm^{-1}) and Their Assignments in the *in Situ* FT-IRRAS Spectra of the $C_2AzoC_{10}SH$ Monolayer on Gold

frequency/cm^{-1}	assignment	band direction
1256/1252	ν_{Ph-O-C}	bipolar
1508	ν_{Ph-N-H}	downward
1613/1603	benzene ring stretch	bipolar
2343	CO_2 in air	random

The notable features arising from the p-polarization spectrum are listed in Table 1. The downward band at 1508 cm^{-1}, which has not been observed in the synthesized molecule, can be assigned to the aromatic N–H bending mode (Ph–N–H),[41,45] showing evidence of the existence of the hydrazobenzene moiety (Ph–NH–NH–Ph) as the reduced product of azobenzene (Ph–N=N–Ph). A similar peak attributed to N–H bending mode was observed at 1514 cm^{-1} by Wang et al. as a reduction product of the Ph–N=N–Ph–O–$(CH_2)_{10}$–SH monolayer on a gold electrode.[34] (Note: $-\Delta R/R$ was used in their work.) The bipolar peak at 1613/1603 cm^{-1} (downward/upward) reflects the band shift of the benzene ring C–C stretch mode[40–42] as a result of the chemical environmental changes during the electrochemical reduction of the azobenzene group. This bipolar band was not reported by Wang et al.[34] The ν_{as}(Ph–O–C) band also shows a bipolar peak at 1252 cm^{-1} (downward) and 1256 cm^{-1} (upward) which can also be considered as due to the conversion of –N=N– to –HN–NH–. A similar bipolar band but a reversed direction was observed by Wang et al.[34] When the –N=N– moiety is reduced to –HN–NH–, the large π-electron conjugated system between the two benzene rings is broken. The reduced –HN–NH– can be considered as an electron-donor group. Therefore, the chemical environment in the reduced monolayer should be changed greatly from that of the oxidized case. A large variation in the electron density and dipole moment in the benzene rings and their substitute groups are expected. Such an effect might play a significant role in the present *in situ* FT-IRRAS spectra. In fact, similar infrared band shifts have been reported, for example, between two molecules with different polar end groups of CH_3CH_2O–Ph–NH_2 and CH_3O–Ph–NO_2, one is NH_2 as an electron

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Scheme 1. Redox Process between Azobenzene and Hydrazobenzene in the Monolayer

Scheme 2. Schematic Drawing of the $C_2AzoC_{10}SH$ Monolayer on Gold
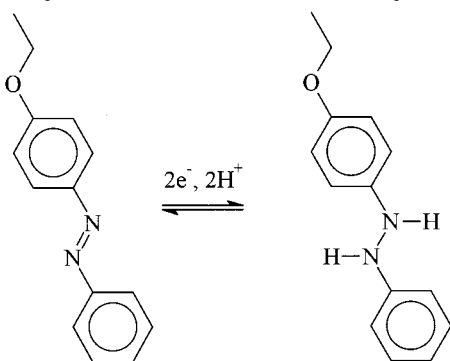
donor, another is NO_2 as an electron acceptor. In that case, ν_{as}(Ph–O–C) shifts from 1233 to 1264 cm^{-1} and benzene ring stretch around 1600 cm^{-1} shifts from 1626 to 1591 cm^{-1}.[46] The same explanation could be applied to the origin for the band shift in the present $C_2AzoC_{10}SH$ monolayer as the –N=N– moiety was reduced to –HN–NH–. Thus, it is reasonable to conclude that the features in the IRRAS spectra are consistent with the reduction of the surface-confined azobenzene to yield the corresponding hydrazobenzene (Scheme 1).

It is interesting to note that the other characteristic IR bands observed in the transmission spectrum of the synthesized molecule such as the stretching mode of CH_2, the amide A (N–H stretch), amide I (C=O stretch), and amide II (N–C=O) have not been found in the IRRAS spectra. We have already shown that amide A and amide I were not observed in *ex situ* grazing incidence reflectance FTIR measurements in the case of an Ph–N=N–Ph–C(O)NH(CH$_2$)$_2$SH (AzoC$_2$SH) monolayer and proposed that this is because the NH bond and C=O bond were primarily parallel to the surface in the monolayer.[9] We suggested that a hydrogen bonding network between neighboring amide moieties, which was expected to highly improve the packing density and the stability of the monolayer, was formed in the monolayer. Similar results relating to the molecular orientation of monolayers have been reported by other groups.[47–49] It is, therefore, reasonable to consider that no bands were observed for the amide group and polymethylene chain (inner layer, see Scheme 2) by the *in situ* IRRAS measurement because of the hydrogen bonding network between neighboring amide moieties. The orientation of the polymethylene chain was unchanged during the redox reaction of the azobenzene moiety. Wang et al. was also unable to find any band in the C–H stretch region in their *in situ* IRRAS measurement, although these bands were found in their *ex situ* infrared reflection measurement, suggesting no orientation change in the long polymethylene chain took place during the redox reaction of the Ph–N=N–Ph–O–(CH$_2$)$_{10}$–SH monolayer. From the decrease of the band for ν_{as}(Ph–O–C), they suggested that an orientation change of the terminal azobenzene group took place when it was reduced electrochemically.[34] Since no band related to the C–H in the end group (CH$_3$CH$_2$O–) of the monolayer was observed in the present study, this kind of orientation change was not confirmed in the present experiment. This
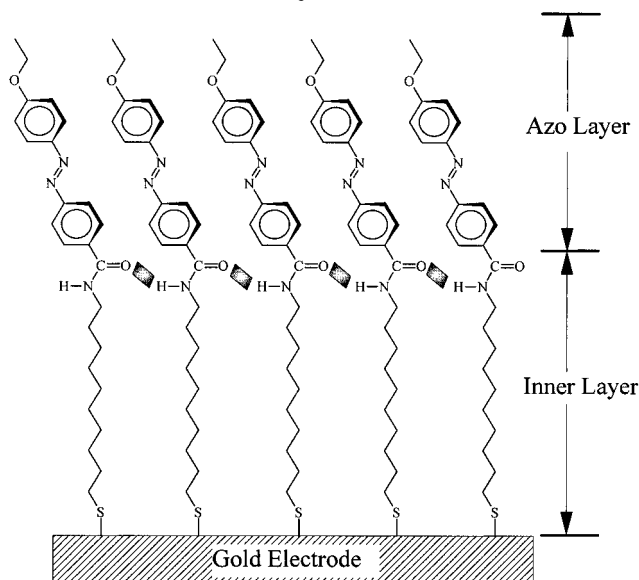
result is also in contrast to the results of the mercaptoalkanenitrile (HSCnCN, n = 2, 7) monolayer[35] and the 11-ferrocenyl-1-undecanethiol (FcC$_{11}$SH) monolayer[37,38] reported recently by our group, where no strong intermolecular hydrogen bonding interaction existed and potential dependent orientation changes in the monolayers were observed.

Since a large peak separation was found in the cyclic voltammogram (Figure 1), sluggish electron transfer behavior of azobenzene in the monolayer was expected. These sluggish electron transfer processes in the azobenzene self-assembled monolayers have been investigated extensively by electrochemical measurements.[1–7] In order to clarify the structure/orientation change and kinetics of the reduction of the azobenzene group in the monolayer, reaction time dependent IRRAS measurement was carried out in the present work. As shown in Figure 3, there are discernible changes in the band intensities, when the reaction time for the reduction process of the $C_2AzoC_{10}SH$ monolayer was extended from 5 to 605 s at −0.1 V before IRRAS spectra were recorded. As clearly shown in the series of spectra (Figure 3), all the bands we described above, including the one for the hydrazobenzene Ph–N–H bending vibration at 1508 cm^{-1}, distinctly increased when the cathodic potential was applied for a longer time, indicating that more azobenzene moieties in the monolayer were reduced. In contrast, as shown in Figure 4, only a small change in the band intensity was found as the oxidation time at the anodic potential (+0.8 V) was extended from 5 to 65 s. After that (65 s), no matter how long we applied the potential for oxidation, no discernible increase was observed in the IRRAS spectra (Figure 4).

Since the band at 1508 cm^{-1} can be considered as a direct indicator of the formation of hydrazobenzene upon the reduction of azobenzene moieties, it is reasonable to estimate the relative amount of hydrazobenzene moieties in the monolayer by using the intensity of this band. The ratios of amounts of hydrazobenzene to azobenzene at different reaction times were determined from the band intensity at 1508 cm^{-1} for the reduction (Figure 3, −0.1 V) and the reoxidation (Figure 4, +0.8 V) process of the monolayer. The ratios were normalized by the band intensity at 605 s for the reduction process (Figure 3) and the band intensity at 185 s for the oxidation process (Figure 4). The results are shown in Figure 5 for the reduction

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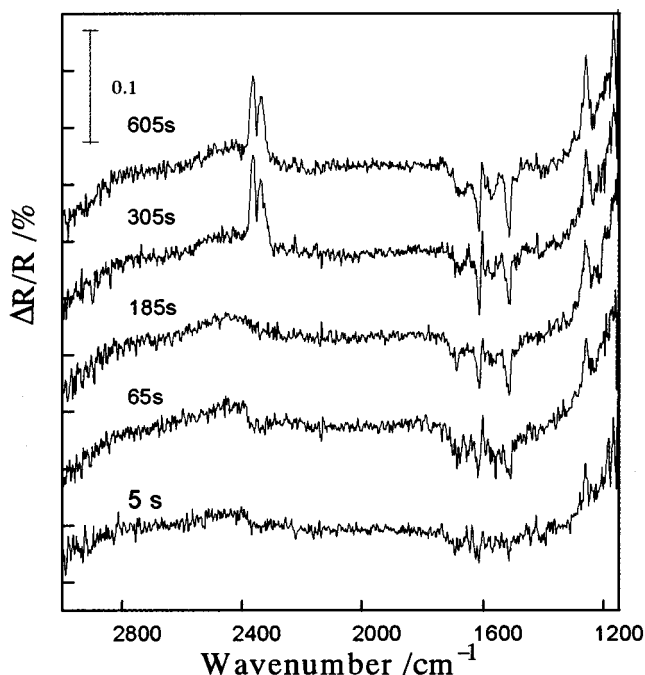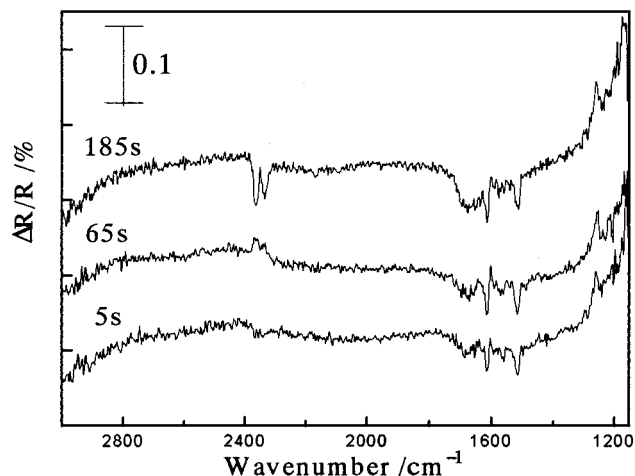
Figure 3. *In situ* IRRAS spectra of the $C_2AzoC_{10}SH$ monolayer on gold as a function of the reaction time at -0.1 V. The collection mode is 16×64 scans. Other conditions are the same as for Figure 2.

Figure 4. *In situ* IRRAS spectra of the $C_2AzoC_{10}SH$ monolayer on gold as a function of the reaction time at $+0.8$ V. The collection mode is 16×64 scans. The reduction time at -0.1 V was 65 s. Other conditions are the same as for Figure 2.

(square) and the oxidation (circle) processes, respectively.

The time dependence of the amount ratios for the reduction and the oxidation processes shown in Figure 5 obviously differs from each other, suggesting different kinetic characteristics for the two reactions. The rate of reduction of azobenzene to hydrazobenzene in the C_2-$AzoC_{10}SH$ monolayer is much slower than that of reoxidation of hydrazobenzene to azobenzene in the same monolayer. Comparing this with the redox kinetics behavior of the $H_2QC_{11}SH$ monolayer on gold we reported recently,[36] the origin for the sluggish kinetics in the present $C_2AzoC_{10}SH$ monolayer might be different since their chemical structures and reaction passways are different in their own. Mirkin and his co-workers[1-4] reported that Fc$-$Ph$-$N$=$N$-$Ph$-$$(CH_2)_4$SH monolayer on a gold electrode has an electrochemically accessible "ferrocene layer" and an electrochemically inactive "azobenzene interior layer" for a closely packed monolayer and recently termed
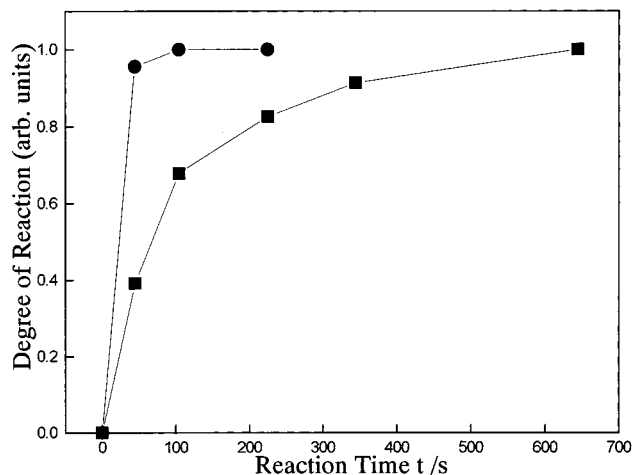

Figure 5. Normalized amount ratio of hydroazobenzene to azobenzene as a function of the reaction time for the reduction (■) and the reoxidation (●) process.

what they found as ion-gated electron transfer.[4] They suggested the prohibited incorporation of charge-compensating ions into the "azobenzene layer" should be responsible for the electrochemical inaccessibility of the azobenzene groups in the monolayer on the electrode. The sluggish reduction of azobenzene to hydrazobenzene we observed in $C_2AzoC_{10}SH$ SAM may be partially attributed to inhibited proton transportation and might be consistent with his hypothesis due to the similarities of these systems.

The relationship between the azobenzene monolayer structures and their respective electrochemical behaviors, especially in aqueous electrolytes, has been studied intensively in our group recently. The results have enabled us to conclude that the electrochemical kinetic behavior of azobenzene monolayers are dominated by closely-packed monolayer structures which interfere with both conformational change and proton transportation during the azobenzene/hydrazobenzene redox process.[1-8] When the hydrazobenzene is formed upon the reduction of the monolayer, conformational changes associated with the conversion of the planar azobenzene group[50] to the kinked hydrazobenzene[51] form must be inhibited by the rigid film structure and this rigidity might have a blocking effect on ion transportation in the meantime. For the $C_2AzoC_{10}SH$ monolayer, the strong hydrogen bonding between neighboring amide groups and the long-alkyl chain might contribute to a more densely packed structure which would make conformational change and proton transportation much more difficult. The alkyl chain under the amino group (inner layer) does not change its orientation when the azobenzene moiety undergoes its redox process, as evidenced by the fact that no bands for C$-$H vibrations and the amide group have been observed in the *in situ* IRRAS spectra, even when we extended the reaction time.

The time dependence of the IRRAS spectra described above are in good agreement with our predictions that the reduction of azobenzene shows a typical sluggish kinetic behavior in the present experimental time scales. Investigating the relationship between the electrochemical accessibility and the monolayer structure of highly organized azobenzene monolayers by means of *in situ* IRRAS method has enabled us to get a much clearer and direct view of this kind of novel molecular assembly

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(51) Pestena, D. C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528.

system. Further investigation with azobenzene monolayers of different structure is being carried out in our laboratory.

Conclusion

An electrochemical *in situ* FT-IRRAS study on the redox behavior of an azobenzene monolayer at a gold/electrolyte interface has been performed. The features observed in the IRRAS spectra arose only from changes in the chemical environments of azobenzene as a result of the azobenzene/hydrazobenzene redox process, and they provided no evidence for any change in the orientation of the polyethylene chains (inner layer) upon the reduction and reoxidation of the azobenzene group. Furthermore, a sluggish reduction of azobenzene, as well as a relatively faster reoxidation have been experimentally addressed for the first time by the time dependent FT-IRRAS measurement. This unique redox kinetic phenomenon was explained by the spatial inhibition of conformational change and hydrated proton transportation. Efforts to probe structure factors leading to the different rates at the oxidation and reduction processes within those monolayers using spectrochemical method may lead to new avenues for the applications of *in situ* spectroscopic studies.