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Notes

Carfagna, C. *Macromolecules* **1989**, *22*, 1600.

3. del Pino, J.; Gomez, M. A.; Ellis, G.; Marco, C.; Fatou, J. G. *Macromol. Chem. Phys.* **1994**, *195*, 2049.

4. Bahadur, B. *Liquid Crystals: Applications and Uses*; World Scientific Publishing Co. Singapore, 1990.

5. Yu, S.-C.; Paek, J.; Yu, K. H.; Ko, S. B.; Cho, I.-H.; Lee, M. *Bull. Korean Chem. Soc.* **1997**, *18*, 773.

6. Lee, M.; Oh, N.-K.; Lee, H. K.; Zin, W. C. *Macromolecules* **1996**, *29*, 5567.

7. Lee, M.; Oh, N.-K. *J. Mater. Chem.* **1996**, *6*, 1079.

8. Williams, K. P. J.; Pitt, G. D.; Smith, B. J. E.; Whitley, A.; Batchelder, D. N.; Hayward, I. P. *J. Raman Spec-*

trosc. **1994**, *25*, 131.

9. Yu, S.-C.; Chung, D.; Yu, K. H.; Kim, D. H.; Oh, N. K.; Lee, M.; Ko, S. B.; Cho, I. H. *Bull. Korean Chem. Soc.* **1996**, *17*, 1004.

10. Wu, P. P.; Hsu, S. L.; Thomas, O.; Blumstein, A. *Polymer Physics* **1986**, *24*, 827.

11. del Pino, J.; Gomez, M. A.; Marco, C.; Ellis, G.; Fatou, J. G. *Macromolecules* **1992**, *25*, 4642.

12. Shilov, S.; Volchek, B.; Zuev, V.; Skorokhodov, S. *Macromol. Chem. Phys.* **1994**, *195*, 865.

13. Thompson, P. A.; Eaton, W. A.; Hofrichter, J. *Biochemistry* **1997**, *36*, 9200.

FT-IR Spectral Analysis of Self-Assembled Monolayer Film of N-(2-Mercaptoethyl)-Anthraquinone-2-Amide on Gold

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Introduction

Redox molecules adsorbed on metal substrates have been regarded to be model systems to understand electron transfer in biological systems.[1] From the fact that quinone derivatives play important roles in biological systems,[2] their redox properties as well as their adsorption behavior on various electrode surfaces have been studied using electrochemical and spectroscopic techniques.[3-5]

The most popular quinoids compounds naturally occurring are anthraquinone derivatives.[6] In a hope eventually to prepare electroactive devices that could be applied as a biosensor, we are currently interested in the adsorption behavior of various anthraquinone derivatives on noble metals such as gold and silver. Recently, we found that a planar molecule, *i.e.*, anthraquinone-2-carboxylic acid, could be self-assembled and close-packed on a silver surface, forming a brick-like architecture.[7] On the other hand, in a molecular dynamics simulation study on benzylthiolate on Au (111),[8] it was found that the methylene group situated at between the sulfur head group and the benzene ring moiety should play a key role for the adsorbate molecules to arrange in a herringbone type structure.[9] On these grounds, we have investigated the adsorption behavior of N-(2-mercaptoethyl)-anthraquinone-2-amide, a flexible nonplanar anthraquinone derivative, on a gold surface, and herein we hope briefly to discuss its orientation on gold that could be deduced from the FT-IR spectroscopic data.

Experimental

N-(2-mercaptoethyl)-anthraquinone-2-amide (AQ-CONH-

C2-SH) was synthesized by coupling 2-aminoethanethiol with anthraquinone-2-carboxylic acid. The product was confirmed from H-NMR, IR, and mass spectra. Unless otherwise specified, all chemicals and gases were reagent grade and used as received.

Gold substrates were prepared by resistive evaporation of titanium (Aldrich, 99.99%) and gold (Aldrich, 99.99%) below 10^{-6} Torr on a batch of glass slides, cleaned previously with a hot piranha solution (30% $H_2O_2 : H_2SO_4 = 1 : 4$) and then sonicated in deionized water. After deposition of approximately 300 nm of gold, the evaporation chamber was backfilled with nitrogen.

Adsorbate solutions were prepared by dissolving weighed portions of AQ-CONH-C2-SH in nitrogen-bubbled anisole to desired concentrations covering the range from 10^{-3} to 10^{-7} M. Precleaned glass vials were used as the self-assembly cells. The gold substrates were immersed subsequently into the adsorbate solutions for a predetermined period of time. After the substrates were removed, they were rinsed with excess ethanol and then subjected to a strong nitrogen gas jet to blow off any remaining liquid droplets on the surface or the edges of the substrates.

The infrared spectra were obtained with a Bruker IFS 113v Fourier transform spectrometer equipped with a Globar light source and a liquid N_2-cooled mercury cadmium telluride detector. The method for obtaining the reflection-absorption infrared (RAIR) spectra has been reported previously.[10,11] Each RAIR spectrum was obtained by averaging 1024 interferograms at 4 cm^{-1} resolution, with p-polarized light incident on the gold substrate at 80°. The Happ-Genzel apodization function was used in Fourier transforming the interferograms. The RAIR spectra are reported as $-\log(R/R_o)$, where R and R_o are the reflectivities of the sample and the bare clean metal substrates, respec-

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tively.

As a supplementary set, the ellipsometric thickness of self-assembled AQ-CONH-C2-SH was estimated using a Rudolph Auto EL II optical ellipsometer. The measurement was performed with a 632.8 nm line of He/Ne laser incident upon the sample at 70°. The ellipsometric parameters, Δ and ψ, were determined for both the bare clean substrates and the self-assembled films. As usual, the refractive index of the AQ-CONH-C2-SH film was assumed to be 1.45.[12] The so-called DafIBM program supplied by Rudolph Technologies was employed to determine the thickness values. At least five different sampling points were considered to get the averaged thickness value.

Results and Discussion

As were the cases with simple aliphatic and aromatic thiols, AQ-CONH-C2-SH self-assembled very favorably on a gold surface. For instance, a complete monolayer seemed to be formed readily within 1 h by contacting the gold substrate with a 10^{-3} M AQ-CONH-C2-SH solution.

The RAIR spectra of AQ-CONH-C2-SH on gold which has been prepared by self-assembling for 24 h in 10^{-6} and 10^{-3} M solutions are shown in Figure 1(a) and 1(b), respectively. As one could certainly expect, the S-H stretching band was completely absent in the RAIR spectra; the band was seen at 2600 cm^{-1} in the transmission spectrum of neat AQ-CONH-C2-SH (not shown here). This indicates that the molecule should chemisorb on gold as thiolate. It is quite surprising that the peak intensities in Figure 1(a) are quite comparable to those in Figure 1(b). This is indicative of the favorable adsorption of AQ-CONH-C2-SH on gold. Hence, we assume that the spectrum shown in Figure 1(b) should correspond to the monolayer of AQ-CONH-C2-SH on gold in a full coverage limit.

Although the overall spectral features in Figure 1(a) are very similar to those in Figure 1(b), the relative peak intensities are clearly different between the two RAIR spectra. It can be attributed to the difference in the orientation of the adsorbed species for the two cases. In addition, the an-
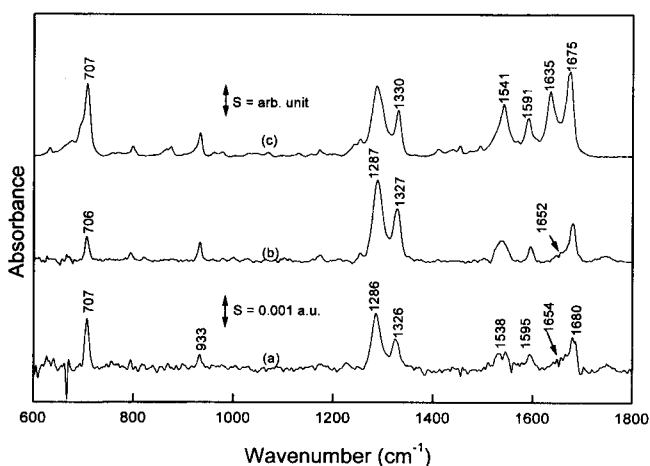
isotropic orientation of the adsorbed species on gold can be anticipated by comparing the RAIR spectra with the transmission infrared (TRI) spectrum of AQ-CONH-C2-SH in KBr matrix shown in Figure 1(c). The peaks in the region of 1500-1700 cm^{-1} are obviously much intense, in a relative sense, in the TRI spectrum than their counterparts in the RAIR spectrum; as far as the peak positions are concerned, all the TRI and RAIR spectra are comparable to one another, and this indicates clearly that the adsorbed species on gold is AQ-CONH-C2-S^{-}.

To deduce the orientation of AQ-CONH-C2-S^{-} on gold from the RAIR spectra, a correct vibrational assignment is a prerequisite. For this end, we consulted the well-established spectral assignments of anthraquinone and *N*-methylacetamide. In our previous work, it was concluded that the vibrational modes of the anthraquinone moiety in anthraquinone-2-carboxylic acid (AQ-2-COOH)[7] correlate well with those of anthraquinone (AQ)[13] itself; namely, the directions of the transition dipoles of AQ-2-COOH ring modes were comparable to those of AQ. A similar correlation is expected to hold even to AQ-CONH-C2-SH. In fact, the major ring vibrational bands appeared at nearly the same positions for both the AQ and AQ-CONH-C2-SH samples in the neat solid state. For instance, the ring vibrational modes whose transition dipoles aligned along the long axis of the anthraquinone moiety (b_{2u} modes) appear at 933, 1286, and 1330 cm^{-1} for AQ-CONH-C2-SH and at 937, 1285, and 1333 cm^{-1} for AQ itself, respectively. The ring modes whose transition dipoles aligned along the short axis of the anthraquinone moiety (b_{1u} modes) appear at 1591 and 1675 cm^{-1} for AQ-CONH-C2-SH and at 1591 and 1679

Figure 1. RAIR spectra of AQ-CONH-C2-SH self-assembled on a vacuum deposited gold substrate for 24 h in (a) 10^{-6} M and (b) 10^{-3} M anisole solutions. (c) TRI spectrum of AQ-CONH-C2-SH in KBr matrix.

Table 1. Infrared spectral data and vibrational assignment of AQ-CONH-C2-SH in neat and adsorbed state on gold[a]

| TRI[b] neat solid | RAIR | | Assignment[c] |
	Au film in 10^{-3} M	Au film in 10^{-6} M	
707 vs[d]	706 s	707 vs	$\nu_{63}(b_{3u})$ C-H bend.(op)[e]
798 vw	794 w	794 vw	$\nu_{62}(b_{3u})$ skeletal def.(op)
933 m	933 m	933 w	$\nu_{47}(b_{2u})$ skeletal def.(ip)[e]
1253 m	1253 w	1253 vw	amide III
1286 vs	1287 vs	1286 vs	$\nu_{44}(b_{2u})$ C-C str.
1330 s	1327 s	1326 s	$\nu_{43}(b_{2u})$ C-C str.
1541 s	1538 m	1538 m	amide II
1591 s	1595 m	1595 m	$\nu_{25}(b_{1u})$ C-C str.
1635 vs	1652 sh	1654 sh	amide I
1675 vs	1680 s	1680 s	$\nu_{24}(b_{1u})$ C=O str.
2600 vw	ND	ND	ν(S-H)
2875 w	2870 vwb	2870 vwb	$\nu_{sym}(CH_2)$
2929 w	2922 vwb	2922 vwb	$\nu_{asym}(CH_2)$
3023 w	3022 w	3022 w	$\nu_{40}(b_{2u})$ C-H str.
3063 w	ND	ND	$\nu_{23}(b_{1u})$ C-H str.
3080 w	3079 vw	3079 vw	$\nu_{39}(b_{2u})$ C-H str.
3300 w	ND	ND	ν(N-H)

[a] Wavenumber in cm^{-1}. [b] Taken in KBr matrix. [c] Assigned based on references 7, 13-15. Symmetry classification and mode labelling conform to those of AQ in D_{2h} point group, taken from reference 13. See text. [d] vs; very strong, s; strong, m; medium, w; weak, vw; very weak, vwb; very weak and broad, ND; no detected. [e] ip; in-plane, op; out-of-plane.

cm^{-1} for AQ, respectively. Although slightly less consonant, the typical out-of-ring modes (b$_{3u}$ modes) appear at 707 and 798 cm^{-1} for AQ-CONH-C2-SH and at 694 and 810 cm^{-1} for AQ, respectively. On the other hand, the peaks at 1634 and 1544 cm^{-1} in the TRI spectrum of AQ-CONH-C2-SH whose counterparts could not be found in the AQ spectrum can be assigned, respectively, to the amide I and amide II bands.[14-16] The vibrational assignments made on these grounds are summarized in Table 1, in which the symmetry types refer to AQ in D$_{2h}$ symmetry.

Recalling the infrared surface selection rule that only the vibrational modes whose dipole moment derivatives have components normal to the metal surface are exclusively infrared active,[16] the appearance of the b$_{1u}$, b$_{2u}$, and b$_{3u}$ type bands altogether in the RAIR spectra suggests that the anthraquinone moiety of the adsorbed AQ-CONH-C2-S$^-$ is neither perpendicular nor flat with respect to the gold surface. Namely, the ring plane seems to have a tilted orientation on the surface.

Figure 2(a) defines the laboratory coordinates so that Z is the direction perpendicular to the surface, while X and Y represent directions at the surface. The angle between the long axis of the anthraquinone moiety and the Z coordinate is defined as θ (*i.e.*, the tilt angle of the long axis away from the surface normal). Similarly, the angle between the plane of anthraquinone moiety and the X-Z plane is defined as Φ, *i.e.*, the twist angle of the plane of AQ moiety. Recalling the theory of RAIR spectroscopy, θ and Φ can be related to the intensity ratios of selected bands in RAIR and TRI spectra using the following equations;[17] herein, a uniaxial model is implicit since the gold substrate is not a single crystal.

$$A_{\parallel}(R)/A^i_{\perp}(R) = [A_{\parallel}(T)/A^i_{\perp}(T)][\cot^2\theta/\cos^2 \Phi] \quad (1)$$

$$A_{\parallel}(R)/A^o_{\perp}(R) = [A_{\parallel}(T)/A^o_{\perp}(T)][\cot^2\theta/\sin^2 \Phi] \quad (2)$$

where $A_{\parallel}(R)$ and $A_{\parallel}(T)$ are the absorbance of a band in the RAIR and TRI spectra, respectively, having transition dipole moments parallel to the long axis (b$_{2u}$ type, and call it as the first kind of band); $A^i_{\perp}(R)$ and $A^i_{\perp}(T)$ are the absorbances of a band in the RAIR and TRI spectra, respectively, having transition dipole moments perpendicular to the long axis and in the plane of the anthraquinone moiety (b$_{1u}$ type, and call it as the second kind of band); and $A^o_{\perp}$ (R) and $A^o_{\perp}(T)$ are the absorbances of a band in the RAIR and TRI spectra, respectively, having the transition dipole moment perpendicular to the long axis but out of the molecular plane (b$_{3u}$ type, and call it as the third kind of band).

Among the first kind of bands, the bands appearing in the 1280-1330 cm^{-1} region are known to be in Fermi resonance with the nearby combination bands.[7] Accordingly, we selected the band at 933 cm^{-1} in Figure 1(c) (as well as in Figure 1(a) and 1(b)) as the typical first kind of band. We selected the C=O stretching band of AQ moiety, appearing at 1675 cm^{-1} in Figure 1(c) and at 1680 cm^{-1} in Figure 1(a) and 1(b), as the typical second kind of band. As a third kind of band, we selected the distinct band appearing at 707 cm^{-1} in Figure 1(a) (as well as in Figure 1(b) and 1(c)). On these grounds, the tilt (θ) and twist (Φ) angles of the AQ moiety are determined to be 50° and 49°, respectively, for the AQ-CONH-C2-S$^-$ monolayer prepared in a 10^{-6} M solution and to be 40° and 35°, respectively, for the mono-
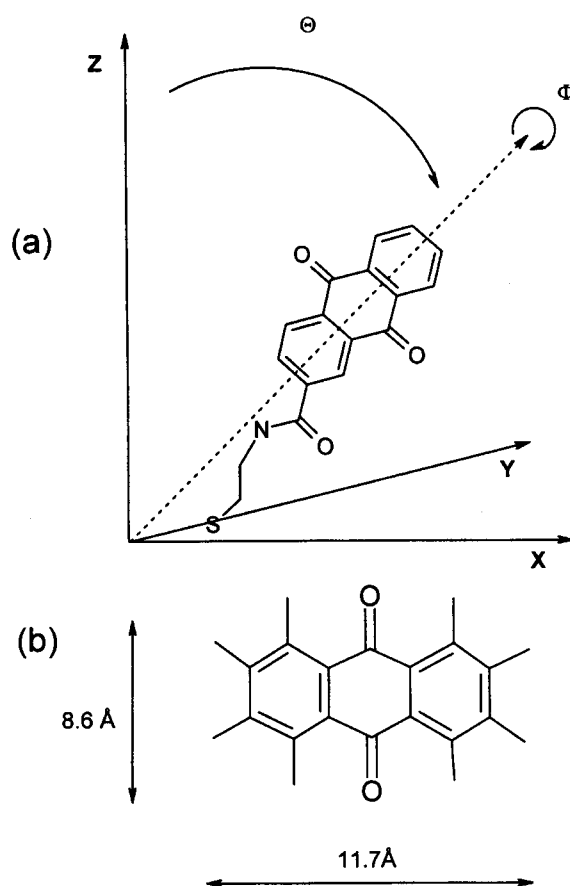

Figure 2. (a) Definition of the tilt (θ) and twist (Φ) angles for the AQ moiety of AQ-CONH-C2-SH adsorbed on gold. (b) Dimension of the AQ moiety of AQ-CONH-C2-SH deduced from the X-ray crystallographic data of neat AQ crystal.

layer prepared in a 10^{-3} M solution. This suggests that the AQ moiety has to be inclined with respect to the surface normal albeit the plane may assume a slightly more perpendicular stance upon the increase in the surface coverage.

Regarding the orientation of other parts of AQ-CONH-C2-S$^-$, any quantitative conclusion can not be made. Nonetheless, a qualitative information seems to be extracted from the infrared spectral features. The amide I band should arise mainly from the C=O stretching vibration.[14,15] Then, it is noteworthy that the N-H stretching and the amide I bands as well as the C=O stretching band of the AQ moiety are considerably weakened in the RAIR spectra compared with those in the TRI spectrum. This suggests that the amide group is co-planar with the AQ moiety and also that the weak bands must be attributed to the twist of the molecular plane with respect to the X-Z plane. Since the amide II band is contributed almost equally by the N-H bending and the C-N stretching modes,[14,15] it is difficult to explain its peak intensity variation. It would be also noteworthy that the symmetric as well as the antisymmetric stretching bands of the CH$_2$ group were hardly seen in the RAIR spectra. This may indicate that the CH$_2$ plane is parallel to the gold substrate so that the C-C bond between the two methylene groups is nearly perpendicular to the metal substrate.[18]

Referring to the X-ray crystallographic data of AQ crystal,[19] the dimension of the AQ moiety in AQ-CONH-C2-S- is es-

timated to be 11.7 Å long, 8.6 Å wide, and 3.6 Å thick, as drawn in Figure 2(b). Using the known bond lengths, bond angles, van der Waals atomic radii, and the approximate distance between the sulfur atom and the gold surface,[20] the thickness of the AQ-CONH-C2-SH monolayer on gold is estimated to be 11.8 and 13.3 Å, respectively, when the tilt and twist angles determined from the RAIR spectra for the samples prepared in 10^{-6} and 10^{-3} M solutions were invoked. It would be desirable to compare these values with the ellipsometric measurement, albeit a direct comparison may be controversial due to the various uncertainties in the ellipsometry measurement (*i.e.*, oxide formation and ambient contamination). Since the solution of the ellipsometry equations, *i.e.*, refractive index and thickness, could not be obtained simultaneously, a refractive index of 1.45 was assumed for the estimation of thickness. From a three phase optical model, the ellipsometric parameters corresponded to the thicknesses of 9.6 ± 1.1 Å and 10.8 ± 0.5 Å for the samples prepared in 10^{-6} and 10^{-3} M solutions, respectively. Although the predicted thicknesses from the RAIR spectral feature do not agree with the measured thicknesses, it is nonetheless informative that the predicted difference in the thicknesses of the AQ-CONH-C2-SH monolayers prepared in 10^{-6} and 10^{-3} M solutions is quite comparable to that measured by ellipsometry.

In summary, we have found that AQ-CONH-C2-SH should chemisorb well on a gold surface. The AQ moiety is concluded to be tilted and twisted with respect to the surface normal in a full surface coverage limit. The present information will be useful in the investigation of the adsorption kinetics and the spectroelectrochemical charactersitics of various AQ derivatives, and eventually in the preparation of AQ-containing electroactive devices that could be applied as a biosensor.

References

1. Murray, R. W. *Molecular Design of Electrode Surface*; Techniques of Chemistry Series; John Wiley & Sons, Inc.: New York, 1992; Vol. XXII.
2. Patai, S.; Rappoport, Z. *The Chemistry of the Quinonoid Compounds*; John Wiley & Sons, Inc.: New York, 1992; Vol. 2.
3. Ye, S.; Yashiro, A.; Sato, Y.; Uosaki, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3813.
4. Stern, D. A.; Wellner, E.; Salaita, G. N.; Davidson, L. L.; Lu, F.; Batina, N.; Frank, D. G.; Zapien, D. C.; Walton, N.; Hubbard, A. T. *J. Am. Chem. Soc.* **1988**, *110*, 4885.
5. Soriaga, M. P.; Soriaga, E. B.; Hubbard, A. T.; Benziger, J. B.; Pang, K. W. P. *Inorg. Chem.* **1985**, *24*, 65.
6. Tomson, R. H. *Naturally Occurring Quinones (2ed)*; Academic Press: New York, 1971.
7. Han, S. W.; Ha, T. H.; Kim, C. H.; Kim, K. *Langmuir* in press.
8. Jung, H. H.; Shin, S,; Kim, K.; Won, Y. D. submitted for publication.
9. Tao, Y.-T.; Wu, C.-C.; Eu, J.-Y.; Lin, W.-L. *Langmuir* **1997**, *13*, 4018.
10. Kim, S. H.; Ahn, S. J.; Kim, K. *J. Phys. Chem.* **1996**, *100*, 7174.
11. Son, D. H.; Ahn, S. J.; Lee, Y. J.; Kim, K. *J. Phys. Chem.* **1994**, *98*, 8488.
12. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.
13. Spanget-Larsen, J.; Christensen, D. H.; Thulstrup, E. W. *Spectrochim. Acta* **1987**, *43A*, 331.
14. Sugawara, S.; Hirakawa, A. Y.; Tsuboi, M. *J. Mol. Spectrosc.* **1984**, *108*, 206.
15. Yu, N. T.; Jo, B. H.; Liu, C. S. *J. Am. Chem. Soc.* **1972**, *94*, 7572
16. Greenler, R. G. *Chem. Phys.* **1968**, *10*, 1963.
17. Young, J. T.; Boerio, F. J.; Zhang, Z.; Beck, T. L. *Langmuir* **1996**, *12*, 1219.
18. Ahn, S. J.; Son, D. H.; Kim, K. *J. Mol. Struct.* **1994**, *324*, 223.
19. Sen, S. N. *Indian J. Phys.* **1948**, *22*, 347.
20. Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 9389.

Direct Synthesis of Benzylamine Derivatives from Aldehydes and Ketones *via* Phenylhydrazones Using BER-Pd(OAc)₂

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Reductive amination is commonly carried out using cyanoborohydrides.[1-3] Borane pyridine (BAP),[4] sodium triacetoxyborohydride[5] and borohydride exchange resin (BER)[6] were also reported as alternative, less expensive and less toxic reagents. Using these methods, secondary and tertiary amines are prepared in very good yields; however, primary amines are obtained in poor to moderate yields using cyanoborohydride[1b] or BER.[6] Alternatively primary amines