# The 6-(10-Mercaptodecoxyl)quinoline Self-Assembled Monolayer on Gold: Spectroscopy and Wettability Investigation

Hao-Li Zhang,* Hua Zhang,† Jin Zhang,* Zhong-Fan Liu,† and Hu-Lin Li*,[1]

*Department of Chemistry, Lanzhou University, Lanzhou 730000, China; and †Center for Intelligent Materials Research (CIMR), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

E-mail: Lihl@lzu.edu.cn

A self-assembled monolayer (SAM) with an exposed basic group has been generated by the adsorption of a novel quinoline derivative 6-(10-mercaptodecoxyl)quinoline (MDQ) on a gold surface. The structure and surface properties of the SAMs of MDQ were characterized by ellipsometry, reflection absorption FTIR (RA-IR), and contact angle titration. It was found that the quinoline moiety of MDQ forms an ordered layer on the top of the film and the alkyl chain exhibits a packing density similar to that of a monolayer of decanethiol. The molecular orientation of MDQ in SAMs was evaluated by RA-IR spectroscopy which indicates that the alkyl chain exhibits a tilting angle of 24 ± 4° with respect to the surface normal and a twisting angle of 50 ± 5° around its axis. Contact angle titration in the pH range between 2 and 12 illustrates that the surface of SAM of MDQ is less hydrophilic for acidic solution than for basic solution, which is in contrast with the previous reports on SAMs that basic groups are located at the ends of the molecules. © 1999 Academic Press

*Key Words:* self-assembled monolayer (SAM); quinoline derivative; reflection absorption infrared (RA-IR) spectroscopy; contact angle.

## INTRODUCTION

Functionalized self-assembled monolayers (SAMs) have attracted increasing attention in the past decade in the fields of interfacial chemistry and materials science research. Such monolayers are densely packed and well ordered; therefore, they have been widely used in the research of wetting, adhesion, catalysis, lubrication, and corrosion inhibition (1). Recently, SAMs modified with acidic or basic groups have been used for studying the ionization behavior at interfaces. Whitesides and co-workers have extensively investigated the wetting of a variety of monolayers with exposed ionizable groups (2, 3). Later, Creager and co-workers reported the results of research on mixed monolayers vs a nonreactive spreading protocol using contact angle titration (4). Liu's group also studied amino-terminal mono-

layers by both contact angle titration and chemical force microscopy (CFM) (5, 6).

Generally, the reports demonstrated that surfaces modified with a monolayer of molecules containing ionizable groups became more wettable as they became more ionized. However, there have been few reports on more complex or more conjugated systems, such as quinoline derivatives, as the basic moiety. In this work, a novel quinoline-containing alkanethiol was synthesized and its monolayer on gold surface was fabricated. Subsequently, the structure of the monolayer was evaluated by ellipsometry and reflection absorption infrared (RA-IR) spectroscopy; in addition, the surface wettability was studied by contact angle titration.

Molecules containing a quinoline group were selected as model systems because of their planar structure and weak basicity (the $pK_a$ of protonated quinoline is about 4.8). We seek to answer two questions. How does a large planar group situated at the end of alkyl chain affect the film structure? Does the quinoline moiety in a SAM exhibit a different titration behavior from the small basic groups studied previously?

## EXPERIMENTAL SECTION

6-(10-Mercaptodecaoxyl)quinoline (MDQ) was synthesized by the following procedure. First, 6-hydroxylquinoline was converted to 6-(10-bromodecaoxyl)quinoline by conventional Williamson ether synthesis. The 6-(10-bromodecaoxyl)quinoline was reacted with thiourea and then hydrolyzed with NaOH aqueous solution to give the product (Scheme 1). The crude MDQ was purified by column chromatography (silica, eluent = chloroform) and the structure was confirmed with EI-MS, ^{1}H NMR, and IR (7). Other reagents were of analytical purity and were used as received. Ultrapure water with a resistivity of above 18 MΩ · cm was used throughout the experiments.

The substrates employed in this study were prepared by evaporating a 200 nm thick layer of gold (99.99%) onto a glass slide (7.5 cm × 2.5 cm) precoated with 10–15 nm chromium. SAMs were prepared by immersing the clean gold substrates
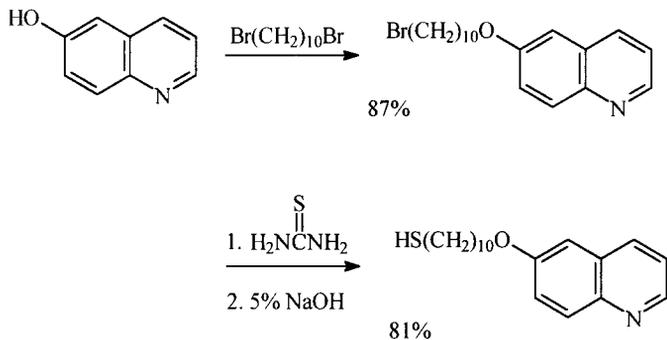
**SCHEME 1.** Synthesis of MDQ.

into a 1.0 mM ethanol solution of quinoline derivative for over 24 h to reach a saturated coverage. Afterwards, the monolayer was washed with ethanol and was dried in N2 prior to the characterization.

The thickness of the monolayer was monitored with use of a Gaertner L116B ellipsometer equipped with a 632.8 nm helium–neon laser. The laser beam is 1.0 mm in diameter with the incident angle is 70° with respect to the surface normal. A three-layer optical mode was applied for calculating the mono-layer thickness with assuming refractive index ($n_f$) of the organic film to 1.5.

RA-IR spectra were measured at 4 cm$^{-1}$ resolution on a Perkin–Elmer System 2000 FTIR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. 500 interferograms were usually collected to achieve an acceptable signal-to-noise ratio. The sample chamber was purged with nitrogen to minimized interference by water va-por. Samples were mounted on a SPECAC variable angle reflection accessory, in which the incident angle of the p-polarized infrared radiation was 86°.

Contact angle titrations were performed with a contact angle goniometer (Model JJC-II, The Fifth Optical Instrument Fac-tory of Changchun) under ambient conditions (15–20°C, 50–60% relative humidity) using yellow light to illuminate the water droplet. Each point represents an average of at least three measurements. Phosphate buffers were used as probe liquids in the contact angle measurement. The ionic strength of the phosphate buffer was maintained at 0.01 mol/L. For the mea-surement of buffered water on the SAMs, readings were taken from free-standing droplets formed at the end of a fine bore capillary tube after it was lowered onto the surface. The cap-illary tube was then removed and the contact angle of the free-standing droplet was measured after 10 to 20 s of expan-sion. Errors in these measurements were usually less than 2°.

## RESULT AND DISCUSSION

### A. Structural Evaluation

It is important to know the molecular structure of the MDQ SAM before studying any of its wet properties studied. The

thickness of MDQ monolayer was measured by ellipsometry as 2.2 ± 0.1 nm. The result is consistent with the molecular length of MDQ being 2.2 nm (which is calculated by assuming the alkyl chain is extended and is an all-trans conformation) and indicates that the molecules in the film are densely packed so that they exhibit a very small tilting angle with respect to the gold surface normal. However, due to the uncertainty of the refractive index ($n_f$) of the organic layer, we found that the information obtained from ellipsometry is very limited and the thickness is not precise enough for further structural evalua-tion. Detailed structural analysis of the monolayer can be performed by infrared spectroscopic techniques.

The RA-IR spectrum of the MDQ SAM between 4000 and 800 cm$^{-1}$ is shown in Fig. 1. For comparison, the transmission spectrum of an isotropic sample of the same compound in a KBr pellet is also shown. Since the IR spectrum of MDQ has not been reported before, it is necessary to give the band assignments for the bulk spectrum first. The assignments are based on the comparison of MDQ spectrum with the spectra of related compounds, e.g. quinoline, 6-hydroxylquinoline, and various alkane thiols. The band positions and assignments (8, 9) are listed in Table 1.

In the spectrum of the KBr pellet, a weak band around 3050 cm$^{-1}$ is assigned to the aromatic C–H stretching modes of the quinoline moiety. Consistent with previous reports, the band assigned to aromatic C–H stretching modes is broad and is split into at lest three bands that may be attributed to stretching of the various aromatic C–H bonds in the molecule (10, 11). The prominent bands between 2800 and 2950 cm$^{-1}$ are easily identified as the stretching vibrations of methylene groups; the symmetric stretching ($\nu_s$-CH$_2$) is at 2851 cm$^{-1}$, and asymmet-ric stretching ($\nu_{as}$-CH$_2$) is at 2923 cm$^{-1}$. The S–H stretching mode gives rise to a small peak at 2566 cm$^{-1}$. Most bands falling in the frequency region of 1700–1400 cm$^{-1}$ are readily assigned to the aryl skeletal stretching vibrations of C=N and C=C bonds in the quinoline fused ring. The band at 1469 cm$^{-1}$ is assigned to an in-plane deformation (scissoring mode) of CH$_2$. The most intense band in the region below 1000 cm$^{-1}$, at 842 cm$^{-1}$, is assigned as an aryl-H out-of-plane wagging mode (12).

On the basis of the selection rule of RA-IR, *only those transitions having the non-zero component of their dipole moment in the direction of the surface normal can bring about absorption,* and several important features in the RA-IR spec-trum of the SAM of MDQ could be seen (Table 1).

Firstly, as noted above, the aryl C–H stretching band at 3050 cm$^{-1}$ in the spectrum of the KBr pellet is rather broad and shows a shoulder at 3079 cm$^{-1}$. In contrast, only a single very weak band at 3076 cm$^{-1}$ is observed in the RA-IR spectrum of the SAM. We think the bands at 3050 cm$^{-1}$ and the shoulder around 3079 cm$^{-1}$ correspond with the stretching vibrations of different aryl C–H bonds in the quinoline ring. Thus, the absence of the 3050 cm$^{-1}$ band in the RA-IR spectrum indi-cates that the corresponding C–H bonds have large angle with
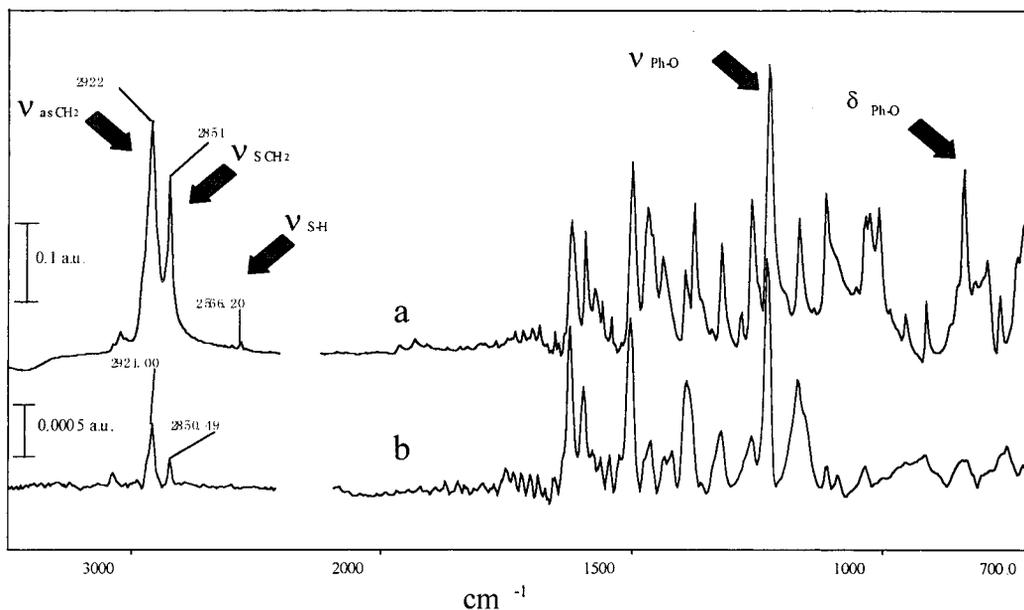
**FIG. 1.** (a) Transmission spectrum of MDQ molecule in KBr pellet and (b) RA-IR spectrum of a SAM of MDQ.

respect to the surface normal. Understanding of the spectrum in this region is still very limited because the exact assignment to the vibrational modes in this region has not yet been achieved.

It is well known that the position, the intensity and the shape of $\nu_s$-CH$_2$ and $\nu_{as}$-CH$_2$ of the CH$_2$ bands are sensitive to the phase state of the polyethylene chain (13, 14). A disordered "liquid-like" SAM is expected to give broader absorption bands and exhibit higher frequency than that in the crystalline state (15). In the RA-IR spectrum of MDQ SAM, $\nu_{as\text{-}CH_2}$ and $\nu_{s\text{-}CH_2}$ are observed at 2921 and 2850 cm$^{-1}$, respectively. It is notable that both of the $\nu_{as\text{-}CH_2}$ and $\nu_{s\text{-}CH_2}$ modes shift toward lower frequency compared with that observed in the transmis-

## TABLE 1
### Assignments of infrared bands

| Vibrational modes | In KBr[a] | In SAM[a] | Direction of dipole moment transition[a] |
|---|---|---|---|
| Aryl $\nu_{C-H}$ | 3079 (shoulder) | 3076 w | ip quinoline rings |
| | 3050 w | | |
| $\nu_{as}$–CH$_2$ | 2922 s | 2921 m | ip CH$_2$, cross H |
| $\nu_s$–CH$_2$ | 2851 s | 2850 m | ip CH$_2$, bisec HCH |
| $\nu_{S-H}$ | 2566 w | Not observed | //S–H bond |
| Aromatic skeleton | 1622 m | 1625 s | ip quinoline rings |
| | 1594 m | 1598 m | ip quinoline rings |
| | 1500 m | 1505 s | ip quinoline rings |
| $\delta_{CH2}$ | 1469 m | 1467 w | ip CH$_2$, bisec. HCH |
| $\nu_{Ph-O}$ | 1228 s | 1231 s | //Aryl C–O bond |
| $\nu_{C-O}$ | 1030 m | 1030 w | //Alkyl C–O bond |
| $\delta_{Ph-H}$ op | 843 s | 842 w | Perpendicular to aryl ring |

[a] s, strong; m, middle; w, weak; op, out of plane; ip, in plane.

sion spectrum of a polycrystalline sample (Table 1). These shifts suggest that the molecules in the MDQ SAM are as densely packed as they are in the solid state (13–15). Generally speaking, introducing a functional group with a large volume into a SAM usually disturbs the packing of hydrocarbon chain (16). It is necessary to discuss how the quinoline group disturbs the alkyl chain. To this end, the SAM of decanethiol, which has same number of methylene groups as the MDQ molecule, has also been studied for reference. In the RA-IR spectrum of the decanethiol SAM, $\nu_{as\text{-}CH_2}$ and $\nu_{s\text{-}CH_2}$ are found around 2920 and 2850 cm$^{-1}$, respectively. Compared with the values for the decanethiol SAM, the methylene stretching vibrations in the spectrum of MDQ SAM are shifted slightly to high frequency (no more than 1 cm$^{-1}$), suggesting that the perturbation of the packing density of alkyl chain introduced by the quinoline group in the SAM of MDQ is not significant. Therefore, it is reasonable to propose that the quinoline group must adopt the orientation in which it has the smallest projection on the substrate. The most probable configuration is that the plane of the quinoline group is parallel with the surface normal.

The very weak S–H stretching vibration at 2566 cm$^{-1}$ in the spectrum of KBr pellet is absent in the spectrum of the SAM of MDQ, which is consistent with the formation of the S–Au bond.

The strength of several bands between 1700 and 1400 cm$^{-1}$ that were assigned to the aryl ring stretching vibrations of C≡N and C≡C bonds in the quinoline fused ring, indicates that the direction of the derivative of these modes is predominately in the plane of the quinoline ring. Thus, the strong bands at 1625, 1598, 1504, and 1422 cm$^{-1}$ in the RA-IR spectrum of MDQ SAM indicate that there is a large angle

between the plane of quinoline ring and the surface of the substrate. In contrast with the medium absorption of the methylene in-plane deformation at 1469 cm$^{-1}$ in the spectrum of the KBr pellet, the fact that the band at 1464 cm$^{-1}$ is very weak in the RA-IR spectrum of the SAM indicates that the alkyl chain exhibits a very small tilting angle with respect to the surface normal.

The two most characteristic bands of the aromatic ether are the stretching vibrations of the aryl C–O bond ($\nu_{C-O}$) and the alkyl C–O bond ($\nu_{C-O}$). In the transmission spectrum, $\nu_{Ph-O}$ is observed as a strong band at 1228 cm$^{-1}$ and $\nu_{C-O}$ is observed as a medium strength absorption at 1030 cm$^{-1}$. For comparison, $\nu_{Ph-O}$ stretching exhibits the strongest band in the RA-IR spectrum of the SAM of MDQ while the $\nu_{C-O}$ stretching is relatively weak. The $\nu_{Ph-O}$ band may be not the pure Ph–O stretching, but may involve the contribution of the out-of-phase C–O–C stretching or mixes with ring vibration (8, 9). However, the greatest contribution comes from stretching of the Ph–O bond, so that the dipole moment transition is roughly parallel with the Ph–O bond. Therefore, the high intensity of $\nu_{Ph-O}$ in RA-IR spectrum suggests that the Ph–O bond is at a very small angle with respect to the surface normal.

By analogous to the benzene and naphthalene derivatives, most medium intense bands in the region from 1400 to 1000 cm$^{-1}$ involve deformation of aryl ring, rocking of methylene and aryl-H in-plane bending in quinoline group. An exact assignments for these bands is not possible at this time. Thus these bands gives little useful information on the orientation of the MDQ molecule. The strongest band below 1000 cm$^{-1}$ in the spectrum of the KBr pellet is the aryl C–H out-of-plane wagging at 842 cm$^{-1}$, but this band is barely detected in the RA-IR spectrum. Since the direction of dipole moment transition of the aryl C–H out-of-plane wagging mode is perpendicular to the plane of quinoline ring, the weak intensity of this band in RA-IR spectrum suggests that the plane of the quinoline ring is roughly perpendicular to the substrate surface.

Several methods of estimating the orientation angle of MDQ molecules in a SAM, by comparing the RA-IR spectrum with that of an isotropic sample have been reported (17–21). In this work, Dete's method (18) was used, which is based on a comparison of the intensity of selected bands in the RA-IR spectrum of the monolayer referenced to those of a bulk sample. The general assumptions of such a comparison are that (i) the oscillator strengths of the vibrations of the adsorbed molecules do not change appreciably upon chemisorption as that in the isotropic reference sample; (ii) the electric field of infrared radiation at the metal surface is not expected to change significantly near the wavelengths of interest, so that the transition dipole moments are all affected equally.

According to the selection rule of RA-IR spectra for metal surfaces, the intensity of a vibrational mode for a molecule adsorbed on a metal surface is given by

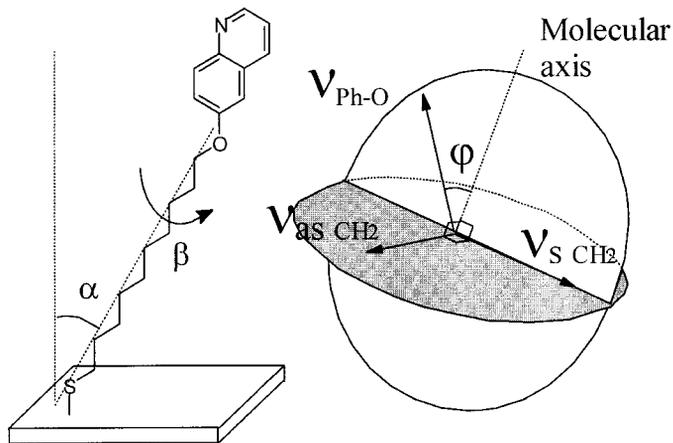$$I \propto |\mathbf{E} \cdot \mu_z|^2, \qquad [1]$$



**FIG. 2.** Definition of molecular orientation in SAM and the related vibrational modes.

where $\mathbf{E}$ is the electric field at the metal surface and $\mu_z$ is the vertical projection of the transition dipole moment.

Three vibrational modes were used to evaluate the orientation of the MDQ moieties of the gold surface. Those were the CH$_2$ symmetric stretching ($\nu_s$-CH$_2$), the CH$_2$ asymmetric stretching ($\nu_{as}$-CH$_2$) and the Ph–O stretching ($\nu_{Ph-O}$), respectively. Expressions for $\mu_z$ for each mode used in our analysis of the MDQ SAM are presented in terms of the dynamic dipole moment for each mode and the tilting($\alpha$) and twisting($\beta$) angles of the monolayer illustrated in Fig. 2 are given by (23):

$$(|\mu_{\nu_{s-CH_2}}|)_z = |\mu_{\nu_{s-CH_2}}|\sin \alpha \cos \beta, \qquad [2]$$

$$(|\mu_{\nu_{as-CH_2}}|)_z = |\mu_{\nu_{as-CH_2}}|\sin \alpha \cos \beta, \qquad [3]$$

$$(|\mu_{\nu_{Ph-O}}|)_z = |\mu_{\nu_{Ph-O}}|(\cos \varphi \cos \alpha + \sin \varphi \sin \alpha \sin \beta). \qquad [4]$$

All three bands are prominent in the transmission spectrum of the KBr pellet of MDQ and exhibit strong enough integrated intensities in the RA-IR spectrum that the errors in measuring accurate integrated infrared bands intensities are small. The value of $\varphi = 35°$ in Eq. [4] was obtained from the geometrical analysis to the molecule using the regular bond angle values.

The ratio of the infrared integrated band intensities for $\nu_{s-CH_2}$ and $\nu_{as-CH_2}$ gives the twisting angle ($\beta$). Based on the correlation between the dynamic dipoles and the infrared intensity and using Eqs. [2] and [3], one obtains

$$\beta = \arctan\left[\left(\frac{I\nu_{as-CH_2}}{I\nu_{s-CH_2}}\right)_{SAM}\left(\frac{I\nu_{s-CH_2}}{I\nu_{as-CH_2}}\right)_{KBr}\right]^{1/2}. \qquad [5]$$

Similarly, the tilting angle, $\alpha$, can be obtained from Eqs. [2] and [4] as:

$$\alpha = \arctan\left(\cos\varphi\,\cos^{-1}\beta\left[\left(\frac{I\nu_{\text{Ph-O}}}{I\nu_{\text{s-CH}_2}}\right)^{1/2}_{\text{SAM}}\right.\right.$$

$$\left.\left.\times\left(\frac{I\nu_{\text{s-CH}_2}}{I\nu_{\text{Ph-O}}}\right)^{1/2}_{\text{KBr}} - \sin\varphi\right]^{-1}\right). \quad [6]$$

By using the above formulas, we obtain from our experiment that the tilting and twisting angles are 24 ± 5° and 50 ± 5°, respectively. The orientation of polymethylene chain in MDQ SAM is consistent with previous reports on SAMs terminated with methyl and various small polar groups (CH$_2$OH, COOH, CO$_2$CH$_3$, CN, etc.), in which the alkyl chain was found to prefer a tilting angle of about 30° (23, 24). With the above results in mind, it is clear that the quinoline moieties form a tightly packed layer in MDQ SAM and do not obviously perturb the alkyl chain layer.

### B. Surface Properties Investigation

Measurement of contact angle permits the surface free energy to be estimated directly (25) and is a sensitive method of studying the surface properties. Contact angle measurements of probe liquids at various pH values on the SAMs, so-called "contact angle titrations," have been widely used to estimated the p$K$ value of functional groups at surfaces (1–6, 25, 26). The contact angle titration curve for an SAM of MDQ for the pH range between 2.0 and 12.0 is displayed in Fig. 3. A plateau is clearly seen at pH values higher than 8.0. The contact angle increases dramatically when the pH of the probe solution decreases from 8.0 to 4.0 and reaches maximum around pH 3.0. Although the variation of the contact angle throughout the pH range we studied was less than 8°, it is readily detectable above the experimental error. Clearly, in the range studied, the SAM of MDQ is less hydrophilic to acidic solutions than to basic solutions.
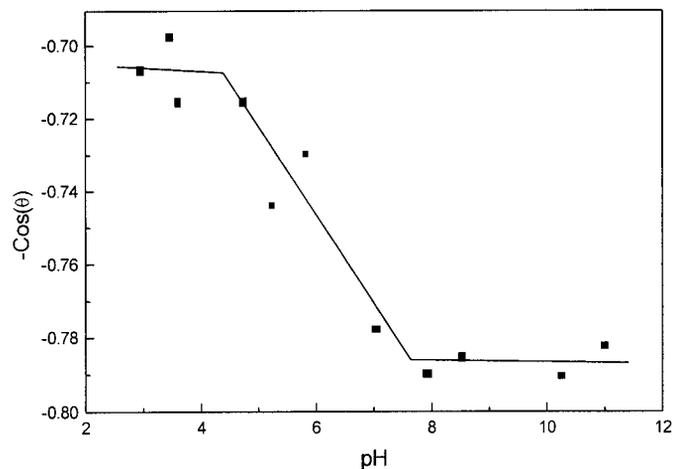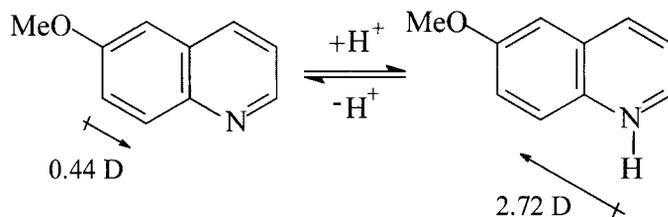


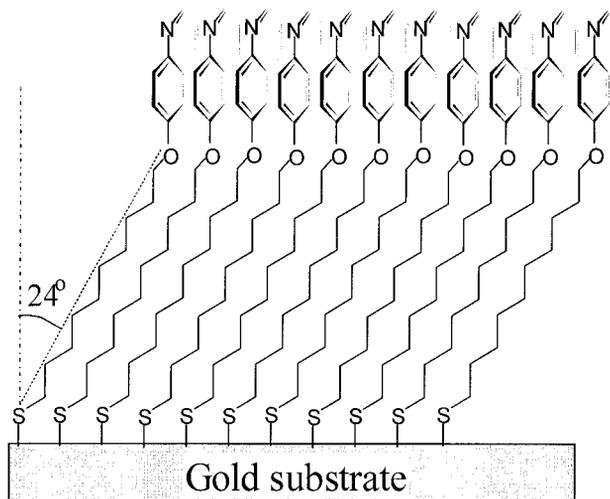**FIG. 3.**   Contact angle titration curve of water on MDQ SAM.



**SCHEME 2.**   Schematic showing the direction of dipole moment change of 6-methoxylquinoline before and after protonation on nitrogen atom.

As may be expected, the change in surface wettability corresponds to the protonation of quinoline group that is expected at low pH. As can been seen in Fig. 3, protonation of quinoline group decreases the surface wettability. In contrast, Whitesides (3) suggested that imidazolo SAMs are more wetting in low pH. We have also reported that the protonation of amino groups at the end of a SAM brought led to an increase in surface wettability (5, 6). Both of these reports show opposite trends to those observed with a SAM of MDQ.

Surfaces that are more readily wet by water usually provide sites for strong intermolecular interactions such as dipole–dipole interactions and hydrogen bonding. Protonation of basic groups at low pH causes the surface to be charged, and thus induces an increase in the surface wettability. In the case of SAMs of MDQ, the unique molecular structure must play important role in its wettability. A small molecule, 6-methoxylquinoline (27), was selected here for investigating the change of dipole moment of its quinoline ring on prontonation since the variation in alkyl substitution is not expected to affect the electronic structure of the quinoline moieties to any great extent. It is well known that nitrogen atom is usually acts as electroattractive group and has surplus negative charge in pyridine and quinoline derivatives (28). It is also known that the oxygen atom in aromatic ethers usually has a positive charge because of conjugation (28) (for example, oxonium ions are very stable compared to the other resonance structures of anisole). In addition, 6-methoxy quinoline moieties exhibit a low dipole moment in the direction from the oxygen atom to nitrogen atom. At low pH, protonation of the nitrogen atom is expected to occur at which point the nitrogen atom is strongly positively charged. We have calculated and found that the dipole moment of 6-methoxylquinoline increases from 0.44 to 2.72 D and that the dipole moment reverses on protonation, see Scheme 2. Despite of any other influences, we expected that the surface wettability would increase on protonation of the nitrogen atom because of the increase in surface dipole moment. However, our observation on the SAM of MDQ gave the opposite result.

An alternative interpretation of the "abnormal wettability" of SAM of MDQ is that the quinoline groups are not fully protonated at the maximum point of the contact angle titration curve. Our infrared spectroscopic studies have suggested that the quinoline moiety is densely packed in the monolayer.

**SCHEME 3.** Proposed structure for the SAM of MDQ.

hydrophilic to acidic solutions than basic solutions in contrast with previous reports on monolayers containing basic groups.

The MDQ SAM provides a good model to investigate the properties of large conjugated and planar basic groups in membrane. Furthermore, the quinoline skeleton is widespread in plants as the main component of various alkoloids. Thus studies of SAMs of MDQ may potentially be used as model systems for further investigation on some biological problems such as determination of the properties of alkoloids at the organ/water interface.

## ACKNOWLEDGMENTS

Therefore, it may be very difficult to protonate all the molecules in monolayer due to the static exclusion force among the neighboring molecules. Remembering that the direction of the dipole moment of 6-methoxyquinoline reverses on protonation, it is possible that both protonated and unprotonated quinoline groups exist in monolayer. If this is the case, the average surface dipole, which is felt by the probe liquid in contact angle measurements, may be lower than that of a totally unprotonated surface, so that the maximum point in the contact angle titration curve will correspond to the minimum of the surface dipole.

The origin of such obvious differences in wettability between MDQ and some other basic groups exposed SAMs is currently not fully understood, and the above hypothesis may be too simplistic. Some other factors, such as hydrogen bonding among prononated MDQ and water, charge–charge interactions in the MDQ monolayer, and changes in the orientation of MDQ when in contact with different solutions may also contribute to the surface wettability (29, 30). Further investigations, including in-situ spectroscopic measurements and investigations by chemical force microscopy (CFM), are being carried out in our laboratory.

## CONCLUSION

A well-ordered, densely-packed basic surface, composed self-assembled monolayer of 6-(10-mercaptodecoxyl)quinoline was obtained. It was found that the quinoline moiety forms an ordered layer on the upper surface of the film and does not appear to perturb the packing of the alkyl chain. The molecular orientation estimated from the RA-IR spectrum indicates that the molecular axis exhibits a tilting angle of 24 ± 5° with respect to the surface normal and a twisting angle of 50 ± 5°. Contact angle titration suggests that a SAM of MDQ is less

## REFERENCES AND NOTES

1. Ulman, A., "An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-assembly." Academic Press, Boston, 1991.
2. Bain, C. D., and Whitesides, G. M., *Langmuir* **5,** 1370 (1989).
3. Lee, T. R., Care, R. I., Biebuyck, H. A., and Whitesides, G. M., *Langmuir* **10,** 741 (1994).
4. Creager, S. E., and Clarke, J., *Langmuir* **10,** 3675 (1994).
5. Yu, H. Z., Zhao, J. W., Wang, Y. Q., Cai, S. M., and Liu, Z. F., *J. Electroanal. Chem.* **438,** 221 (1997).
6. Zhang, H., He, H.-X., Wang, J., Mu, T., and Liu, Z. F., *Appl. Phys. A* **66,** S269 (1998).
7. The spectral data of MDQ: $^1$H NMR 7.1–8.7 (m, 6H, Ar-H), 4.1 (t, 2H, -O-CH$_2$), 2.5 (m, 2H, S-CH$_2$), 1.85 (m, 2H, CH$_2$), 1.6 (m, 2H, CH$_2$), 1.5 (m, 2H, CH$_2$), 1.3–1.4 (m, 11H, CH$_2$, SH): MS (EI) M$^+$/e 317.
8. Lin-Vien, D., Colthup, N. B., Fateley, W. G., and Grasselli, J. G., "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules." Academic, Boston, 1991.
9. Bellamy, L. J., "The Infrared Spectra of Complex Molecules." Chapman and Hall, London, 1975.
10. Finnegan, W. J., Henry, R. A., and Olsen, A. L., *J. Am. Chem. Soc.* **77,** 4420 (1955).
11. Tallent, W. H., and Siewers, I. J., *Anal. Chem.* **28,** 953 (1956).
12. Miller, F. A., and Crawford, B. L., *J. Chem. Phys.* **14,** 282 (1946).
13. Snyder, R. G., Strauss, H. L., and Elliger, C. A., *J. Phys. Chem.* **86,** 5145 (1982).
14. Snyder, R. G., Maroncelli, M., and Strauss, H. L., *J. Phys. Chem.* **90,** 5623 (1986).
15. Nuzzo, R. G., Korenic, E. M., and Dubois, L. H., *J. Chem. Phys.* **93**(1), 767 (1990).
16. Evans, S. D., Urankar, E., Ulman, A., and Ferris, N., *J. Am. Chem. Soc.* **113,** 4121 (1991).
17. Allara, D. L., and Nuzzo, R. G., *Langmuir* **1,** 52 (1985).
18. Dete, M. K., *J. Appl. Phys.* **55,** 3354 (1984).
19. Siniah, K., Chen, J., Terretttaz, S., Reutt-Robey, J. E., and Miller, C. J., *J. Phys. Chem.* **99,** 14500 (1995).
20. Wesch, A., Dannenberger, O., Woll, Ch., Wolff, J. J., and Buck, M., *Langmuir* **12,** 5330 (1996).
21. Young, J. T., Boerio, F. J., Zhang, Z., and Beck, T. L., *Langmuir* **12,** 1219 (1996).
22. His, A., Uvdal, K., and Liedberg, B., *Langmuir* **9,** 733 (1993).
23. Dubois, L. H., and Nuzzo, R. G., *Annu. Rev. Phys. Chem.* **43,** 437 (1992).

24. Nuzzo, R. G., Dubois, L. H., and Allara, D. L., *J. Am. Chem. Soc.* **112,** 558 (1990).
25. Adamson, A. W., "Physical Chemistry of Surface." Wiley, New York, 1982.
26. Holmes-Farley, S. R., Bain, C. D., and Whitesides, G. M., *Langmuir* **4,** 921 (1988).
27. The atomic electron density and molecular dipole moment of 6-methoxyl-quinoline was calculated with Gaussian 94 (Gaussian, Inc., Pittsburgh, PA, 1994).
28. Streitwieser, A., Clayton, Jr., and Heathcock, H., "Introduction to Organic Chemistry," 3rd ed., p. 665 and 1023. Macmillan Publishing Company, New York, 1985.
29. Bain, C. D., and Whitesides, G. M., *J. Am. Chem. Soc.* **110,** 5897 (1988).
30. Evans, S. D., Sharma, R., and Ulman, A., *Langmuir* **7,** 156 (1991).
31. Ong, T. H., Ward, R. N., and Davies, P. B., *J. Am. Chem. Soc.* **114,** 6243 (1992).